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CHARACTERIZATION OF SWELLING PACKER EPDM ELASTOMERS

1. INTRODUCTION

As a reliable wellbore tools, swelling packers have reached their popularity and usability top owing to easy deployment and applicability in HP/HT well conditions. Made of rubbery swelling/sealing element and only few steel parts, packer's operating simplicity advanced the efficiency of oilfield operations these devices are used in, and that is casing cementation, intelligent well completions, coiled tubing systems, sand control, hydraulic fracturing, horizontal well completions and so on [1]. A typical swelling packer consists of an inner tube, a swelling elastomer and the end rings supporting the swelling elastomer. Sometimes, several layers can be found inside the swelling elastomer body – high swelling intensity core, low swelling intensity core and diffusion barrier (Fig. 1).
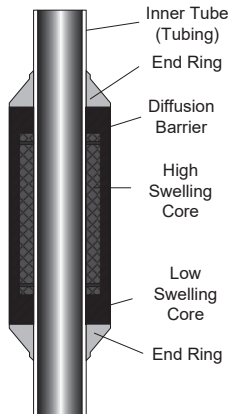

Fig. 1. Cross section view of swelling packer

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Each of the aforementioned layers has its purpose. Outer layers typically delay the onset of swelling depending on the time needed to run the swelling packer string. The inner layer has fast swelling properties.

Generally speaking, when talking about swelling processes, swelling packers are divided into two major groups: *Water Swelling Packers* and *Oil Swelling Packers*. For the purpose of this paper oil swelling packer elements were introduced and swelled through diffusion processes that occur as hydrocarbon molecules enter the rubber matrix due to a natural affinity of elastomer polymer and hydrocarbon molecules. This paper is focused on EPDM elastomers testing and characterization in an attempt to design and tailor a proper swelling element for the packer. For this purpose six different rubber samples were prepared.

Previous rubber testing in general was performed by many authors. References [2–7] show only a few examples. Some of the tests (performance assessment) on oil swelling elastomers were conducted by Al-Yami et al. [8, 9].

2. EXPERIMENTAL PART

Materials

Raw EPDM rubber (Dutral TER 4437 – 87%; Nordel IP 4725 P – 13%).
Solvent – crude oil ($\rho = 0.832$ kg/dm^3).

Compounding and vulcanization

The very first step in sample preparation is the rubber vulcanization which takes place after the homogenization process of all ingredients – raw EPDM rubber, sulfur as a crosslinking agent, vulcanization accelerators, zinc oxide (ZnO) as vulcanization activator, stearic acid as plasticizer, titanium oxide (TiO$_2$), clay and silica fillers, reclaimed rubber and swelling agent. The exact composition is given in Table 1.

Table 1
Composition of EPDM samples

Component	EPDM-1	EPDM-2	EPDM-3	EPDM-4	EPDM-5	EPDM-6
	PHR (parts per hundred)					
Raw EPDM rubber (Dutral TER 4437)	86.94	86.94	86.94	86.94	86.94	86.94
Raw EPDM rubber (Nordel IP 4725 P)	13.06	13.06	13.06	13.06	13.06	13.06
Fillers (clay and silica)	58.77	58.77	58.77	58.77	58.77	58.77
Stearic acid	1.22	1.22	1.22	1.22	1.22	1.22
Titanium dioxide (TiO$_2$)	8.98	8.98	8.98	8.98	8.98	8.98
Zinc oxide (ZnO)	0.82	0.82	0.82	0.82	0.82	0.82
Vulcanization accelerators	5.63	4.90	5.63	5.63	5.63	5.63
Sulfur (Rhenogran S-80)	0.73	0.73	2.44	0.73	0.73	0.73
Reclaimed rubber	–	–	–	–	61.22	102.00
Swelling agent	–	–	–	10.20	10.20	10.20

Vulcanization compounds were prepared in a vulcanization laboratory where they were homogenized and further put to press for the vulcanization maintaining temperature of 180°C for 7 minutes. From the obtained 2 mm sheets samples (80 × 40 × 2 mm) were cut for the swelling testing.

Swelling testing methods

Swelling in a glass dish

Swelling intensity of rubber samples in crude oil solvent at the room temperature in a glass dish was observed every 24 hours by drying and weighing through the period of swelling until the thermodynamic equilibrium state occurred. The state has been reached when no substantial swelling was noted. Swelling degree (α) was then determined as a difference in the mass of samples after and before the swelling, calculated by equation (1).

$$\alpha = \frac{m_2 - m_1}{m_1} \cdot 100\% \tag{1}$$

where:

m_1 – nonswollen sample mass [kg],
m_2 – swollen sample mass [kg].

The equilibrium swelling is expressed as a volume fraction of the polymer (rubber) sample in a swollen gel (φ), which is a fluid obtained by rubber-solvent interaction. It is calculated through equation (2).

$$\phi = \frac{\dfrac{m_1}{\rho_2}}{\dfrac{m_1}{\rho_2} + \dfrac{m_2 - m_1}{\rho_1}} \tag{2}$$

where:

ρ_1 – solvent density [kg/m³],
ρ_2 – sample density [kg/m³].

Swelling in Dynamic Linear Swell meter

OFITE Dynamic Linear Swell meter (Fig. 2) is a measuring device containing four units with cells inside where the swelling process takes place.
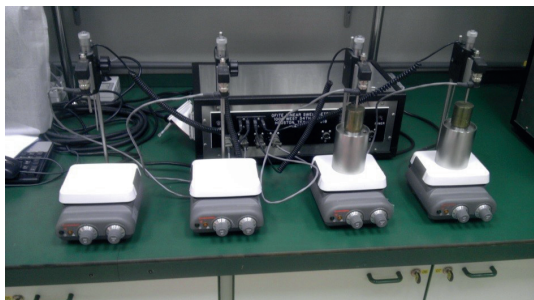

Fig. 2. OFITE Dynamic Linear Swell meter

The desired system temperature is maintained through the heater. Each testing cell has its own magnetic mixing system with a Teflon holder below the sample collet. Swelling intensity is recorded through vertical movement of the metal pin connecting the sample and increment of the moving recorder. The swelling intensity of rubber samples was performed in both room (20°C) and high temperature conditions (90°C) concerning the sample thickness – equation (3).

$$\alpha_0 = \frac{h_2 - h_1}{h_1} \cdot 100\%$$ (3)

where:

α_0 – swelling degree [%],
h_1 – sample thickness before the swelling process [m],
h_2 – sample thickness after the swelling process [m].

Crosslinking density determination

Crosslinking density of the sample (ν) can be determined by applying the following steps.
1. As every crude oil component has its own Hildebrand solubility parameter, an average value for the solvent (δ_s) is determined through the molar fractions of the crude oil components. The Hildebrand solubility parameter for the rubber (δ_p) is determined with regard to a rubber type (in this case EPDM).
2. Enthalpic contribution to the Flory–Huggins interaction parameter (χ_H) is calculated through the following equation:

$$\chi_H = \frac{V_s}{RT} \cdot \left(\delta_s - \delta_p\right)^2$$ (4)

where:

χ_H – enthalpic component of the Flory–Huggins interaction parameter,
V_s – molar volume of the solvent [cm³/mol],
T – temperature [K],
R – gas constant, 8.3144621 J/kg·mol,
δ_s – Hildebrand solubility parameter for solvent [J$^{1/2}$/cm$^{3/2}$],
δ_p – Hildebrand solubility parameter for rubber [J$^{1/2}$/cm$^{3/2}$].

3. The enthropic contribution to the Flory–Huggins interaction parameter (χ_s) is determined, which is equal to 0.34 if the value of dielectric constant for the non-polar solvent systems is less than 15 ($\xi_r = 1.5 \div 4.5$).
4. Flory–Huggins interaction parameter (χ) is equal to a sum of enthalpic and enthropic component of the parameter – equation (5).

$$\chi = \chi_H + \chi_S$$ (5)

5. Crosslinking density of the rubber sample (ν) is then calculated using the equation (6).

$$\nu = -\frac{\left[\ln\left(1-\phi\right) + \phi + \chi\phi^2\right]}{V_s\left(\phi^{\frac{1}{3}} - 0,5\phi\right)}$$ (6)

where ν – crosslinking density [mol/cm³].

6. Molecular weight of the rubber sample (M_c) is calculated using the equation (7).

$$\nu = \frac{\rho_2}{M_c} \tag{7}$$

where M_c – molecular weight [kg/mol].

3. RESULTS AND DISCUSSION

As EPDM samples have different crosslinking density the same goes for a swelling degree. Figure 3 and Table 2 represent the results of swelling research showing that each sample swells with a different intensity and degree. Sample EPDM-6 is of the highest swelling degree (164.64%) with thermodynamic equilibrium state reached after 14 days of swelling. On the other hand, sample EPDM-3 swelled with the lowest degree (72.96%) for only 6 days. Generally speaking, from Figure 3 it can be seen that samples EPDM-4, EPDM-5 and EPDM-6 reached very good swelling degree values while samples EPDM-1, EPDM-2 and EPDM-3 swelled less than the above mentioned. From the given results it can be seen that the composition and crosslinking density of each sample is different.

The swelling rate (v) of each sample was calculated as well (Tab. 2). Samples EPDM-4 and EPDM-3 achieved the highest and the lowest rate (101.12% and 55.38% per day).
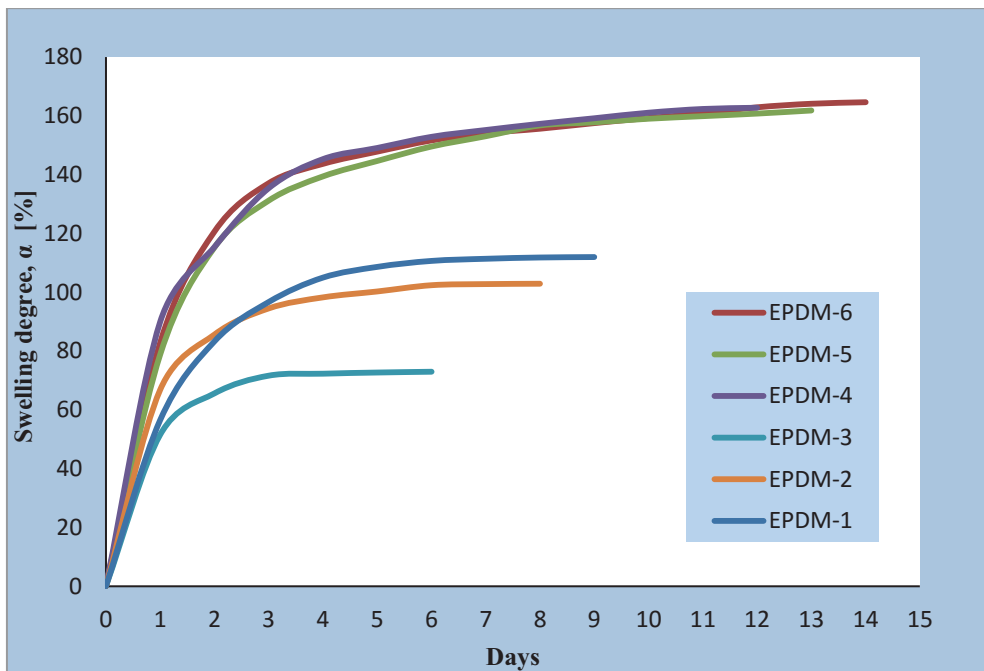

Fig. 3. Swelling degrees of EPDM samples in correlation with swelling time

It is very well known from the literature [10–12] that the crosslinked rubber swells slower with low degree and vice versa. As the structural network is created inside the rubber matter, space between the crosslinking knots becomes smaller with a low swelling potential. Added swelling agent expands the space between the crosslinking knots creating larger pores able to absorb solvent. Besides the swelling agent, reclaimed rubber also affects the swelling degree in term of more intensified swelling and acts as a softener.

Table 2

Swelling degree and rate values of EPDM samples

	EPDM-1	EPDM-2	EPDM-3	EPDM-4	EPDM-5	EPDM-6
α_0 [%]	111.94	102.88	72.96	162.74	161.82	164.64
v [% /day]	59.02	78.95	55.38	101.12	84.11	90.00

Calculated crosslinking densities, molecular weights, fractions of the polymer in a swollen gel and sample densities are shown in Table 3 and Figure 4. It can be clearly seen that each sample is different in its composition and network structure. As a different concentration of sulfur is used to vulcanize the samples it is expected for them to be differently structured.

The least value of volume fraction of the polymer sample in a swollen gel was attained by sample EPDM-1 ($\varphi = 0.3928$) which nicely corresponds to the lowest value of crosslinking density. In other words, this sample has the best ability to absorb the solvent. On contrary, sample EPDM-3 attained the highest value of the mentioned volume fraction ($\varphi = 0.4975$) with a very high crosslinking density value. Molecular weights shown on Figure 4 represent the distance between the crosslinking knots and depends on the crosslinking density and the density of the sample. The highest value of molecular weight is addressed to EPDM-1 ($M_c = 6.561 \cdot 10^3$ g/mol) and the lowest to EPDM-4 ($M_c = 2.241 \cdot 10^3$ g/mol).

It can be said that the sample EPDM-3 was vulcanized using the most content of sulfur. Addition of the swelling agent and reclaimed rubber has gradually lessened the crosslinking density in samples EPDM-4, EPDM-5 and EPDM-6. Increase in reclaimed rubber content in samples EPDM-5 and EPDM-6 is the main reason for crosslinking density decrease which contributed to more intensive swelling.

Table 3

Values of volume fraction of the polymer sample in a swollen gel (φ), crosslinking density (v) and samples densities (ρ_p)

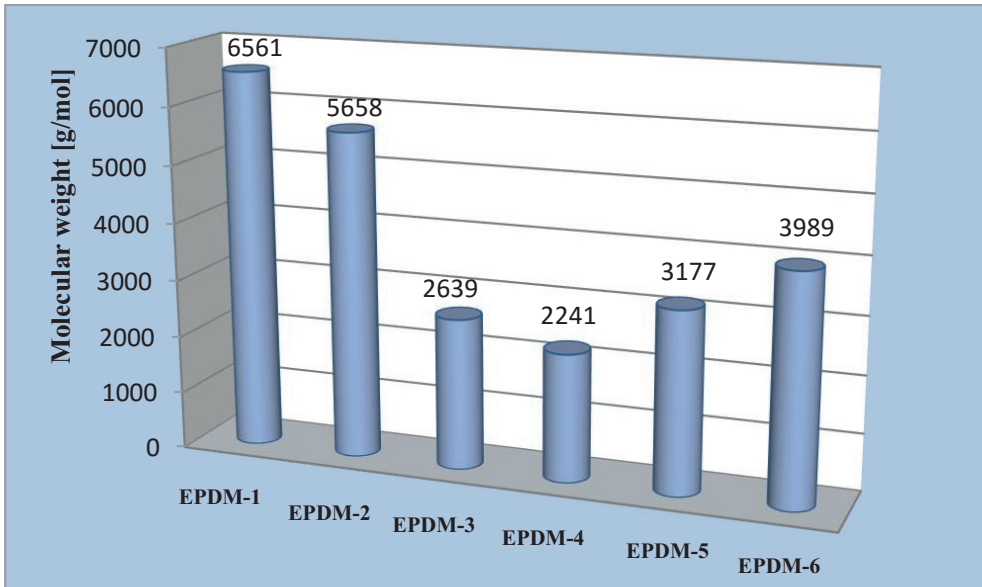| Samples	φ	v [mol/cm³]	ρ_p [kg/m³]
EPDM-1	0.3928	$1.744 \cdot 10^{-4}$	1143.97
EPDM-2	0.4098	$2.049 \cdot 10^{-4}$	1159.26
EPDM-3	0.4975	$4.344 \cdot 10^{-4}$	1146.46
EPDM-4	0.4456	$2.825 \cdot 10^{-4}$	633.15
EPDM-5	0.4191	$2.232 \cdot 10^{-4}$	709.31
EPDM-6	0.4009	$1.885 \cdot 10^{-4}$	751.69

Fig. 4. Molecular weights of the samples

Figures 5 and 6 show the swelling process in different swell meter temperature conditions. At 20°C the highest swelling degrees were reached by samples EPDM-1, EPDM-2 and EPDM-3 (32.4%; 30.27%; 25.3%) while the sample EPDM-4 achieved the least swelling degree of 23.5%.
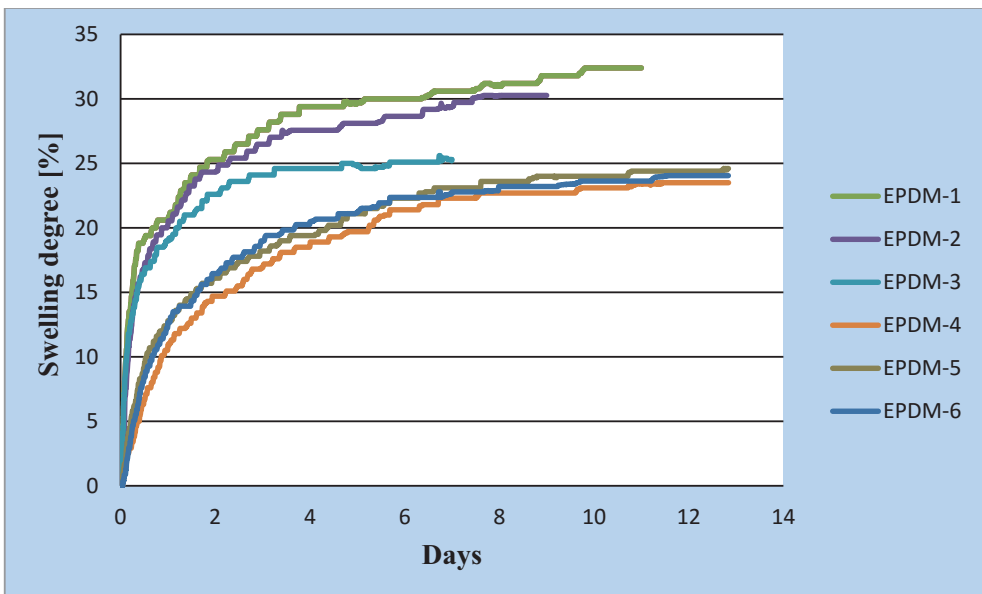

Fig. 5. Swelling degrees of EPDM samples in correlation with swelling time at 20°C
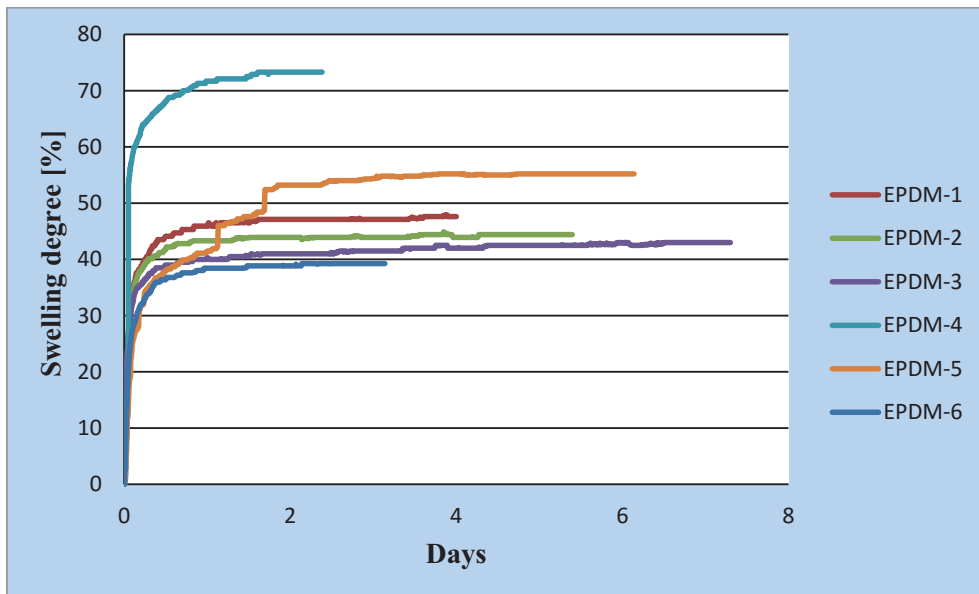
Fig. 6. Swelling degrees of EPDM samples in correlation with swelling time at 90°C

It is obvious that during the swelling process in samples EPDM-4, EPDM-5 and EPDM-6 swelling agent did not contribute the same way like with swelling in a glass dish.

Thermodynamic equilibrium state in samples EPMD-1, EPDM-2 and EPDM-3 oc-curred earlier (11, 9 and 7 days).

Swelling at 90°C pretty much differs from room temperature swelling. Although, two important properties come to the surface when we compare the swelling mechanism at room temperature and 90°C and that is swelling rate and swelling degree. The swelling rate (pace) at room temperature is significantly lower which means that the thermodynamic equilibrium state occurs much later. Diagrams from the mentioned figures show that the time needed to swell the EPDM samples at room temperature ranges from 7–13 days, while the very first day was crucial when samples swelled at 90°C – the swelling degree almost reached its maximum. The difference between the swelling degree values is 14–50% in favor of 90°C swelling.

So, as the highest swelling degrees at 90°C were reached by samples EPDM-4 and EPDM-5 (73.3% and 55.2%), they have shown the most intensive difference in swelling degrees when comparing room temperature and 90°C environment.

4. CONCLUSIONS

There are few conclusions coming up from the laboratory research done with EPDM samples meant to be engineered for the swelling packer elastomer.
– Each EPDM sample has different crosslinking density and thus different molecular weight.
– Each sample swells with different intensity and degree.

- Composition of EPDM samples influences and imposes different physical properties and network structure.
- A swelling agent expands the space between the crosslinking knots (M_c) creating larger pores able to absorb solvent which leads to a greater swelling degree.
- Reclaimed rubber affects the swelling degree in term of more intensified swelling and acts as a rubber softener.
- Swelling at 90°C pretty much differs from room temperature swelling. Swelling rate at room temperature is significantly lower which means that the thermodynamic equilibrium state occurs much later.
- Additional laboratory research should be commenced to delay such a fast swelling rate at high temperatures if swelling packers are to be set within a time margin without premature activation of swelling elastomers.

NOMENCLATURE

h_1 – sample thickness before the swelling process [m]
h_2 – sample thickness after the swelling process [m]
M_c – molecular weight [kg/mol]
m_1 – nonswollen sample mass [g]
m_2 – swollen sample mass [g]
R – gas constant, 8.3144621 J/kg·mol
T – testing temperature [K]
V_s – molar volume of the solvent [cm³/mol]
α – swelling degree [%]
α_0 – swelling degree for swell meter [%]
δ_s – Hildebrand solubility parameter for solvent [J$^{1/2}$/cm$^{3/2}$]
δ_p – Hildebrand solubility parameter for rubber [J$^{1/2}$/cm$^{3/2}$]
ν – crosslinking density [mol/dm³]
ρ_1 – solvent density [kg/dm³]
ρ_2 – sample density [kg/dm³]
φ – volume fraction of polymer in a swollen gel
χ – Flory–Huggins interaction parameter
χ_H – enthalpic component of the Flory–Huggins interaction parameter
χ_s – enthropic component of the Flory–Huggins interaction parameter

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