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Effect of Lead and Borax Powder on the Swelling Behavior of EPDM Rubber Composite in Toluene

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Abstract

Synthetic EPDM reinforced, with carbon-black (N-220) as filler, was cured by sulfur with other ingredients. Three groups of samples were prepared. The 1st group contains different concentration (phr) of lead, the 2nd group contains different phr of borax, and the 3rd group contains 25phr borax and different phr of lead. The swelling test was carried out for all samples in the toluene. Swelling parameters such as the rubber volume fraction, crosslinking density, swelling index etc. were calculated. The results showed that the crosslinking density increase as the concentration of lead increase and the ability of the sample to swell decrease. In contradiction, it is observed that the samples contain different phr lead and 25phr borax the crosslinking density decreased, and the samples swelled to high extent. Adding borax only to the samples had no considerable effect on the crosslinking density and on the swelling behavior. Also, the swelling index has been obtained to all samples. The result showed that n ~ 0.5 which Fickian diffusion. Two models (Kraus and Cunnen – Russel) were applied to test the filler rubber interaction. The models give a good result with the experimental data.

One way ANOVA statistical analysis was applied to find out more information about the effect of lead, borax and both of them on the swelling behavior through the calculated coefficients. The statistical results confirmed the practical results, and consequently the post-test Tukey was used to assess the significance of differences between pairs of group means.

Keywords: EPDM; Rubber volume fraction; Crosslinking density; Diffusion coefficient; ANOVA; Tukey method

1. Introduction

Ethylene propylene diene monomer (EPDM) rubber is the fastest growing synthetic rubber [1, 2]. It represents one of the popular synthetic rubbers due to its resistance to polar solvents such as water, acids, alkalis, ketone, and alcohols [3]. EPDM is widely used in the automobile industry [4, 5]. In some accessories of automobile, EPDMs are used in the manufacturing of Hoses for radiators and heaters, window and door seals, O-rings and gaskets etc.

In EPDM, the ethylene and propylene monomers attached to the main chain with unsaturated diene, which has the ability to accept high loading of fillers. By means of a chemical curing process called the vulcanization process, EPDM can be solidified. During this process, the long macromolecules will join together by covalent and/or ionic interactions. Due to the low crosslinking density, the resulting structure exhibits an elastic and soft characteristic and cannot flow even after being reheated [6, 7]. Using the vulcanizing system and heating to the curing temperature, the elastomer will cure. **Figure (1)** illustrates the chemical structure of the EPDM monomer.

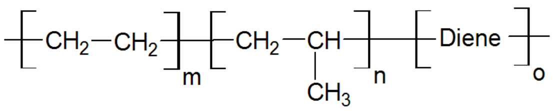

Figure (1): *Chemical structure of ethylene-propylene-diene monomer (EPDM)*

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The swelling of rubbers by the solvent is an important aspect to be considered especially for sealing applications. When solvent, a swelling process happens. The surface of rubber will degrade under the action of an acidic liquid solution humid air, which may deteriorate its surface performance and eventually lead to the loss of bulk properties and reduce the service life time [7, 8].

During the swelling process, a mass transfer takes place and the liquid penetrant through the rubber. This process is controlled by the well-known Fickian diffusion mechanism.

Many researchers interested in the study of the diffusion mechanisms of liquid in different types of rubber [9, 10], including EPDM rubber[11, 12]. Some also were interested in studying the solubility parameters of EPDM rubber in different liquids [12, 13]. The effect of vulcanization parameters (temperature, time, weight%, etc.) on the phenomenon of swelling of EPDM rubber represents another research direction [14, 15].

Boron and their derivatives are used in many industries[16, 17], the most important of which is the automobile industry. Many parts of the car use polymer and rubber as an essential component, such as power cables, tires, and others. Researchers are always motivated to develop such parts to comply with climatic conditions, operating conditions and improve its performance. Sealants also have a share in these industries and others industries and the main component of sealants is the rubber in various forms (such as a natural or synthetic, blend and/or composite etc.)[18, 19]. Hence it is important to study the effect of additives on rubber properties (i.e EPDM) and examining their validity to be used in the appropriate applications.

Borax decahydrate ($Na_2B_4O_7 .10H_2O$) represent one of the non-toxic materials which can be used for different applications [20]. The addition of borax to some polymers will increase its viscosity due to formation of complex compound between the borax ions and the hydroxyl function groups of the polymer. It also used in the field of pharmaceutical and biochemistry fields. Also, Borax is widely used in the industry of detergents and cleaning materials

In this article, the effect of adding borax, lead and a mixture of them on the swelling process of EPDM rubber are investigated. The article will also deals to the application of two models to characterize the interaction between rubber and filler. The two models are the Kraus and Cunne - Russel equation, which were originally derived from the Lorentz gardens

2. Experimental work

2.1. Sample Preparation

A synthetic EPDM reinforced, with carbon-black (N-220) as filler, was cured by sulfur. Zinc oxide acid as an inorganic activator and stearic acid as an organic acid activator were used to activate the accelerator used in the vulcanization process. All these ingredients have been mixed using a laboratory scale two roll mill at room temperature. During mixing these ingredients, paraffin oil added gradually as softener.

The obtained master batch has been weighted and divided into equal parts and lead powder or Borax powder was added separately or together to the prepared product. The composites were mixed again using the two roll mill and vulcanized (cross-linked) by a compressive method under temperature of 153 °C and pressure 4 Mpa. The prepared composite was compressed in the form of a circular disk of diameter of 10 cm and 4 mm thick.

The main components and ingredients used in sample preparation are listed in **Table (1)**. All of the values are in phr (Parts per Hundred Rubber). The lead, borax and lead /borax concentration are illustrated in **Table (2)**.

Table (1): The chemical formulation and ingredient used for samples preparation (in phr)

Material	Role	Amount (phr)
EPDM	Rubber base	100 phr
carbon – black (N – 220)	Reinforcement (filler)	50 phr
Paraffin Oil	Softener (plastizes)	50 phr
Steric acid	Activator	2 phr
ZnO	accelerator	5 phr
Z.K	accelerator	3 phr
Sulfur	Curing agent	3 phr
Lead powder	additive − reinforcing filler	Variable 0,100,200,300,400)
Borax	non reinforcing filler	Variable (0,25,50,75,100)

Table (2): show the lead and borax percentage for the samples used in the swelling measurements

Sample symbol	Borax (phr)	Lead (phr)
E0B0Pb	0	0
E0BxPb	0	100, 200, and 400
E25BxPb	25	100, 200, and 300
ExB0Pb	25, 50, 75, and 100	0

2.2. Swelling measurement and swelling parameters:

Samples with the dimension of ~ 0.5 cm radius and 0.4 cm height (cylindrical shape) were cut from the composite sheet. Four similar parts were cut from the same patch to decrease the error of mass measurements. The test pieces were weighted as the initial weight m_o then immersed in toluene solvent. At a periodic intervals (15min) the test samples were removed from the liquid containers, and extra solvent on the surface was wiped out quickly with filter paper, then the samples were weighted immediately (m_t). After weighting the samples were placed back into the original test bottles, such operations were conducted several times until arriving at equilibrium swelling rate Q_f.

The swelling ratio Q (t) % of the EPDM rubber in the solvent was calculated by the equation

$$Q(t)\,\% = \frac{m_t - m_o}{m_o} \times 100 \quad (1)$$

2.3. Statistical analysis

The presented data were submitted to statistical analysis (one-way ANOVA) to compare the group means. Analysis of variance (ANOVA) was performed with the objective of analyzing the influence of the fillers and filler weight ratio on swelling parameters (crosslink density, rubber volume fraction and swelling index) of the prepared EPDM composite sample. The significance level was taken as P=0.1, i.e., for a level of confidence of 90%. The study was followed by Tukey's test as post hoc used to compare the means. Results of ANOVA analysis are given in the supplementary material.

2.4. Background for swelling parameters:

2.4.1. Rubber volume fraction Vr:

Rubber volume fraction is a measurement of the percentage volume swelled, and is given by

$$V_r = \frac{w_r/\rho_r}{w_r/\rho_r + w_s/\rho_s} \quad (2)$$

Where w_r and w_s represents the Weight of the EPDM rubber and the absorbed of toluene solvent respectively and ρ_r and ρ_s represents the rubber and solvent densities respectively (ρEPDM = 0.92 gm /cm3, ρtoulene = 0.87 gm/ cm3).

Equation (2) can be written as

$$V_r = \varphi = \frac{\frac{m_1}{\rho_r}}{\frac{m_1}{\rho_r} + \frac{m_2 - m_1}{\rho_s}} \quad (3)$$

where m_1 is the non-swollen sample mass (gm), m_2 is the swollen sample mass (gm) at saturation. From the values of rubber volume fraction one can determine the value of crosslink density directly using Flory – Rehner equation [21] according to the following equation

$$\nu_e = -\frac{[\ln(1 - v_r) + v_r + \chi v_r^2]}{V_s\left(v_r^{\frac{1}{3}} - 0.5\, v_r\right)} \quad (4)$$

where χ is a free energy parameter called Flory-Huggins interaction parameter between solvent and polymer and χ is equal to the sum of enthalpic and entropic component of the parameter

$$\chi = \chi_H + \chi_s \quad (5)$$

The enthropic contribution to the Flory – Huggins interaction parameter χ_S is determined, which is equal to 0.34 for nonpolar systems. Enthaplic contribution to the Flory–Huggins interaction parameter χ_H is also determined which equal to 0.15 , henceχ = 0.49. Equation (3) can also take the form [22].

$$V_r = \frac{1}{1 + \frac{m_2 - m_1}{m_1}\frac{\rho_r}{\rho_s}} = \frac{1}{1 + Q_\infty \frac{\rho_r}{\rho_s}} \quad (6)$$

One can write:

$$V_r = \frac{1}{1+Q} \quad (7)$$

Where $Q = Q_\infty \frac{\rho_r}{\rho_s}$ (the volume swelling ratio)

2.4.2. Kraus and Cunneen–Russel Models

These model are theoretical model predict the interaction between the filler and rubber matrix. Kraus equation written as:

$$\frac{V_{r_o}}{V_{r_f}} = 1 - m\frac{Z}{1-Z} \quad (8)$$

¬Where V_{r_o} is the rubber volume fraction for the pure gum, V_{r_f} is the rubber volume fraction for the rubber loaded by the filler, and Z is the volume fraction of filler in the vulcanizate. The parameter m obtained from the slope of the $\frac{V_{r_o}}{V_{r_f}}$ vs. $\frac{Z}{1-Z}$

Another model used which has the from

$$\frac{V_{r_o}}{V_{r_f}} = ae^{-Z} + b \quad (9)$$

Another form of eqn. (9) in terms of swelling of filler reinforced vulcanizates

$$\frac{Q_f}{Q_g} = ae^{-Z} + b \quad (10)$$

Where Q is the amount of the solvent imbedded per unit weight of the rubber, "f" and "g" refer to filled and gum mixes. "a" and "b" are two constants which depend on the filler activity. High value of "a" and low value of b indicate strong polymer attachment.

2.4.3. Fick's law model for diffusion:

The swelling behavior was explained by applying different kinetic models such as Fickian diffusion and Schott second order dynamic model [23].

For fractional capacity $F = \frac{Q_t}{Q_\infty} < 0.6$)

The following equation was used $\frac{Q_t}{Q_\infty} = Kt^n$ (11)

K: is the gel characteristic constant.

n: is the swelling index.

Where k is the gel characteristic constant that depends both on the molecular structure of the rubber and on the interaction between the rubber and solvent n is the swelling index. The value of n indicates the nature of transport mechanism. n = 0.5 which is considered as Fickian.

Putting n = 0.5 in eqn. (11)

$$\frac{Q_t}{Q_\infty}=Kt^{\frac{1}{2}} \quad (12)$$

diffusion coefficient (D) is calculated in accordance with the Fick's law model

$$\frac{Q_t}{Q_\infty} = \frac{4}{h_o}\sqrt{\frac{D}{\pi}}\; t^{\frac{1}{2}} \quad (13)$$

A plot of Q_t versus $t^{\frac{1}{2}}$ is a linear at short time

$$D = \pi\left(\frac{h_o\,\theta}{4Q_\infty}\right)^2 \quad (14)$$

Where θ is the slope of the nearly linear portion of the curve ho is the thickness of the sample.

4. Results and discussion

4.1. Swelling test

There are many parameters can be used to represent the diffusion of solvent through materials (mass change (Δm), swelling ratio (Q), mole percentage uptake (%Qt), etc.). In the present work the swelling ratio will be used. The swelling ratio (Q) can be expressed as following:

$$Q = \frac{w_t - w_d}{w_d} \quad (15)$$

where w_t and w_d represent the weights of the swollen sample at time t and the weight of the dried sample (initial weight) respectively. To ensure the reliability of the work and the benefit of data in the statistical analysis, experiments were carried out on 4 samples for each concentration (Pb and/or Borax) within each group (E0BxPb, E25BxPb, and ExB0Pb groups). The data to be displayed represents the arithmetic mean of these four samples. **Figure (2)** illustrates the dependence of mass on time and the swelling ratio on $\sqrt{t}$ for the three groups of samples.

From **Figure (2)** and by following the change of mass over time for all samples, one can note that the behaviour follows the same trends for all samples, as the mass increases at a high rate due to the absorption of the solvent. This behaviour is attributed to the large concentration gradient difference inside and outside the samples, then the rate of mass change decreases as the concentration inside the samples approaches to the equilibrium state.

Figure (3) represents the data by vertical graph as well as 3D Pipe chart for the three groups after swelling time of 225min. It is also noticed that for the samples which contain a different concentration of lead and zero borax (E0BxPb), the swelling ratio increases with the increase of the lead concentration, as well as the sample that contains a fixed concentration of borax (E25BxPb), but the rate of change is relatively less than E0BxPb group.

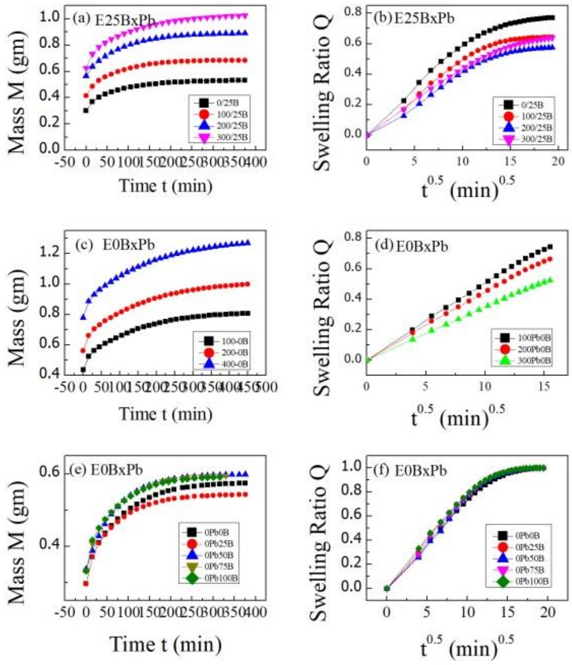

Figure (2):. Swelling kinetic curves for EPDM composite samples in toluene (a, c, e) mass change vs. time (min) and (b, d, f) swelling ratio vs. $t^{0.5}$ relations

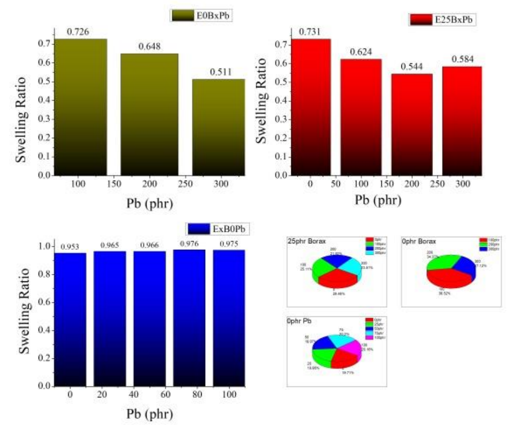

Figure (3): Vertical graph and 3D-Pipe chart presentation for the three groups of samples after swelling time of 225min

The calculated values of the swelling parameters (rubber volume fraction (V_r), swelling ratio percentage Q_∞% at equilibrium or saturation, crosslink density (ν_e), swelling index (n), and the diffusion coefficient (D)) are listed in **Table (3)**, **Table (4)**, and **Table (5)** for the three groups of samples.

Table (3): The calculated swelling parameters for the group E0BxPb

Sample	Mnon (gm)	Ms (gm)	V_r	$Q\infty$ %	υ_e x 10^{-4}	n	D × 10^{-4} cm^2/sec
E0B0Pb	0.30	0.58	0.50	91.71	11.76	0.50	1.62
E0B100Pb	0.44	0.81	0.53	84.30	14.97	0.49	1.11
E0B200Pb	0.56	0.99	0.55	77.56	17.26	0.49	1.00
E0B400Pb	0.77	1.25	0.60	62.61	24.47	0.49	0.92

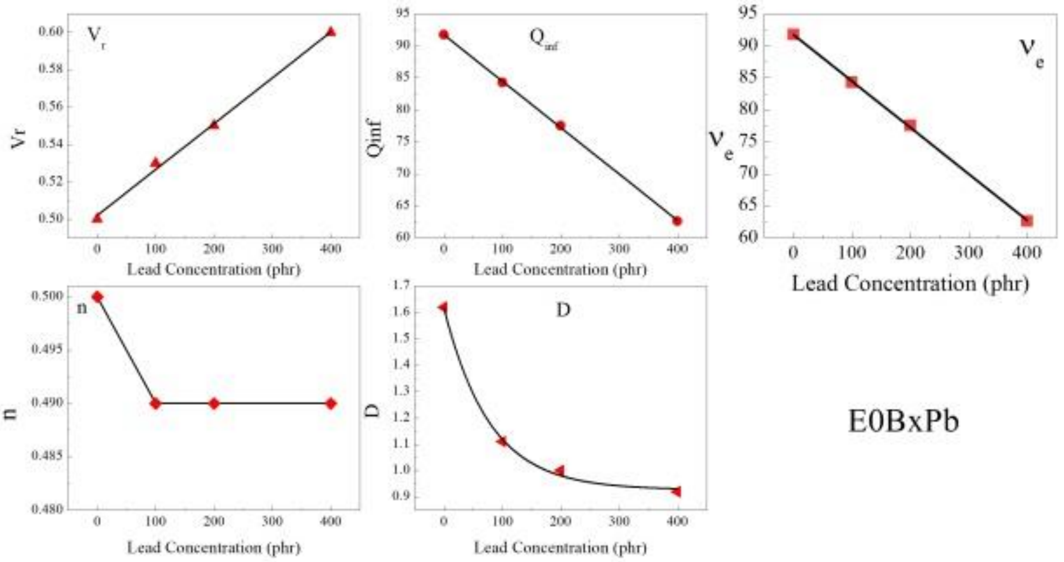

Figure (4): Graphic presentations for the swelling parameters for samples loaded with 100, 200, and 400phr lead and zero borax

For the 1st group (E0BxPb), the crosslink density increases as the lead concentration increase, this can be attributed to the increases of the interaction between the filler and the EPDM rubber (**Table (3)**) and so, the free volume, between EPDM molecules, is reduced. Also, the distance between crosslinks shortens. This in turn will leads to less solvent swelling. The experimental result showed that as the reinforced lead filler increase the percentage of volume swelled decrease. Adding 400phr lead increase the crosslink density to 24.47 $\times10^{-3}cm^{-3}$ (108%) and the swelling at saturation decrease to 62.61% (29%). Also, the diffusion coefficient (which represents the degree of flow of solvent through the crosslinks of the polymer) decrease to 0.924 cm^2/sec (i.e. 43%). The rubber volume fraction increases from 0.5 to 0.6 (20%) for sample loaded with 400phr lead. The value of the swelling index remains around 0.5 for all samples loaded with lead without borax loading.

The values of **Table (3)** are graphically represented in **Figure (4)**. The parameters V_r, Q_∞, and ν_e can be represented as straight lines and the fitting parameters were listed on the figures. The diffusion coefficient decreases exponentially and can be represented by exponential decay function with the fitting parameters listed on the figure.

The results of adding 25phr borax to the samples of EPDM rubber loading with 0, 100, 200, and 300phr lead powder (E25BxPb) are shown in **Table (4).** The addition of borax and lead together leads to a decrease in the crosslink density and the rubber volume fraction decrease. This can explain as follow, chemical reaction occurs between lead borax and the energy of the reaction break the weak covalent bond (σ bond π bond)

Table (4): The calculated swelling parameters for the group E25BxPb

Sample	Mnon (gm)	Ms (gm)	Vr	$Q\infty$ (%)	$\upsilon_e \times10^{-4}$	n	D × 10^{-4} (cm^2/sec)
E25B0Pb	0.30	0.54	0.54	78.95	15.65	0.45	1.84
E25B100Pb	0.43	0.71	0.49	67.16	9.05	0.53	1.95
E25B200Pb	0.56	0.90	0.44	62.15	7.84	0.52	1.92
E25B300Pb	0.64	1.06	0.39	65.92	5.27	0.43	1.25

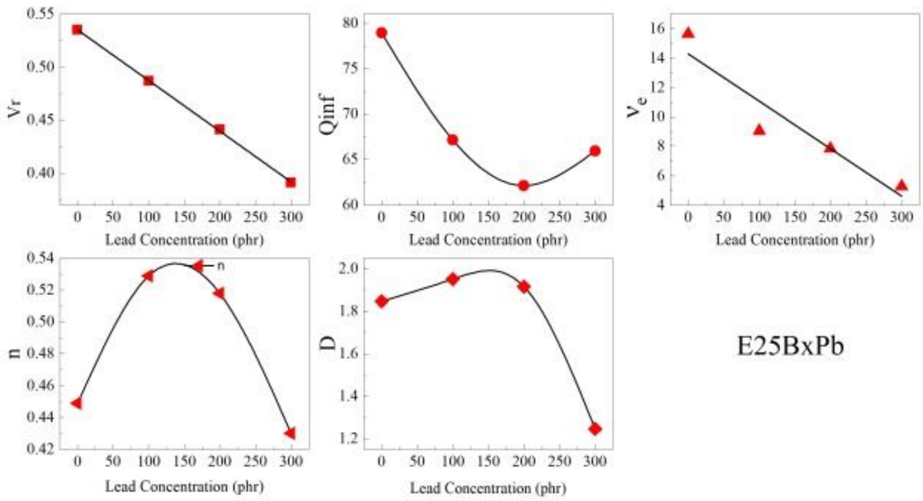

Figure (5): Graphic presentations for the swelling parameters for samples loaded with 25phr borax and 100, 200, and 300phr lead.

It is evident from **Table (5)** that adding borax alone to the EPDM samples (ExB0Pb) had no appreciable impact on either the crosslink density or swelling behaviour. **Figure (6)** shows the data graphically, and it can be seen that there is no discernible trend in the data.

The results of **Table (3)** for group E0BxPb, agree with theoretical expressions such as the equation developed by kroaus and Cunneen – Russell, which originally derived by Lorentz parks, one find that V_{rf} of the rubber filled with lead always much higher than in the pure gum V_{or}, so that the ratio V_{or} / V_{rf} decreases with increase the filer loading also $\frac{Q_f}{Q_g}$ is decreases with increase the filler loading, as shown in **Table (6)**

Table (5): The calculated swelling parameters for the group ExB0Pb

Sample	Mnon (g)	Ms (g)	Vr	$Q\infty$ (%)	υ_e x10^{-4}	n	D × 10^{-4} (cm^2/sec)
E0B0Pb	0.30	0.58	0.50	91.71	11.76	0.50	1.62
E25B0Pb	0.30	0.54	0.54	78.95	15.65	0.45	1.85
E50B0Pb	0.32	0.60	0.50	88.72	11.36	0.46	1.59
E75B0Pb	0.34	0.60	0.51	78.06	12.91	0.48	1.83
E100B0Pb	0.33	0.59	0.52	76.49	11.12	0.45	1.70

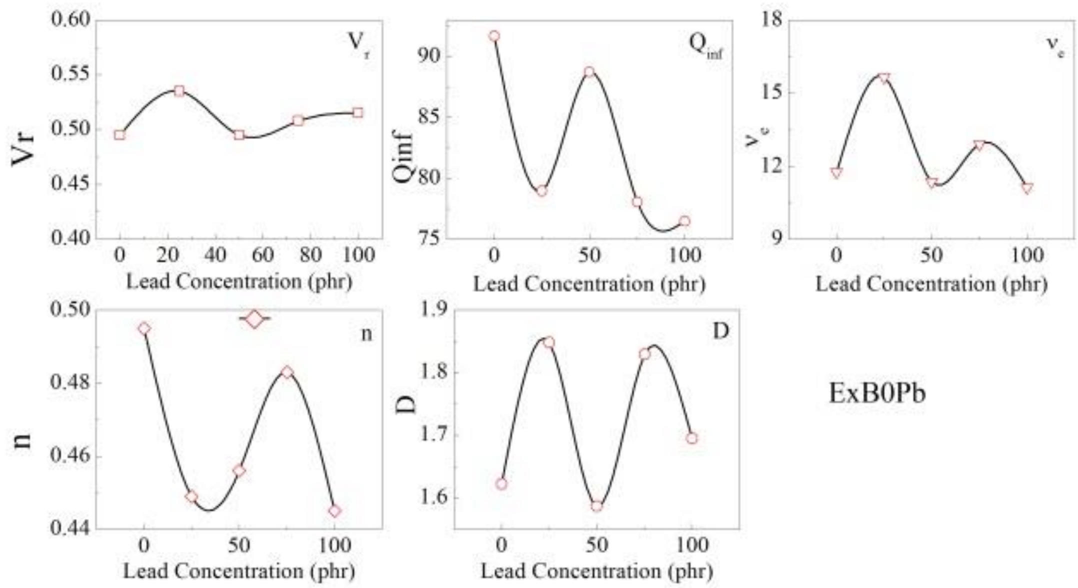

Figure (6): Graphic presentations for the swelling parameters for samples loaded with 0,25, 50, 75, and 75 borax and zero phr lead

***Table (6)**: The values of $\frac{V_{ro}}{V_{rf}}$ ratio, swelling at saturation, $\frac{Q_f}{Q_g}$ ratio, and filler volume fraction V_r.*

Sample	Vr	$\frac{V_{ro}}{V_{rf}}$	Q	$\frac{Q_f}{Q_g}$	Z	e^{-z}	$\frac{z}{1-z}$
E0B0Pb	0.50	1	91.71	1.00	0.00	1.00	0
E0B100Pb	0.53	0.94	84.30	0.92	0.038	0.96	0.03
E0B200Pb	0.55	0.90	77.56	0.85	0.071	0.93	0.08
E0B200Pb	0.60	0.83	62.61	0.68	0.131	0.88	0.15

4.2. ANOVA analysis

Moreover, to verify the significance of the lead, borax and borax/lead fillers on the swelling properties of EPDM rubber, one way ANOVA statistical analysis were implemented on the results obtained from the swelling which are reported in **Tables (7)** by using Minitab 17 software. During the one-way ANOVA, effect of weight ratio of lead powder, borax, lead/borax (wt%) on the crosslink density (υ_e), Rubber volume fraction (V_r) and swelling index (n) were examined independently. The results of one-way ANOVA are given in **Table (7)**. In **Table (7)**, df indicates degrees of freedom, SS shows sum of squares, MS indicates mean square. Moreover, F, Fcrit, and P values are essential to decide whether the significance of the input parameters (filler weight ratios) have an effect on the swelling parameters (V_r, n and υ_e) because F and P values are used to establish null hypotheses [24].

The normal distribution of the original data was determined by plotting residual graphs, as shown in **Figure (7)**. The response for the input parameters (n, V_r and υ_e) percentage followed the normal distribution and there is no obvious problem with normality and that no response transformation is required. The non-systematic behavior of the plot in **Figure (8)** implies that the variance of the original data remains constant for each value of the response.

Using the Boxplot method **(Figure (9))**, the effect of adding lead and borax can be investigated individually for the three groups (E0BxPb, ExB0Pb, and E25BxPb). **.** From the figure, one can conclude that the variability or the range of change in the values of the swelling parameters is large for the groups that contain lead (ExB0Pb and E25BxPb) than the group of borax (ExB0Pb). It was also noticed that there is an overlap between the values of the response parameters for both groups ExB0Pb and E25BxPb, while there is a significant change, whether increase or decrease for E0BxPb.

Through these results, it is clear that lead plays a major role in influencing swelling parameters, and this is consistent with the previously presented results.

Tukey pairwise comparisons[25]

The post-tests must be used in order to pinpoint which pairs of those groups are responsible for the differences between the three groups in our study. It is well recognized that post-tests are not utilized when comparing only two groups, but that they must be used when comparing more than two groups. In this work, we'll tackle this issue using the Tukey pairwise comparisons test. Tukey's simultaneous test for differences of means of the response factor will be achieved after the means are paired, the differences between the means are calculated, and the results are presented. **Table (8)** contains the results for each response factor.

The pairs that have p-values below the 0.1 level of significance are significantly different from one another. The results are summarized in **Table (8)** and graphically represented in **Figure (10).**

Remark: The means that do not share the same letter are significantly different from each other.

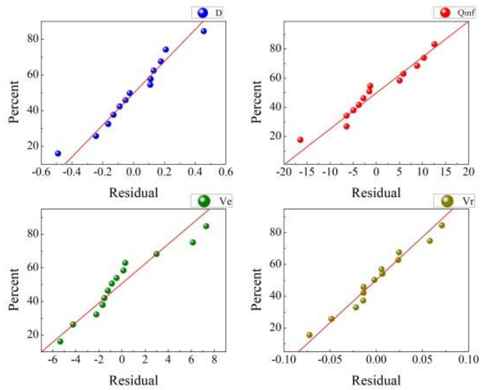

Figure (7): Graphs of normality (percent vs. residuals) for (a) Diffusion (b) Qinf (c) Crosslink density (d) Rubber volume fraction

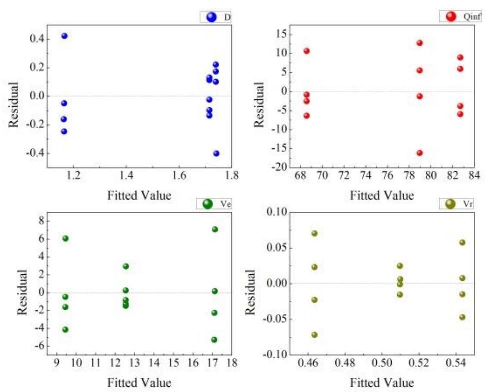

Figure (8): Graphs of normality (fitted value vs. residuals) for (a) Diffusion (b) Qinf (c) Crosslink density (d) Rubber volume fraction

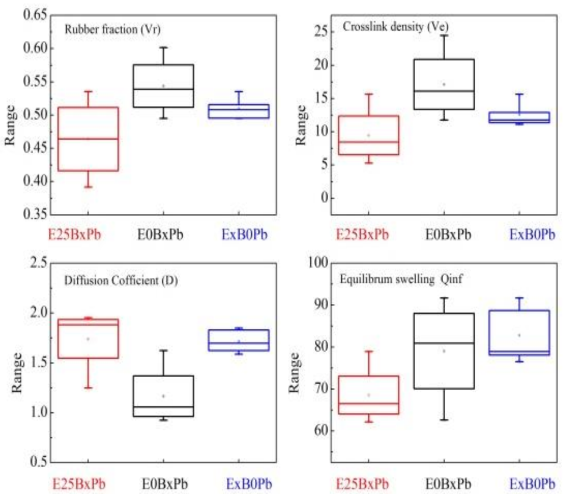

Figure (9): One-way ANOVA results in a boxplot form on each of the swelling parameter's D, Vr, υe and n respectively

The following observations can be prompted from the analysis of the Tukey test:

- There are statistically significant differences between the group E0BxPb and the group E25BxPb for the three swelling parameters υ_e, V_r, and D.
- With regard to the swelling parameter Q_∞, there are statistically significant differences between the group (ExB0Pb) and the other containing lead (E25BxPb).
- The diffusion coefficient shows statistically significant differences between the borax group ExB0Pb with the lead group (E0BxPb), while no significant difference appears for the rest of the treatments. This result for the diffusion coefficient can be expected by looking at the boxplot.

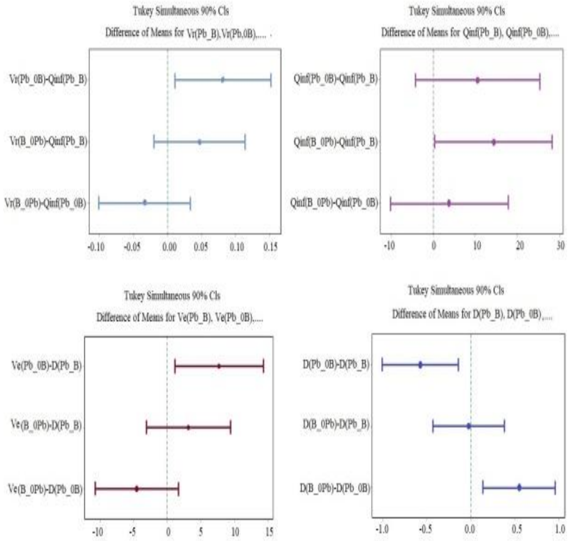

Figure (10): Tukey test results, with significance level of 0.1for the swelling parameters V_r, Q_∞, υ_e, and D

Table (7): One way ANOVA statistical analysis for the swelling parameters (response factors)

Rubber Volume Fraction (Vr)						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.013	2	0.006	3.48	0.07	4.10
Within Groups	0.019	10	0.002			
Total	0.031	12				
Swealing at Equilibrium (Qinf)						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	469.1	2	234.5	2.89	0.10	4.10
Within Groups	809.8	10	80.97			
Total	1278.8	12				
Crosslink Density (υe)						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	119.0	2	59.5	3.72	0.06	4.10
Within Groups	159.9	10	16.0			
Total	278.9	12				
Diffusion Coefficient (D)						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.88	2	0.44	6.40	0.01	4.10
Within Groups	0.68	10	0.07			
Total	1.56	12				
Swelling Index (n)						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.01	2	0.01	0.90	0.44	4.10
Within Groups	0.01	10	0.01			
Total	0.01	12				

Table (8): Grouping Information Using the Tukey Method and 90% Confidence

Factor		N	Mean	Grouping	
Rubber volume fraction (Vr)					
Pb_0B	Group1	4	0.5437	A	
B_0Pb	Group2	5	0.5099	A	B
Pb_B	Group3	4	0.4638		B
Swealing at Equilibrium (Qinf)					
B_0Pb	Group1	5	87.87	A	
Pb_0B	Group2	4	79.04	A	B
Pb_B	Group3	4	68.55		B
Diffusion Coefficient (D)					
Pb_B	Group1	4	1.741	A	
B_0Pb	Group2	5	1.716	A	
Pb_0B	Group3	4	1.165		B
Crosslink Density (υe)					
Pb_0B	Group1	4	17.110	A	
B_0Pb	Group2	5	12.560	A	B
Pb_B	Group3	4	9.450		B

5. Conclusion:

The main objective of this study was to prepare a group of rubber composites based on EPDM and loaded with different concentrations of lead powder and borax and investigate the effect of these additives on the swelling properties of the composite samples. The host composite sample was prepared using the two-roll mill technique at room temperature. Several additives, such as carbon black, zinc oxide acid, and stearic acid were used in the preparation process. The sample was vulcanized using sulfur. Three groups of the composite were prepared in addition to the basic (host) composite sample. The first group was loaded with different phr of lead powder, while the second group was loaded with different phr of borax, and finally, the third group was loaded with different phr of lead and borax together. The results showed that the crosslink density increase as the amount of lead increase and the ability of the sample to swell decrease. In contradiction, it is observed that the samples contain different phr lead and 25phr borax the crosslink density decreased, and the samples swelled to high extent. Adding borax only to the samples had no considerable effect on the crosslink density and on the swelling behavior. Also, the swelling index has been obtained to all samples. The result showed that n ~ 0.5 which Fickian diffusion. Two models (Kraus and Cunnen – Russel) were applied to test the filler rubber interaction. The models give a good result with the experimental data.

One-way ANOVA statistical analysis was used to learn more about the impact of lead, borax, and the two substances together on swelling behavior. The statistical findings supported the practical findings, and the post-test Tukey method was employed to determine the significance of differences between group averages.

6. Conflicts of interest

"The authors have no relevant financial or non-financial interests to disclose."

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8. References

[1] J.W. Noordermeer, Ethylene–propylene elastomers, Encyclopedia of polymer science and technology, (2002).

[2] R. Mounir, M.M. El-Zaya, Thermal and Physico-Mechanical Properties of Irradiated Aluminum Oxide Filled Ethylene Propylene Diene Monomer Rubber Composites, Arab Journal of Nuclear Sciences and Applications, 54 (2021) 89-95.

[3] L. Valentini, M.A. Lopez-Manchado, Classification of rubbers and components for harsh environmental systems, in: High-Performance Elastomeric Materials Reinforced by Nano-Carbons, Elsevier, 2020, pp. 1-14.

[4] A. Kumar, R. Choudhary, A. Kumar, Characterisation of asphalt binder modified with ethylene–propylene–diene–monomer (EPDM) rubber waste from automobile industry, Road Materials and Pavement Design, 22 (2021) 2044-2068.

[5] A.B. Bhattacharya, A.T. Raju, T. Chatterjee, K. Naskar, Development and characterizations of ultra-high molecular weight EPDM/PP based TPV nanocomposites for automotive applications, Polymer Composites, 41 (2020) 4950-4962.

[6] N. Uthaipan, M. Jarnthong, Z. Peng, B. Junhasavasdikul, C. Nakason, A. Thitithammawong, Effects of cooling rates on crystallization behavior and melting characteristics of isotactic polypropylene as neat and in the TPVs EPDM/PP and EOC/PP, Polymer Testing, 44 (2015) 101-111.
[7] C.-W. Lin, C.-H. Chien, J. Tan, Y.J. Chao, J. Van Zee, Chemical degradation of five elastomeric seal materials in a simulated and an accelerated PEM fuel cell environment, Journal of Power Sources, 196 (2011) 1955-1966.
[8] T. Cui, Y. Chao, J. Van Zee, Stress relaxation behavior of EPDM seals in polymer electrolyte membrane fuel cell environment, international Journal of hydrogen energy, 37 (2012) 13478-13483.
[9] Y. Jing, Z. Cui, H. Zou, J. Tu, X. Jiang, X. Shi, Z. Yong, S. Liu, G. Liu, Three-dimensional solubility parameters of natural rubber and its predictive power in diffusion coefficients, Journal of Applied Polymer Science, 139 (2022) 51473.
[10] N. Kumar, K.P. Singh, A. Giri, S.P. Singh, Transport mechanism and diffusion kinetics of kerosene through polynorbornene rubber/natural rubber blends, Polymer Bulletin, (2021) 1-21.
[11] H. Gao, F. Chen, R. Cai, S. Ye, F. Tan, W. Xiong, Y. Yi, W. Hu, The diffusion of components from propellant and liner at the interfaces of EPDM insulation, Propellants, Explosives, Pyrotechnics, 46 (2021) 460-467.
[12] X. Jiang, X. Yuan, X. Guo, F. Zeng, G. Liu, Determination of three-dimensional solubility parameters of HNBR/EPDM blends and the transport behaviors in ester solvents, Journal of Applied Polymer Science, 139 (2022) e52881.
[13] X. Jiang, X. Yuan, X. Guo, F. Zeng, H. Wang, G. Liu, Study on the application of Flory–Huggins interaction parameters in swelling behavior and crosslink density of HNBR/EPDM blend, Fluid Phase Equilibria, 563 (2022) 113589.
[14] M.D. Stelescu, A. Airinei, A. Bargan, N. Fifere, M. Georgescu, M. Sonmez, M. Nituica, L. Alexandrescu, A. Stefan, Mechanical Properties and Equilibrium Swelling Characteristics of Some Polymer Composites Based on Ethylene Propylene Diene Terpolymer (EPDM) Reinforced with Hemp Fibers, Materials, 15 (2022) 6838.
[15] İ.K. Akbay, A. Güngör, T. Özdemir, Optimization of the vulcanization parameters for ethylene–propylene–diene termonomer (EPDM)/ground waste tyre composite using response surface methodology, Polymer Bulletin, 74 (2017) 5095-5109.
[16] C. Vidyasagar, B.M. Flores, V. Jiménez-Pérez, P. Gurubasavaraj, Recent advances in boron-based schiff base derivatives for organic light-emitting diodes, Materials today chemistry, 11 (2019) 133-155.
[17] R. Kumar, A. Karkamkar, M. Bowden, T. Autrey, Solid-state hydrogen rich boron–nitrogen compounds for energy storage, Chemical Society Reviews, 48 (2019) 5350-5380.
[18] C. Li, Y. Ding, Z. Yang, Z. Yuan, L. Ye, Compressive stress-thermo oxidative ageing behaviour and mechanism of EPDM rubber gaskets for sealing resilience assessment, Polymer Testing, 84 (2020) 106366.
[19] V. Kumar, P.K. Koorata, U. Shinde, P. Padavu, S.C. George, Review on physical and chemical properties of low and high-temperature polymer electrolyte membrane fuel cell (PEFC) sealants, Polymer Degradation and Stability, (2022) 110151.
[20] F.B. Gul, N. Baydoganb, Synthesis of Poly (methyl methacrylate) with Borax Decahydrate Adition for Energy Applications, ICSEEC: Sustainable Energy and Energy Calculations, (2020) 21.
[21] M. Barlkani, C. Hepburn, Determination of crosslink density by swelling in the castable polyurethane elastomer based on 1/4-cyclohexane diisocyanate and para-phenylene diisocyanate, Iranian Journal of Polymer Science & Technology, 1 (1992) 1-5.
[22] G. Ovejero, P. Perez, M. Romero, I. Guzman, E. Dı, Solubility and Flory Huggins parameters of SBES, poly (styrene-b-butene/ethylene-b-styrene) triblock copolymer, determined by intrinsic viscosity, European polymer journal, 43 (2007) 1444-1449.
[23] N. Yavari, S. Azizian, Mixed diffusion and relaxation kinetics model for hydrogels swelling, Journal of Molecular Liquids, 363 (2022) 119861.
[24] J. Shreffler, M.R. Huecker, Hypothesis testing, P values, confidence intervals, and significance, in: StatPearls [Internet], StatPearls Publishing, 2022.
[25] T.-a. Shiraishi, All-Pairwise Comparison Tests, in: Multiple Comparisons for Bernoulli Data, Springer, 2022, pp. 31-43.