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Molecular Transport Kinetics of Non-Polar Solvents Through AGNP Filled EPDM Elastomeric Composites

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Abstract

EPDM Based rubber composites can be used in tank and pipe lining works. In these applications one of the major requirements is that the composite must have good fluid permeability and chemical degradation resistances in their working environment. In order to enhance the performance of EPDM rubber to suit these applications, scientists and engineers are trying to develop novel nanocomposites by incorporating nano fillers. In the present work, to ensure the proper miscibility with the matrix, functionalized nano filler namely amine functionalized graphene nanoplatelets (AGNP) is used as the nano filler material and six composite samples were prepared by varying the AGNP filler content from 0 to 25 phr in steps of 5 phr. Comprehensive experimental studies were carried out to determine the optimal filler content based on their swelling characteristics and solvent diffusion stabilities in non-polar solvents such as benzene and $CCl_4$and compared with that of virgin EPDM blend. Furthermore, mathematical modeling of solvent transport kinetics is adopted to obtain better understanding of the composite's diffusion characteristics. Results demonstrated that the composite with 15 phr AGNP exhibited superior performance across all the evaluated parameters required for membranous lining applications, indicating it as the most promising optimum nano filler content.

Keywords: EPDM rubber, amine-functionalized graphene nanoparticles (AGNP), solvent diffusion, solvent transport kinetics, mathematical modeling

INTRODUCTION

The increasing demand for advanced materials with tailored properties has led to the exploration of elastomer composites, where rubber matrices are reinforced with functional fillers to achieve superior performance. Among the synthetic elastomers, EPDM (Ethylene Propylene Diene Monomer) rubber stands out due to its excellent thermal, mechanical, electrical, and weathering properties, making it suitable for diverse engineering applications [1–3]. Despite its versatility, the properties of EPDM can be further enhanced by the incorporation of fillers, enabling it to meet the specific requirements of advanced applications.

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Traditionally, carbon black (CB) has been extensively used as a reinforcing filler in elastomers. However, the limited availability of CB, coupled with its environmental concerns and black staining issues, have driven researchers toward alternative filler materials [4–5]. In this context, nanofillers have emerged as a promising class of reinforcements. These fillers, due to their high surface area and unique properties, enhance the performance of composites, including diffusion, dielectric [7–8], damping [9–10], mechanical [11-12], and thermal characteristics [6]. Graphene-based nano-materials, in particular, have gained prominence as efficient reinforcements for elastomers [13–15].

One major challenge with incorporating nanofillers into elastomeric matrices is achieving uniform dispersion, as nanoparticles tend to agglomerate at higher concentrations. To address this, functionalized nanofillers [16–17] such as amine-functionalized graphene nanoplatelets (AGNP) have been developed to improve compatibility and dispersion within the matrix. Following this approach, this study focuses on reinforcing EPDM rubber with AGNP as the sole filler.

The present study investigates about the solvent transportation and molecular transport behaviors of non-polar solvents such as benzene and CCl_4 on prepared EPDM-AGNP nanocomposites by varying the AGNP filler content from 0 to 25 phr in steps of 5 phr. These composites, along with the virgin EPDM blend, were experimentally evaluated and compared. Furthermore, mathematical modeling such as Zeroth order Kinetics, first order Kinetics, Higuchi, Peppas-Shalin, Korsmeyer Peppas models of solvent transport kinetics were adopted to obtain better understanding of the composite diffusion characteristics. The findings not only highlight the enhanced performance of the EPDM-AGNP composites but also identify the optimal filler content for achieving the properties required for membranous applications.

EXPERIMENTATION

The experimental framework adopted for the present study is detailed with the materials used for composite preparation and the methodologies employed to investigate their diffusion and solvent transport characteristics. The procedures were systematically designed to ensure reproducibility and accuracy in assessing the interaction behavior between the polymer matrix and selected solvents.

Materials

For this study, EPDM (Ethylene Propylene Diene Monomer) rubber was selected as the base material due to its exceptional mechanical, thermal, and electrical properties, making it suitable for diverse engineering applications. The rubber was reinforced with amine-functionalized graphene nanoplatelets (AGNP) (purity :99%, thickness ~5-10nm, lateral dimension~5-10 microns, layers~5-10 layers, amine content~2-5% surface treated), a nano-filler recognized for its high surface area and unique structural properties, which enhance the overall performance of elastomeric composites. Additional chemicals and additives essential for the preparation of these composites were carefully sourced to ensure compatibility and uniformity in the formulation. The constituents used for composites development are detailed in Table 1.

Table 1. Formulation of composites prepared (in phr).

Ingredients	Virgin EPDM blend	EPDM-AGNP5 composite	EPDM - AGNP 10 composite	EPDM - AGNP15 composite	EPDM - AGNP 20 composite	EPDM - AGNP25 composite
EPDM rubber	100	100	100	100.0	100.0	100.0
Amine functionalized Graphene nano platelets	-	5	10	15	20	25
Napthenic oil	7.5	7.5	7.5	7.5	7.5	7.5
ZINC OXIDE	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TMTD (Tetra-methyl thiuram Disulfide)	0.5	0.5	0.5	0.5	0.5	0.5
SULPHUR	1.5	1.5	1.5	1.5	1.5	1.5
CBS (N-cyclohexyl-2 benzothiazolesulfenamide)	0.5	0.5	0.5	0.5	0.5	0.5
ZDC (Zinc diethyldithiocarbamate)	0.5	0.5	0.5	0.5	0.5	0.5
ANTIOXIDANT (4020)	1	1	1	1	1	1

EPDM-AGNP composites were prepared using a two-roll mill to ensure uniform mixing. After masticating EPDM, AGNP was gradually added atrequired amount as per formulation for consistent dispersion. Antioxidants, activators, and plasticizers were then added, followed by curing agents like stearic acid and sulfur. These blends were cured under optimized conditions of heat and pressure, determined via rheometric analysis. From the cured sheets the test samples were prepared and tested for their diffusion characteristics.

Methods

Solvent transportation and diffusion study. To study the diffusion kinetics of the composites, the selected solvents, benzene (molecular mass: 78.11 g/mol; molar volume: 89.4 cm^3/mol; density: 0.8765 g/cm^3; solubility parameter: 18.8 MPa^0.5) and carbon tetrachloride (molecular mass: 153.82 g/mol; molar volume: 97.1 cm^3/mol; density: 1.594 g/cm^3; solubility parameter: 17.8 MPa^0.5) were specifically employed for the swelling and diffusion studies, procured from Sigma Aldrich, were selected as representative solvents. The followed procedure adhered to ASTM D0471-16a standards to ensure consistency and reliability. Composite samples, cut into uniform dimensions (15 mm × 15 mm × 2 mm) were then immersed in airtight containers containing 25 ml of the respective solvents at room temperature. The initial mass of each sample was carefully recorded before immersion. At regular time intervals, the samples were removed, gently blotted to remove excess solvent, and weighed using a high-precision Ohaus Adventurer balance with a 0.001 g accuracy. To minimize vaporization losses, each weighing was completed within 20–25 seconds. This process was repeated until equilibrium solvent absorption condition reached. This swelling data will provide crucial insights into the transportation behaviours (diffusion characteristics and interaction mechanisms) of the solvents within the composite matrix. The polymer–solvent interaction parameter (χ) is commonly estimated using the equation based on solubility parameters: $\chi = (Vs/RT)(\delta p - \delta s)2$, where,$\chi$ = polymer–solvent interaction parameter, Vs= molar volume of solvent (cm^3/mol), R = universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), T = absolute temperature (K) ,δp = solubility parameter of EPDM (16.5 MPa^0.5) ,δs = solubility parameter of solvents (MPa^0.5).

RESULTS AND DISCUSSIONS

The experimental results and their corresponding analyses to elucidate the structure–property relationships within the developed EPDM/AGNP composites are presented below . Emphasis is placed on understanding how the incorporation of amine-functionalized graphene nanoplatelets influences the morphological features, diffusion behavior, and overall physicochemical interactions of the composite system. The subsequent subsections discuss these findings in detail, supported by experimental evidence and theoretical considerations.

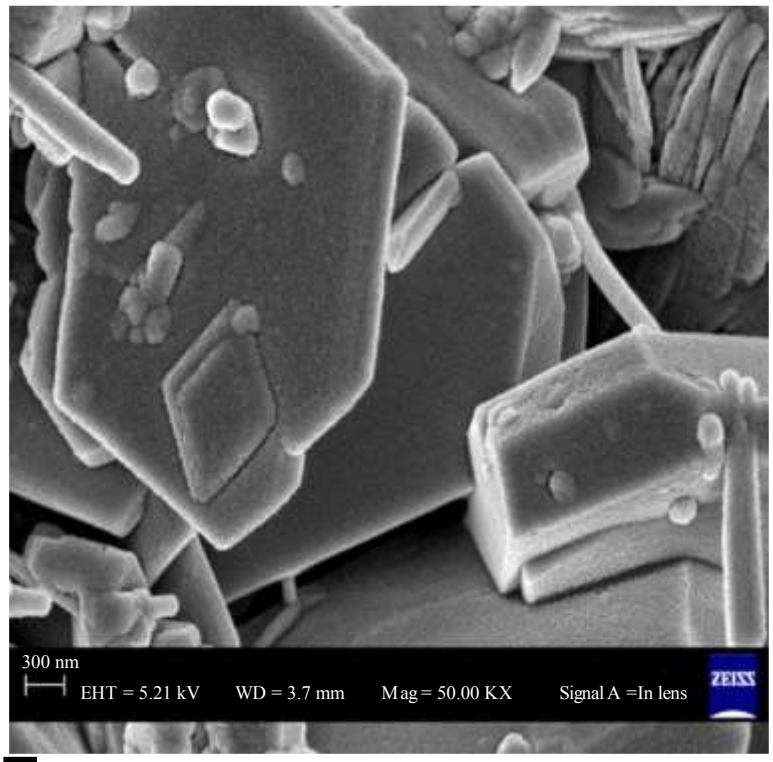
Morphology of Composites

The fracture surface morphology -FESEM images of the virgin EPDM blend, and amine functionalized EPDM composites at 15 phr and 25 phr loading are shown in Figures 1(a-c) respectively. The surface appears to be smooth, and it is observed that the cracks and vicinity were the main features of the EPDM without filler as seen in Figure 1(a) [17]. It was observed in Figure 1(b) that the AGNP seems to be more randomly oriented more or less aligned in the matrix, and further they were distributed more uniformly inside the EPDM matrix [17]. The fracture surface becomes rougher due to the uniform dispersion of optimum filler content in the matrix. A good dispersion of the filler in the rubber matrix reduced the filler–filler interaction and increased the rubber–filler interaction. Because of such exceptional interactions and interfacial adhesion between the EPDM rubber matrices and AGNP augmented the performance of the composite. Figure 1(c) demonstrates the agglomeration of AGNP nanoparticles beyond 15 phr results in reduced performance compared to optimum 15 phr AGNP loading.

Diffusion Kinetics and Solvent Transport Mechanism

Solvent diffusion kinetics and molecular transportation describe the process by which solvent molecules penetrate and move through polymer matrices, driven by concentration gradients. This

phenomenon is crucial in diverse applications, such as swelling in elastomers [19], controlled drug delivery systems, and membranous/barrier properties of polymers [20-21]. The transportation process is typically governed by Fick's laws of diffusion. Fick's first law describes steady-state diffusion, where the flux of solvent molecules is proportional to the concentration gradient. Fick's second law, on the other hand, governs non-steady-state diffusion and predicts the temporal evolution of concentration profiles. The diffusion, sorption, and permeability coefficients are the key parameters that can characterize these processes.



(a)

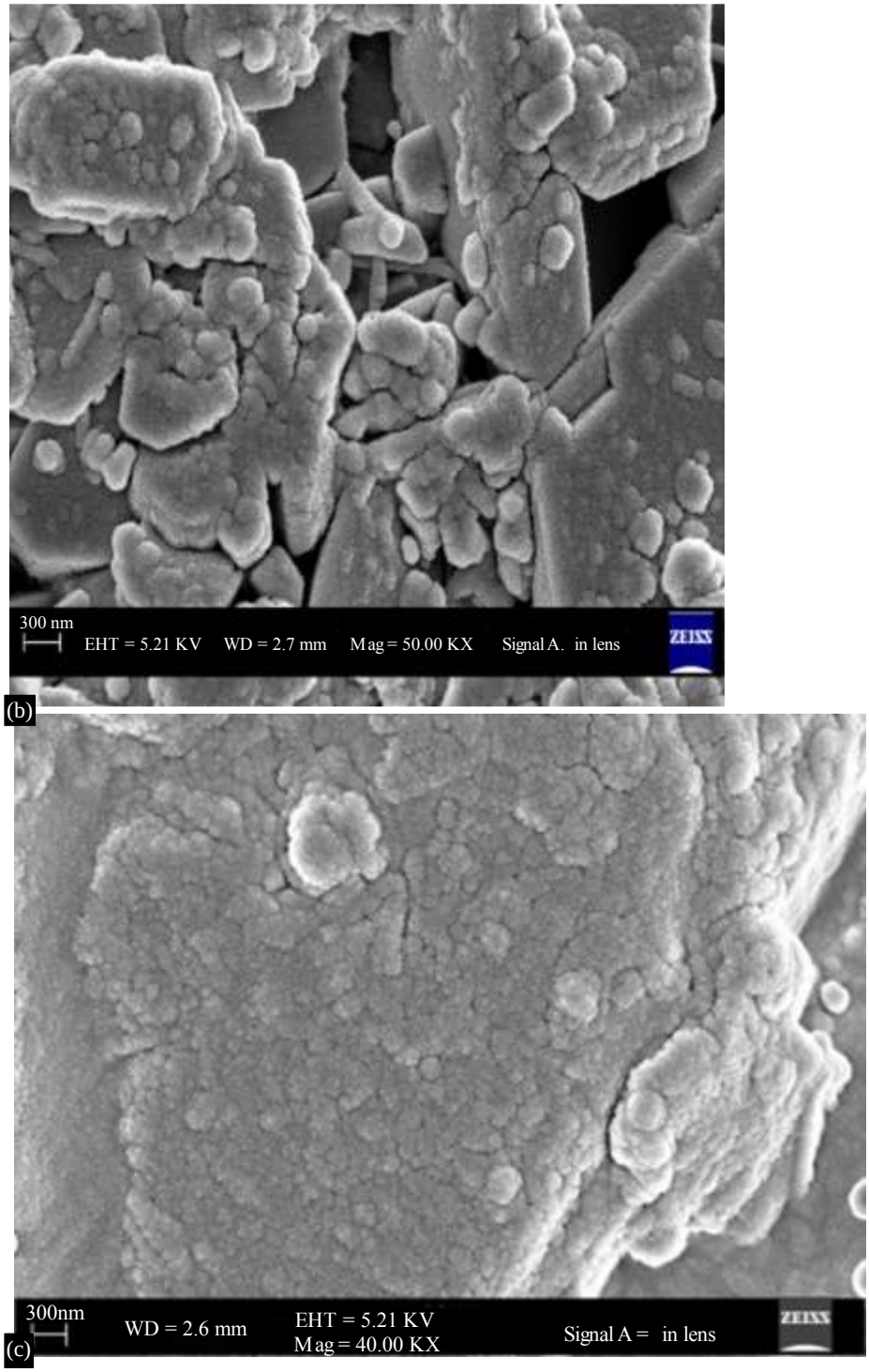


Figure 1. FESEM images of (a) Virgin EPDM blend and (b) AGNP 15phr filled nanocomposite and (c) AGNP 25phr filled nanocomposite.

The diffusion coefficient (D) quantifies the rate at which solvent molecules migrate through a polymer matrix. It is influenced by the molecular size of the penetrant, polymer structure, temperature, and solvent-polymer interactions. The higher D value indicates faster diffusion. The sorption coefficient (S) measures the equilibrium concentration of the solvent absorbed by the polymer and reflects the polymer's affinity for the solvent. It is defined as the ratio of the solvent concentration in the polymer to that in the surrounding environment. The permeability coefficient (P) is a product of the diffusion

and sorption coefficients (P=D×S), representing the overall ability of the solvent to penetrate through the material.

Several models are used to describe solvent transportation kinetics and molecular release mechanisms. The Higuchi model [22] is a foundational approach that assumes one-dimensional diffusion, constant diffusion coefficient, and negligible swelling of the polymer. It relates the amount of solvent (or solute) released to the square root of time as

$$Q = k_H t^{\frac{1}{2}} \quad (1)$$

where Q is the release amount, kH is the Higuchi constant, and t is time. This model is mostly applied to systems dominated by Fickian diffusion. The Korsmeyer-Peppasmodel[23] generalizes diffusion analysis to include both Fickian and non-Fickian transport. It uses a power-law relationship given by

$$\frac{M_t}{M_\infty} = k_P t^n \quad (2)$$

where Mt/M∞ is the fraction of solvent released, kP is the kinetic constant, t is time, and n is the release exponent. The value of n indicates the mechanism involved, Fickian diffusion (n≤0.5), anomalous diffusion (0.5<n<1), or Case II (n=1) non-Fickian transport. This model is flexible and accommodates systems with variable geometries and release mechanisms. The Peppas-Sahlin model [24–25] further refines this analysis by including contributions from both diffusion and polymer relaxation. It is expressed as

$$\frac{M_t}{M_\infty} = k_1 t^m + k_2 t^{2m} \quad (3)$$

where k1and k2 are constants representing Fickian and relaxation contributions respectively and m is an exponent describing the kinetics. This model is especially useful for systems where polymer swelling or relaxation significantly impacts transportation behavior. Together, the diffusion, sorption, and permeability coefficients along with these mathematical models provide a comprehensive framework for understanding solvent-polymer interactions. They enable the prediction and analysis of swelling, release rates, and barrier properties, making them indispensable for designing elastomer composites, membranes, and controlled release systems.

The swelling behavior and transport properties of virgin EPDM and EPDM nanocomposites filled with amine-functionalized graphene nanoplatelets (AGNP) at various loadings (5 to 25 phr) were analyzed in non-polar solvents: benzene and CCl_4 are indicated in Table 2. The swelling index and swelling coefficient decreased progressively with increasing AGNP content, demonstrating improved solvent resistance. For example, in the case of benzene solvent, the swelling index decreased from 155.71% of virgin EPDM to 126.42% of EPDM AGNP25 composite, representing an 18.8% reduction. CCl_4 exhibited the higher swelling indices, with values decreasing from 427.94% of virgin EPDM to 335.78% of EPDM AGNP25. This trend reflects the reinforcing effect of AGNP, which restricts polymer chain mobility and reduces solvent uptake. The swelling coefficient also followed a similar pattern, with values in benzene decreasing from 1.776 of virgin EPDM to 1.44 of EPDM AGNP25 nanocomposite while in case of CCl_4, it reduced from 2.684 to 2.107.

The cross-link density of EPDM nanocomposites peaks at AGNP15 loading, enhancing the polymer network's strength and restricting solvent penetration. Beyond this point, higher AGNP loadings lead to agglomeration, reducing reinforcing efficiency. In benzene and CCl_4, cross-link density rises with AGNP incorporation up to AGNP15 before declining at AGNP25. This highlights AGNP15 as the optimal filler loading for effective network formation, crucial in applications like elastomeric membranous barriers.

Key parameters such as the diffusion constant, equilibrium sorption level, and permeability rate offer valuable metrics to interpret this behavior. The diffusion constant (D) indicates how swiftly solvents navigate through the matrix, being dependent on molecular dimensions, polymer microstructure, and

the extent of molecular interactions between solvent and polymer. Equilibrium sorption (S) estimates the solvent retention capability of the matrix, reflecting its affinity for absorption. Permeability (P), which arises from the interplay of diffusion and sorption, provides an aggregate measure of a solvent's penetration capacity within the system.

Various theoretical models have been proposed to explain the kinetics of solvent diffusion and the mechanisms governing molecular navigation of solvents. One of the most established approaches is the Higuchi model, which provides a framework based on the assumptions of one-dimensional diffusion, a uniform diffusion coefficient, and minimal polymer swelling. This model establishes a relationship between the release amount of a solvent (or solute) and the square root of time, offering insights into systems dominated by linear diffusion dynamics.

$$Q = k_H t^{\frac{1}{2}} \tag{4}$$

To understand solvent transportation more effectively, multiple kinetic models have been introduced. Higuchi's formulation, tailored for systems dominated by linear diffusion, associates solvent migration to the square root of time, while the Korsmeyer-Peppas model extends this approach by incorporating both Fickian and non-Fickian mechanisms of transport through a power-law expression. For more complex systems involving polymer relaxation, the Peppas-Sahlin framework provides additional precision by factoring in both diffusion and polymer relaxation contributions, highlighting the interplay between transport kinetics and polymer dynamics.

In this context, Q represents the quantity of solvent released, k_H is the constant associated with the Higuchi model, and t signifies time. This model is primarily applicable to systems where diffusion is governed by Fickian principles. Expanding on this, the Korsmeyer-Peppas model [23] broadens the scope of diffusion analysis by accommodating both Fickian and non-Fickian mechanisms, employing a power-law equation to describe the release behavior.

The fraction of solvent released, represented as M_t/M_∞which reflects the progression of the release process over time. Here, k_P is the kinetic constant, t signifies time, and n denotes the release exponent. The value of n determines the nature of the transport mechanism: Fickian diffusion is characterized byn, if $n \leq 0.5$, and anomalous (or non-Fickian) diffusion occurs when $0.5<n<1$and $n=1$ which corresponds to case II transport. This model exhibits adaptability, making it applicable to systems with diverse geometries and release profiles. Building upon this, the Peppas-Sahlin model [24-26] offers an enhanced framework by incorporating both diffusion and the relaxation behavior of polymers. It effectively accounts for scenarios where polymer swelling or relaxation plays a significant role in the transportation mechanism. The expression for this refined model is given as:

$$\frac{M_t}{M_\infty} = k_1 t^m + k_2 t^{2m} \tag{5}$$

The behavior of virgin EPDM and its nanocomposites, developed with amine-functionalized graphene nanoplatelets (AGNP) with different filler content and were systematically analyzed in non-polar solvents such as benzene and carbon tetrachloride. The results displayed a progressive reduction in solvent uptake and swelling levels with increasing AGNP content, reflecting the filler's capacity to restrict polymer chain mobility and enhance solvent resistance. For instance, benzene initially demonstrated higher swelling indices in the pure EPDM matrix, experienced a substantial decline in solvent uptake upon the addition of AGNP. Among the solvents, carbon tetrachloride exhibited the greatest interaction with the matrix.The study found that cross-link density increased with AGNP incorporation, peaking at moderate filler levels at 15 phr loading. Beyond this point, agglomeration reduced efficiency, emphasizing AGNP's dual role as a stabilizer and, at excessive levels, a source of structural inefficiency.

The coefficients such as sorption, diffusion and permeability are obtained mathematically from the solvent uptake data of the prepared composites and are presented in Figure 2 for the different solvents taken for study. The sorption coefficient exhibited a consistent decline with AGNP addition. In benzene,

the sorption coefficient decreased from 2.557 of virgin EPDM to 2.264 of EPDM AGNP25. CCl_4 had the higher sorption coefficient values across all samples, reducing from 5.279 to 4.358, indicating its strong interaction with the polymer matrix. The reduction in the sorption coefficient is attributed to the tortuous path and decreased void space created by AGNP filler, which limits solvent absorption.

Table 2. Swelling parameters and diffusion kinetic constants of virgin EPDM blend and EPDM AGNP nanocomposites in benzene and CCl_4 solvents.

Samples	Solvents	Swelling index (%)	Swelling coefficient	Cross link density (g/mol/cc)	Sorption coefficient	Diffusion coefficient (cm^2/s)	Permeability coefficient (cm^2/s)
virgin EPDM blend	Benzene	155.71	1.776	2.94e-04	2.557	5.97e-06	1.53e-05
	CCl_4	427.94	2.684	1.89e-04	5.279	4.15e-06	2.19e-05
EPDM AGNP5	Benzene	151.76	1.73	2.95e-04	2.518	5.96e-06	1.50e-05
	CCl_4	400.56	2.51	1.94e-04	5.006	3.92e-06	1.97e-05
EPDM AGNP10	Benzene	142.81	1.63	3.03e-04	2.428	5.92e-06	1.44e-05
	CCl_4	379.45	2.38	1.98e-04	4.795	3.66e-06	1.76e-05
EPDM AGNP15	Benzene	131.38	1.49	3.31e-04	2.314	5.91e-06	1.37e-05
	CCl_4	348.3	2.185	2.13e-04	4.483	3.51e-06	1.57e-05
EPDM AGNP20	Benzene	128.60	1.47	3.19e-04	2.286	5.64e-06	1.29e-05
	CCl_4	342.34	2.148	2.11e-04	4.423	3.41e-06	1.51e-05
EPDM AGNP25	Benzene	126.42	1.44	3.11e-04	2.264	5.12e-06	1.16e-05
	CCl_4	335.77	2.10	2.08e-04	4.35	3.37e-06	1.47e-05

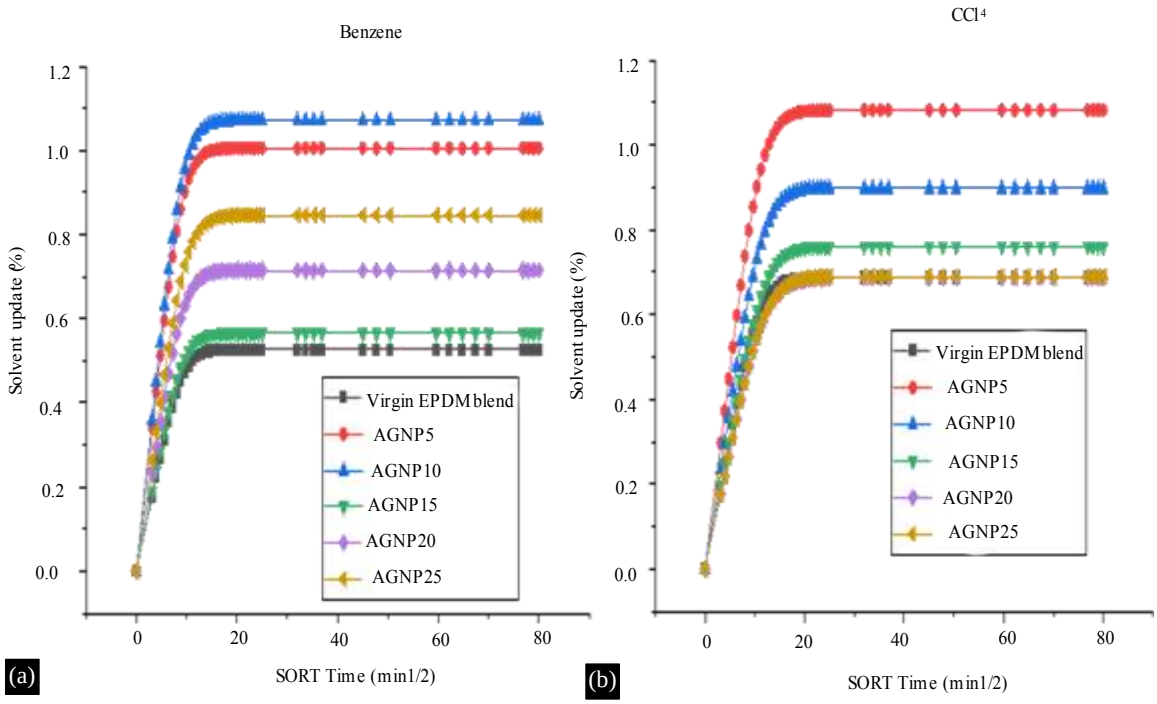


Figure 2. Solvent uptake data of prepared samples in (a) Benzene and (b) CCl4 solvents.

The diffusion coefficient decreased with increasing AGNP content, highlighting the barrier effect of the filler. In benzene, it dropped from 5.97×10^{-6} cm²/s for virgin EPDM to 5.12×10^{-6} cm²/s for EPDM AGNP25, while CCl_4 showed a decline from 4.15×10^{-6} cm²/s to 3.37×10^{-6} cm²/s due to restricted solvent mobility. Similarly, the permeability coefficient reduced with AGNP incorporation. For instance, in benzene, it fell by 24.2%, from 1.53×10^{-5} cm²/s to 1.16×10^{-5} cm²/s, while CCl_4

exhibited the higher permeability, decreasing from 2.19×10^{-5} cm²/s to 1.47×10^{-5} cm²/s. These trends underscore AGNP's role in limiting solvent diffusion and permeability.

The incorporation of AGNP significantly improved the barrier properties of EPDM composites by reducing swelling, sorption, diffusion, and permeability coefficients across the solvents. But CCl_4 consistently exhibited the higher swelling and transport parameters, indicating strong interactions with the polymer matrix. In contrast, benzene showed relatively lower values of swelling parameters compared to $CCl_4$and this may be attributed to its steric factors [18]. The results demonstrate that AGNP filler effectively enhances the solvent resistance of EPDM by creating a denser and more tortuous network, thereby limiting solvent uptake and transport of composite.

The kinetic analysis of solvent transportation in virgin EPDM and EPDM-AGNP composites across solvents-benzene and carbon tetrachloride (CCl_4) offers valuable insights into the mechanisms governing diffusion and uptake in these elastomeric systems. Various mathematical models, including zero-order kinetics, first-order kinetics, Higuchi model, Korsemayer-Peppas model, and Peppas-Sahlin model, were employed to evaluate the transportation behavior and is presented in Figure 3 for benzene solvent for visual presentation only. The kinetic diffusion parameters obtain from curve fitting the mathematical models are presented in Table 3, with benzene solvent discussed in detail.

The zero-order kinetic model, characterized by a constant-rate coefficient (k), exhibited poor fitting across all composites and solvents, with the highest norm error values (e.g., 4.8277 for virgin EPDM in benzene and 2.7255 for EPDM-AGNP15). These results indicate that solvent uptake does not follow a constant-rate mechanism. The simplistic assumptions of this model fail to capture the complexities of solvent transportation, making it unsuitable for these systems.

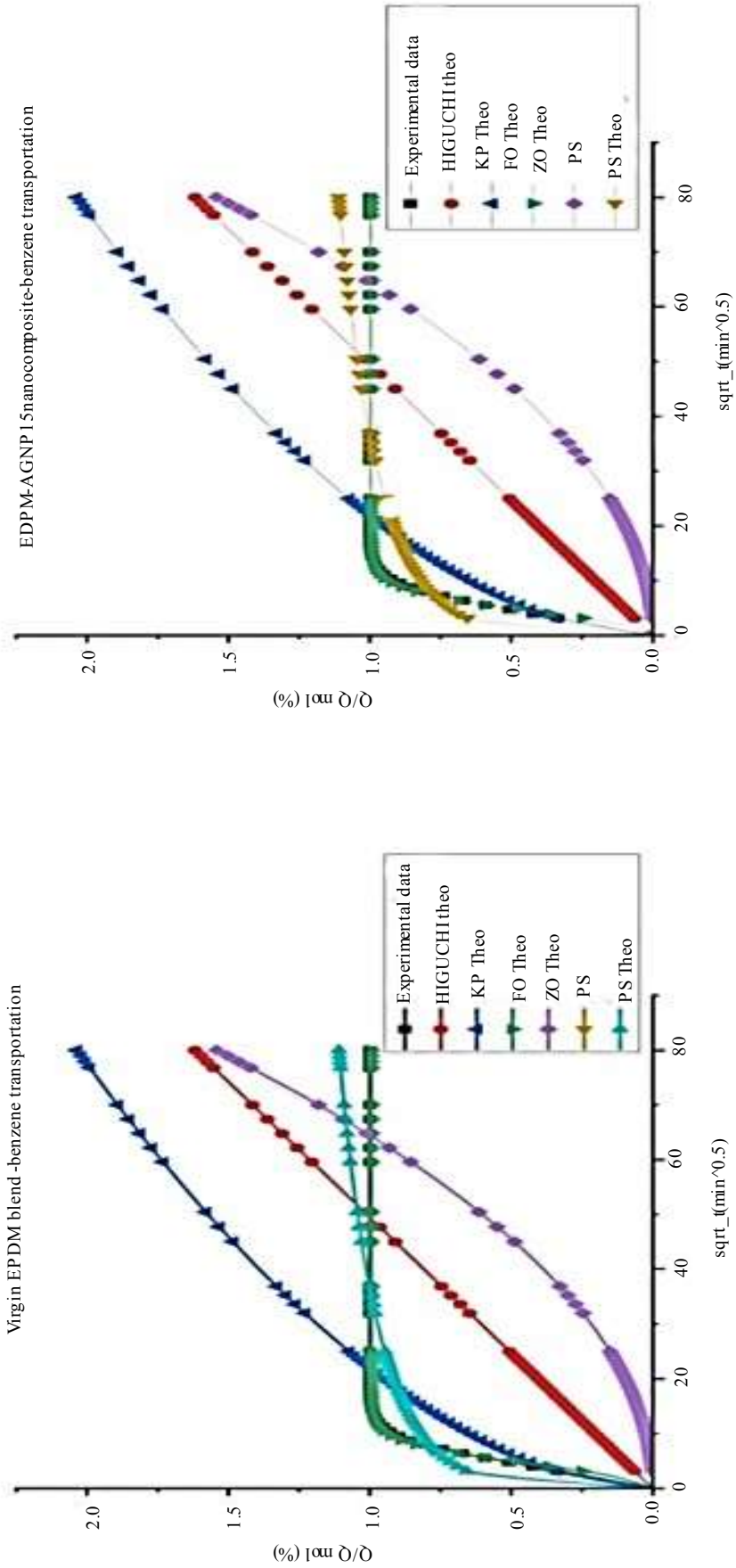


Figure 3. Solvent transportation and diffusion kinetic model fittings of virgin EPDM blend and EPDM-AGNP-15 nanocomposite.

The first-order kinetic model demonstrated significantly better fitting, with lower norm error values (e.g., 0.137 for virgin EPDM in benzene and 0.0779 for EPDM-AGNP15). The rate constants (k) varied across solvents and composites, reflecting differences in solvent-polymer interactions. For benzene, virgin EPDM exhibited a higher rate constant (0.0289) compared to EPDM-AGNP15 (0.0286), suggesting faster diffusion in the unmodified matrix. Similar trends were observed for other solvents, highlighting the role of filler incorporation in reducing diffusion rates due to enhanced cross-link density and restricted chain mobility.

The Higuchi model, widely used for diffusion-controlled mechanisms, provided moderate fitting with norm error values ranging from 1.9985 (EPDM-AGNP15 in benzene) to 3.5417 (virgin EPDM in benzene). The nearly constant diffusion rate constants (kH) indicate that solvent transportation involves a combination of diffusion and swelling. EPDM-AGNP composites consistently showed lower norm error values and kH compared to virgin EPDM, reinforcing the impact of filler on reducing solvent uptake.

Table 3. Kinetic parameter coefficients and constants obtained for benzene and $CCl_4$of different models taken for study.

Models		**Pure**	**AGNP 5**	**AGNP 10**	**AGNP 15**	**AGNP 20**	**AGNP 25**
Benzene							
Zero-order kinetics	k	0.0002	0.0002	0.0003	0.0001	0.0002	0.0002
	Error norm	4.8277	4.8523	5.1634	2.7255	3.4329	0.0002
First-order kinetics	k	0.0289	0.0288	0.0287	0.0286	0.0274	0.0249
	Error norm	0.137	0.1378	0.1473	0.0779	0.1017	0.1281
Higuchi model	kH	0.0202	0.0203	0.0216	0.0114	0.0145	0.0171
	Error norm	3.5417	3.5595	3.7867	1.9985	2.5120	2.9319
Korsemayer- peppas model	k	0.6067	0.6064	0.6051	0.6044	0.5939	0.5723
	n	0.0679	0.0679	0.0682	0.0683	0.0706	0.0753
	Error norm	3.0539	3.0537	3.0527	3.0523	3.0446	3.0292
Peppas-sahlin model	k1	0.797	1.563	-4.56	2.31911	3.653	-7.43
	k2	1.44	1.949	4.9	2.74811	4.047	7.784
	m	0.031	0.0539	0.027	0.0396	0.0312	0.0173
	Error norm	0.00011	0.000001	0.000007	0.000014	0.000001	0.000018
CCl_4 (Carbon tetra-chloride)							
Zero-order kinetics	k	0.0002	0.0003	0.0002	0.0002	0.0002	0.0002
	Error norm	3.1940	5.0016	4.1165	3.4701	3.1212	3.1269
First-order kinetics	k	0.0204	0.0193	0.0181	0.0174	0.0170	0.0168
	Error norm	0.1172	0.1906	0.1641	0.1417	0.1297	0.1309
Higuchi model	kH	0.0138	0.0217	0.0180	0.0151	0.0137	0.0138
	Error norm	2.3022	3.5934	2.9455	2.4772	2.2229	2.2266
Korsemayer- peppas model	k	0.5256	0.5126	0.4968	0.4881	0.4814	0.4790
	n	0.0860	0.0892	0.0931	0.0952	0.0969	0.0975
	Error norm	2.9991	2.9917	2.9833	2.9790	2.9759	2.9748
Peppas-sahlin model	k1	-39.712	-4.625	-5.839	-1.776	-2.009	-5.727
	k2	39.7294	4.513	5.863	1.893	2.108	5.833
	m	0.005155	0.0439	0.031	0.064	0.0556	0.0255
	Error norm	0.000875	0.004742	0.000215	0.002891	0.026827	0.001533

The Korsemayer-Peppas model, accounting for anomalous transportation mechanisms, provided better fitting compared to the Higuchi model. Norm error values were relatively low (e.g., 3.0539 for virgin EPDM and 3.0523 for EPDM-AGNP15 in benzene), and the diffusion exponent (n) values ranged from 0.0679 to 0.0952 across all systems and solvents. These n values suggest that Fickian diffusion dominates the transportation mechanism. The reduced rate constant (k) for EPDM-AGNP composites, particularly EPDM-AGNP15, highlights the role of filler in mitigating solvent transportation by increasing matrix tortuosity and cross-link density.

The Peppas-Sahlin model, which combines Fickian diffusion and relaxation mechanisms, emerged as the most accurate model, offering the lowest norm error values (e.g., 0.00011 for virgin EPDM and 0.000014 for EPDM-AGNP15 in benzene). The coefficients (k1 and k2) and relaxation parameter (m) varied significantly across composites and solvents, reflecting the interplay between diffusion and polymer relaxation. For benzene, virgin EPDM exhibited higher k1 and k2 values (-0.797 and 1.44, respectively) compared to EPDM-AGNP15 (-2.319 and 2.748, respectively), indicating stronger diffusion-driven transportation in the unmodified matrix. Similar trends were observed for other solvents, with EPDM-AGNP composites showing a greater contribution from relaxation mechanisms due to filler incorporation.

In contrast, in CCl_4 solvent, demonstrated lower values of diffusion coefficients than benzene highlighting a weaker interaction with the polymer chains. These trends emphasize the role of solvent polarity (Hansen/Hildebrand solubility parameter), molecular structure, and compatibility in determining the swelling and transport kinetics in EPDM and EPDM-AGNP nanocomposites. Additionally, the incorporation of AGNP consistently reduces the swelling and diffusion across both the solvents due to enhanced cross-link density and barrier properties, reaffirming its role in improving the solvent resistance of EPDM nanocomposites.

Overall, the incorporation of fillers in EPDM-AGNP nanocomposites, particularly EPDM-AGNP15 nanocomposite, consistently reduced swelling indices and diffusion coefficients, attributed to increased cross-link density and restricted chain mobility. The reduced permeability coefficients further confirm the role of fillers in enhancing the barrier properties of the composites. Among the models, the Peppas-Sahlin model provided the most accurate description of solvent transportation behavior pattern, capturing both diffusion and relaxation contributions. The Korsemayer-Peppas model also offered valuable insights of dominance of Fickian diffusion.

In conclusion, EPDM-AGNP nanocomposites, especially EPDM-AGNP15 nanocomposite, exhibit superior resistance to solvent swelling and transportation compared to virgin EPDM. This improvement is due to synergistic effects of enhanced filler-polymer interactions, higher cross-link density, and increased matrix tortuosity, etc. These enhancements are particularly notable in non-polar solvent CCl_4 than aromatic non-polar benzene, where compatibility between the filler and polymer matrix is more pronounced. These findings underscore the potential of EPDM-AGNP nanocomposites for membranous applications requiring high solvent resistance and low permeability.

CONCLUSIONS

From swelling experimental studies and from analyzesof molecular transportation behavior of solvents in the virgin EPDM and EPDM-AGNP nanocomposites it was found that the incorporation of 15 phr AGNP filler improved the performance of EPDM-AGNP15 nanocomposites by reducing the swelling index and diffusion coefficients for the non-polar solvents taken for study. For all the samples the Peppas-Sahlin model was found to be the best fit model which indicates that the solvent transportation behavior follows Fickian diffusion model and the solvent transportation is supported by combined effect of both diffusion and relaxation phenomena. It was also noted that in all the samples the diffusion rate is greater for benzene than $CCl_4$and in the case of swelling reverse trend is noticed.

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