The link between swelling ratios and physical properties of EPDM rubber compound having different oil amounts

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Abstract
This new observation demonstrated that an increase in oil amounts within ethylene propylene diene monomer (EPDM) compounds decreased the crosslink density and the storage modulus but increase the elongation at break after tensile testing. The compounds with high oil amounts were observed to release oil particles when dissolved in toluene solutions and that increased their swell ratios. Consequently, the crosslink density had a perfect negative linear correlation with the elongation at break and a strong power-law correlation with the swell ratios. This work guides the material chemists and engineers during compound formulations when an increase in oil amounts is required.

Keywords Crosslinking network density · Storage modulus · EPDM rubber · Processing oil · Swell ratio

Introduction
Many synthetic elastomers are used in rubber formulation companies as gloves, seals in pipes, roofing sheets etc. [1]. Generally, the crosslink networks after vulcanization of those synthetic rubbers are fixed by the vulcanization agents such as sulphur and accelerator amounts and at times on their ratios used [2]. The crosslink density which is the fraction of crosslinking junctions per unit volume in a polymer network promotes stiffer material when the number of junctions is high [3]. One of the important rubber recipes that lower the viscosity and improve the mixing and processing of the rubber compound is the processing oil [4, 5] but the addition of the processing oil also promotes good compatibility between the ingredients, reduces the forces between the rubber polymer chains and lowers their glass transition temperatures because they act as plasticizers [6]. After vulcanization, the influence of the processing oil amount on the crosslink densities within synthetic rubber compounds has not been studied. This work investigates how the oil amount in vulcanized synthetic rubber compounds affects the crosslinking density and goes further to illustrate how to calculate/estimate the various parameters that are associated with swelling, crosslinking density as well as determining morphologies obtained as a result of increasing oil amount.

Ethylene propylene diene monomer (EPDM) rubber compound which is normally used in sealing, construction, pipeline, heat dissipation, insulation and water separation applications [7] was used because the compound has good resistance to ozone, water and weathering [8, 9]. The EPDM elastomer which consists of terpolymerization of ethylene, propylene, conjugated diene was mixed with a varied amount of processing oil while maintaining other recipes such as accelerator, anti-oxidant, and vulcanizing agent [10, 11].

The swelling of polymers is normally influenced by their crosslinking densities [12] such that the lower the chain network density, the higher their capacity to accommodate more solvent molecules [13, 14]. Conversely, higher crosslink density makes the polymer chains hard to stretch and that minimises spaces between the chains as well as limits the solvent molecule absorptions into the networks. In the swelling method, the swell ratio which is the maximum equilibrium swelling state reached during the absorption of the solvent molecules can be determined [15, 16]. In that method, the swell ratio is determined by measuring the swollen polymer's volume or weight increment until swelling equilibrium is reached [17]. In this work, the swell ratio is defined as:
swell ratio\( (\nu_r) = \frac{(w_s + w_d)}{w_d} \)  \hspace{1cm} (1)

where \( w_d \) is the initial weight of the rubber, and \( w_s + w_d \) is the weight of swollen rubber which is the total weight of the rubber \( (w_d) \) and the solvent \( (w_s) \) \([17]\).

Using Flory-Rehner’s equation \([18]\), the swell ratio can be related to the crosslink density \( (\rho_c) \) by;

\[
\rho_c = -\frac{[\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2]}{V_s(\phi_2^{1/3} - \phi_2/2)} \hspace{1cm} (2)
\]

where \( V_s \) is the molar volume of solvent. \( \phi_2 \) is the ratio of the volume of an unswollen network to the volume of the swollen network at equilibrium \([19]\) and given calculated by;

\[\phi_2 = 1/V_r\]  \hspace{1cm} (3)

The \( \chi \) is the Flory–Huggins interaction parameter \([20]\), which can be determined by;

\[
\chi \cong 0.34 + \frac{V_s(\delta_s - \delta_r)^2}{RT} \hspace{1cm} (4)
\]

where \( \delta_s \) is the solubility parameter of solvent, \( \delta_r \) solubility parameter of polymer, \( R \) is the gas constant (i.e. 8.3144598 J/mol) and \( T \), the environmental temperature.

Normally, the crosslinking densities can be modified by varying the vulcanizing agents (i.e. accelerator and ratio contents) \([21, 22]\). The vulcanizing agents were found to influence the crosslink concentrations when conventional, semi-efficient, efficient and nitrosamine-safe systems were used \([22]\). Other curing composition systems (i.e. zinc oxide, accelerator, sulphur, carbon black, and processing equipment, etc.) age when they come into contact with other solvents such as toluene.

Materials and methodology

EPDM compound design of experiment

The compound recipe shown in Table 1 was designed with the sole aim of keeping most of the constituents constant but varying the amount of the processing oil. To achieve this, both a dry EPDM polymer and an oil EPDM polymer known as Vistalon 3666 \([25]\) were used to provide good mixing and processing while maintaining the required stiffness values. The activators, plasticizer, sulphur, carbon black, and accelerator amounts were all kept constant but the paraffin oil contents were varied as shown in Table 1. All the compounds were mixed and cured at 165 °C for 10 min by LOSCA 20 TON Compression Molder at Clwyd Compounders Ltd, Wrexham, United Kingdom, and were delivered as vulcanized EPDM rubber compounds having 0, 15, 25, 35 and 45 phr oil contents. The company reported shore A hardness values of 80, 65, 60, 55 and 50 for the 0, 15, 25, 35 and 45 phr oil contents, respectively. For the swelling investigations, samples were prepared from each EPDM compound material by cutting square size samples of about 2 cm x 2 cm with thicknesses of about 2.5 mm. The samples for the physical properties were cured in their respective sizes and were treated under the same conditions.

Analytical methods

Tensile test

Dumbbell-shaped material specimen sizes according to ISO 37:2017 \([26]\) were stamped out from flat vulcanized plates (~2 mm thicknesses) and were tested at room temperatures. An Instron 4301 tensile testing machine with an LT extensometer was used for the investigations at a strain rate of 500 mm/min.
Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) was used to determine the loss factor (i.e. tan delta), storage and loss moduli of the compounds. The test was done on a TA Instruments AR200 rheometer using a 20 mm diameter plate geometry and a gap of 2500 µm. All measurements were conducted at 25 °C with frequency sweeps between 0.01 and 200 Hz at 1.0% strain.

Scanning electron microscopy (SEM) measurements

SEM measurement was performed by TESCAN MIRA-3 FEG SEM and this was supported by a field emission scanning electron offering multiple images to a computer. For this experiment, the rubber samples were coated with thin film conductive layers [27] because EPDM rubber compound is a non-conductive material which cannot reflect electrons. To do this, thin gold films of about 10 nm were sprayed on the samples to obtain high-quality SEM images and the images were captured by an accelerating voltage of 5 kV and a working distance between 6.0 mm to 6.5 mm.

Swelling experiment

The swelling experiments were performed by immersing square-sized samples into toluene solutions placed within separate glass dishes (Fig. 1). Each glass dish was filled with 75 ml of toluene and watch glasses were used to cover the dishes to prevent the evaporation of the toluene.

Table 1  EPDM compound recipe having different oil contents

| Formulation recipe | 45 phr oil (%) | 35 phr oil (%) | 25 phr oil (%) | 15 phr oil (%) | 0 phr oil (%) |
|--------------------|----------------|----------------|----------------|----------------|---------------|
| EPDM Polymer       | KEP 240        | 40             | 40             | 40             | 40            | 80            |
| Oil EPDM Polymer   | Vistalon 3666  | 105            | 105            | 105            | 105           | 35            |
| Effective Activator| Stearic Acid   | 1              | 1              | 1              | 1             | 1             |
| Effective Plasticizer| Rhenosin C100 | 2              | 2              | 2              | 2             | 2             |
| Sulphur            | S M300 80      | 2.5            | 2.5            | 2.5            | 2.5           | 2.5           |
| Low grade Carbon Black | FEF N550 ULTRA | 100           | 100           | 100           | 100           | 100           |
| Activator for Sulfur| Zinc Oxide    | 5              | 5              | 5              | 5             | 5             |
| Paraffin oil       | PAR Oil        | 45             | 35             | 25             | 15            | 0             |
| Semi-ultra accelerator | MBT 80      | 1.88           | 1.88           | 1.88           | 1.88          | 1.88          |
| Rhenogran® TMTM-80= Accelerator | TMTM 80  | 1              | 1              | 1              | 1             | 1             |
| Rhenogran ZDBC= Accelerator | ZDBC 80  | 3.13           | 3.13           | 3.13           | 3.13          | 3.13          |

Phr Parts per hundred rubber

Fig. 1  Swelling of EPDM samples in toluene solvents. Samples within the set-up are from the a 0, b 15, c 25, d 35 and e 45 phr oil compounds
solutions. The samples were periodically removed, dried on paper (to remove excess toluene) and weighed until no more absorption or changes in weights were observed. For each compound, the average weight obtained from three specimens was used to calculate the swell ratio using Eq. (1). This enabled the calculation of the $\phi_2$ value which is the volume of the unswollen network to the volume of the swollen network at equilibrium as defined in Eq. (3).

In this experiment, $V_s$ and $\delta_s$ for toluene solvent were 106.5 cm$^3$/mol and 18.2 (MPa)$^{1/2}$ [28], respectively, while $\delta_r$ for EPDM was 16.3 (MPa)$^{1/2}$ [29], $R$ value used was 8.3144598 J/mol.K and $T$ is at 300 K. The $\chi$ used in our experiment was calculated using Eq. (4) as shown below:

$$\chi \cong 0.34 + \frac{106.5(18.2 - 16.3)^2}{8.3144598 \times 300} \quad (5)$$

$$\chi \cong 0.34 + \frac{106.5 \times \left(\frac{cm^3}{mol} \times (1.9 \times J^{1/2} \times cm^{-3/2})^2}{8.3144598 \times \left(\frac{J}{mol.K}\right) \times 300K} = 0.494 \quad (6)$$

(Note: 2.045 $J^{1/2} \times cm^{-3/2} = 2.045$ MPa$^{1/2}$). The $\chi$ obtained is in agreement with previous of $\chi = 0.4913$ [28].

Results

Physical properties of the EPDM compounds

The coercive stiffness of the materials measured, with the tensile test, revealed that the stiffness decreases with increasing oil amount (Fig. 2) and this confirms the shore A values produced by the manufacturer. This means that compounds with less or no oil turned out to be very elastic than those with more oil. Consequently, there was lower elongation at break and high storage modulus (i.e. more elastic) for the 0 phr oil content material than the 35 and 45 phr oil content compounds. The recorded Young moduli of 6.93, 3.40, 3.00, 2.70 and 2.50 MPa were obtained for the 0, 15, 25, 35 and 45 phr oil compounds, respectively.

There was also an observable increase in the surface roughnesses found on the SEM images (Fig. 3) which gave new evidence of the fact that the surface textures or roughnesses were increasing with the oil amount. Referring to Fig. 3, it can be seen that the morphology of the 0 oil is smoother than that of the 45 phr amount compound. The rough surface morphologies from the higher oil amount compounds were attributed to the residual oil particles after vulcanization that might have diffused to the material-air interface due to space requirements. It may also be argued that there were difficulties in obtaining good oil particle dispersion within the samples when the oil amount is high but this was not verified.

During the DMA experiments, there were no significant changes in the loss factor and modulus results but the storage modulus data showed some differences in the dynamic stiffness of the compounds at low frequencies (Fig. 4). Normally, certain frequency sweeps measured at constant temperatures can be compared to temperature sweep measurements that provide similar required results [30] by using the William-Landel-Ferry equation when shift factors are used to establish a temperature master curve [31]. In Fig. 4, the peaks at low frequencies suggest that the less oil content compounds have higher stiffness (i.e. more elastic at low temperature) than the more oil compounds which might also be attributed to more crosslink network densities within the zero oil compounds because there were less free volumes as a result of the unavailability of plasticization within the chains. In previous studies [32–34], the elastic peak positions on the storage modulus were linked to the glass transition temperature ($T_g$) which is dependent on both the crosslink density and the crosslinking type but this was outside the scope of this investigations. It is also known that the dynamic stiffness can also be varied by altering the amount of fillers such as carbon black, accelerators, sulphur, etc. [35–37] within the compound.

Swelling results

During the swelling experiment, the average weights of the specimens shown in Fig. 1 were measured at specific periods. Table 2 shows the measured average weights of the specimens after six (6) days. The protocol described in
Appendix A were followed until no significant changes in the weights were observed. That indicated that the equilibrium swelling points were reached.

As described under the materials and methodology section concerning the calculation of the swell ratios and the crosslink densities, the data in Table 2 were used to calculate $\phi_2$ values using Eqs. (1) and (3) and the resulting data at the specific periods are as shown in Fig. 5. From Fig. 5, it is clear that there is a significant change in the absorptions of toluene solvent molecules and that is evident in the decreasing $\phi_2$ values until absorption limits are reached at the bottom. At equilibrium, the $\phi_2$ values remained almost constant and careful detailed analyses were made to get the average equilibrium points as the reported $\phi_2$ in table 5.

The changes in the swellability of the compounds as a result of the oil variations are very intriguing (Fig. 5) because they suggest that the oil particles influenced the crosslinking process by preventing them to have an effective crosslinking network because of the large free volume produced by the oil plasticization. It was also fascinating to see a similar trend in the DMA results because the lower oil compound had higher storage modulus peak (i.e. at lower frequencies) than those with the high oil amounts. Both results indicate that the more the oil amount, the less stiff the compound and the more absorption of the toluene molecules because the residual oil particles might have allowed toluene molecules to dissolve them and occupy their spaces.

Using Eq. (2), the $\phi_2$ values obtained were used in the calculation of the crosslink densities ($\rho_c$) as shown in Table 3. In the calculation (i.e. Table 3), $V_s = 106.5 \text{ cm}^3/\text{mol}$

### Table 2

| Time (h) | 0 phr oil | 15 phr oil | 25 phr oil | 35 phr oil | 45 phr oil |
|----------|-----------|------------|------------|------------|------------|
| 0        | 3.55      | 5.07       | 4.37       | 4.73       | 4.21       |
| 2        | 4.56      | 6.71       | 5.91       | 6.44       | 5.89       |
| 4        | 4.88      | 7.30       | 6.46       | 7.06       | 6.47       |
| 6        | 5.23      | 7.87       | 6.99       | 7.65       | 7.00       |
| 24       | 6.02      | 8.89       | 7.80       | 8.56       | 7.62       |
| 26       | 5.98      | 8.86       | 7.74       | 8.50       | 7.60       |
| 28       | 6.05      | 8.86       | 7.75       | 8.50       | 7.58       |
| 30       | 6.06      | 8.84       | 7.72       | 8.47       | 7.58       |
| 48       | 5.99      | 8.67       | 7.50       | 8.26       | 7.36       |
| 50       | 5.97      | 8.66       | 7.51       | 8.26       | 7.34       |
| 52       | 5.98      | 8.65       | 7.54       | 8.29       | 7.37       |
| 144      | 5.90      | 8.53       | 7.42       | 8.12       | 7.22       |

Fig. 3 SEM images showing surface morphologies of the a 0, b 15, c 25, d 35 and e 45 phr oil compounds

Fig. 4 DMA results showing plots of the storage modulus versus frequency sweep for the 0, 15, 25, 35 and 45 phr oil compounds
and $\chi = 0.494$ (from Eq. (6)) were used together with the $\phi_2$ values obtained to determine the corresponding $\rho_c$ for each compound. The $\rho_c$ values obtained were all in agreement with previous studies that obtained a maximum crosslink density of $0.0034 \text{ mol/cm}^3$ for EPDM even though efficient (i.e. less sulphur), semi-efficient (i.e. moderate sulphur), and conventional (i.e. more sulphur) vulcanization systems were used [38].

### Discussions

First of all, it can be concluded that the high the oil amounts, the lower the crosslink density (Table 3) and this is a new observation of how oil amount influences the crosslink densities of EPDM compounds. The implications are that increasing oil amount, improves mixing and processing and reduces the hardness of the compound but this new result adds to the fact that increasing oil amounts also reduce the crosslink densities. The influence of oil amount on the storage modulus can be understood because the oil particles can increase the dissipation energy of the compound such that the loss modulus and the tan delta would be increased with increasing oil amount [39]. Nevertheless, this work provides evidence for the fact that the softness and the decrease in dynamic stiffness can be attributed to the decrease in the crosslink densities because the residual oil amount that lowered the stiffnesses may have been displaced by the toluene solvent molecules during the swelling process.

In addition, results from this work can be compared to the slow curing rate of aliphatic chain length of fatty acids with zinc oxide in isoprene rubber that decreased the crosslink density and which was attributed to the high melting temperature associated with higher steric hindrance in the structure which made it more difficult to further react with the curing agents [40]. In this work, the implication is that those oil particles trapped within the chains (i.e. residual) might have caused the chains to swell and limit the formation of more crosslink networks during the vulcanization process. Hence, as illustrated in Fig. 6, enough free volumes may have been created when the toluene molecules dissolve those oil particles in the high oil amount compounds and allowed more toluene molecules to enter the less crosslinked network (Fig. 6d–f). On the other hand, there were no or fewer hindrances in the formation of crosslinks within the zero or less oil amount compounds during vulcanization. Thus, there was less dissolution of oil particles (Fig. 6a–c) and fewer toluene molecules could enter the highly crosslinked chains.

The above explanations can be backed by the detailed visual observations of the toluene solvents after the experiments found in Fig. 1. In Fig. 1, and the end of the swelling experiment, it can be seen that the toluene solutions around the more oil compounds became darker than that obtained from the zero or fewer oil amounts which were very clear and transparent. Further analysis after the experiment also revealed that there were some oil residuals in the beakers after filtering and drying the solvents in the fume hood. This gave evidence illustrated in Fig. 6 on the fact that some of the oil particles were displaced by the toluene molecules. Moreover, EPDM chains are easily absorbed by mineral and aromatic hydrocarbon oils [41] and that can also allow the EPDM chains to release the initial oil particles after vulcanization and accommodate the aromatic toluene molecules.

To produce a piece of plausible and understandable information on the measured results (i.e. Table 3), further analysis of the results revealed a linear positive correlation between the crosslink density and the maximum peak positions obtained from the storage modulus at small frequencies (Fig. 7a). The storage modulus was found to be sensitive to the crosslinking density within a poly(methyl methacrylate) polymer and was described to be due to the limitations of

### Table 3 A summary of results

| Oil content (Phr) | $\phi_2$ | $\rho_c$ ($10^{-3}$) | Storage Modulus* (MPa) | Elongation at break (%) |
|-------------------|---------|---------------------|------------------------|------------------------|
| 0                 | 0.593   | 2.30                | 0.890                  | 186.10                 |
| 15                | 0.572   | 2.00                | 0.658                  | 393.86                 |
| 25                | 0.563   | 1.88                | 0.153                  | 444.72                 |
| 35                | 0.555   | 1.78                | 0.224                  | 457.80                 |
| 45                | 0.553   | 1.75                | 0.130                  | 478.68                 |

Values were obtained from the highest peaks found on the storage modulus curves between 2 and 4 Hz.

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Fig. 5 A plot showing the ratio of unswollen network volume to the volume of the swollen network at equilibrium measured at different times for the 0, 15, 25, 35 and 45 phr oil amount compounds

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Fig. 6 A plot showing the ratio of unswollen network volume to the volume of the swollen network at equilibrium measured at different times for the 0, 15, 25, 35 and 45 phr oil amount compounds

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Values were obtained from the highest peaks found on the storage modulus curves between 2 and 4 Hz.
the chain mobility that enabled the storage of more energy because the chains are not allowed to slide past each other [42].

Another interesting observation is the negative linear correlation between the crosslink density and the elongation at break obtained from the tensile testing measurements (Fig. 7b). This means that the higher the crosslink, the higher the static stiffness and chain mobilities are hindered and it is very interesting to see that a similar result was also obtained when natural rubber vulcanizates with different vulcanization systems were used to vary the crosslink densities [43]. Using EPDM rubber compound with varied oil amounts, this result (Fig. 7b) promoted a very good correlation coefficient (i.e. square of the correlation coefficient, \(r^2 = 0.96\)) [44, 45] and could be used to extrapolate crosslink densities when the elongation at breaks are known.

Furthermore, another astonishing observation is the relation between the crosslink and the swell ratio that was modelled perfectly with the power law. This new observation proves that there is a power-law correlation between the crosslink network density from EPDM and swell ratio which can be used in modelling future theoretical and practical experiments.

**Conclusion**

In summary, the project has demonstrated a clear guide for calculating the Flory–Huggins interaction parameter, the swell ratio and the crosslink density that are beneficial to the material experimentalist. In addition to the above information, the results demonstrate how the crosslinking densities can be varied by using variation in oil amounts within EPDM compounds and showed variations in the storage moduli, elongation at breaks and the surface morphologies. It was noted that compounds with the same recipe but having 0, 15, 35 and 45 phr oil contents decreased in crosslink network densities and storage moduli but had increased elongation at break with increasing oil contents. The elongated at break and the crosslinking density values correlated with a negative linear correlation while the relation between the swell ratio and the crosslink density values were fitted superbly with the power law.

Furthermore, observations revealed that the toluene molecules were able to replace the processing oil particles in compounds with high oil amounts during the swelling process and increase their swell ratios. This work aims to guide material chemists and engineers to be cautious when increasing oil amounts in compound formulations.

**Appendix A**

**A.1 Equipment needed for the swelling experiment**

- Fume hood and toluene (minimum 100 mL per specimen).
- Weighing scales – must be an enclosed system.
- Glass dishes – 1 per specimen (must be at least 60 mm diameter and at least 8 mm deep) and watch glasses (suitable for covering the glass dish).
- Syringe – the larger the size the better. 20 mL minimum, 100 mL would be ideal (for transporting solvent from the toluene bottle to the glass dish).
- Stopwatch, tweezers and digital calliper/micrometer for measuring specimen dimensions.
Fig. 7 Analysis of the measured data showing plots of crosslinking density versus storage modulus (a), elongation at break (E@B) during the tensile testing (b) and swell ratio obtained from the swelling experiment (c).
A. 2 Method

1. Place all necessary apparatus, including the specimens and weighing scales, in the fume hood.
2. The samples must be weighed and the dimensions of the samples recorded.
3. Transfer 75 mL of toluene from the bottle to each glass dish using the syringe. The quantity of toluene will vary depending on the dimensions of the glass dishes but must cover at least the first 4 mm of the glass dish depth to ensure the samples are fully submerged.
4. Place the samples into the toluene filled dishes and record the start times.
5. The samples must be immersed in toluene until they are fully saturated with toluene solutions. This may take up to 5 days (or longer for certain chemical resistant rubber formulations).
6. The samples should be removed daily, dried on paper for a short period (30 s) and the weights recorded. If the weights remain approximately constant for two subsequent days then the samples are fully saturated.
7. The final weights and dimensions of the swollen samples must be recorded.
8. Toluene may evaporate during the experiment, therefore the quantity of toluene in the glass dishes should be checked and topped up daily.
9. Once the experiment has been completed, the specimens must be left in the fume hood to dry over a night and their weights must be recorded to ensure that they are similar to the initial weights.
10. The remaining toluene solutions in the dishes at the end of the experiment may be allowed to evaporate at the back of the fumehood. The glass dishes can then be cleaned once they are free from the solvents.

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Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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