Optimization of hybrid oil/water-swelling ethylene/ propylene/diene monomer compounds

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Abstract

Hybrid swell packers are rubber products capable of swelling in (saline) water and hydrocarbon oils, by exploiting the hydrocarbon diffusion properties of an nonpolar elastomer with the osmotic swelling of a water absorbent (WA). In this study, a variety of modified natural and synthetic WAs and mixtures thereof have been screened in a rubber compound with respect to swelling in decalin, demineralized, and saline water, respectively. We aimed at achieving high and fast swelling in all used media. Mixing of the various WAs in an ethylene/propylene/diene monomer (EPDM)/carbon black masterbatch at an addition level of 75 phr did not pose any problems, although it was found that the WAs did affect the sulfur vulcanization. Decalin swelling of the vulcanizates is very fast, reaching high equilibrium swelling within 1.5 days. Swelling in demineralized or saline water is much slower, with up to 300% swelling in water and up to 100% swelling in saline water. Significant leaching of the organic WA from the EPDM vulcanizates to the water phase occurs. Some combinations of WAs show synergetic effects for swelling in water. To our knowledge, such a systematic study of hybrid swelling elastomers constitutes a novelty in the open literature.

KEYWORDS

elastomers, oil and gas, rubber, swelling

1 | INTRODUCTION

The development and use of horizontal drilling techniques in the mid 2000's led to a widespread growth in the use of hydraulic fracturing techniques (so-called "fracking") to

enable the release of large reserves of oil and gas, trapped underground in layers of shale rock. [1] There are different versions of the fracking process, one of which involves the positive annular isolation of an uncemented liner using zonal isolation swell packers, providing a high degree of fracture control. [2] Swellable elastomer packers were introduced into the oil and gas recovery process in the 2000's as a lower cost and highly practical alternative to more conventional cementing, mechanical, and open-hole packer technologies. [3] Three rubber compounding approaches to swellable elastomer packers are commonly used [4] : the first is a compound based on an nonpolar elastomer that swells by diffusion

when exposed to hydrocarbon oils and gases; the second approach is based on an elastomer compound that is susceptible to swelling in water by a process of osmosis, as in the case of a polar rubber containing a water absorbent (WA), such as a super-absorbent polymer; and the third variant is based on a hybrid compound, which can swell in both water and hydrocarbon oils and gases by exploiting the hydrocarbon diffusion properties of an nonpolar based elastomer, mixed with WA's to enable osmotic swelling in water. Such hybrid systems provide advantages when there is uncertainty as to whether the underground swell fluid is predominantly water or oil based and allows a greater control of swelling rate through adjustments of temperature, solubility, and viscosity characteristics of the swelling oil, or the salinity level of the water.

For the development of a hybrid swelling rubber packer compound, first the right base elastomer has to be chosen. Elastomers are (organic) polymers typically composed of carbon and hydrogen with optionally nitrogen, oxygen, fluorine, silicon, or chlorine as heteroatoms. [5,6] As a result, most common elastomers are relatively nonpolar polymers compared to water, with solubility parameters ranging from 13 to 21$(J/cm^3)^{0.5}$.[7] These elastomers as such do not dissolve in water nor upon cross-linking do they swell in water. Therefore, hybrid swell of rubber products in both oil and water is achieved by combining a rubber, which swells in oil with a WA. Crude oil is an nonpolar liquid (solubility parameter 15 to 16$(J/cm^3)^{0.5}$), thus nonpolar elastomers like natural rubber (NR; 17 $(J/cm^3)^{0.5}$), polybutadiene rubber (BR; 17$(J/cm^3)^{0.5}$) and ethylene/propylene/diene rubber (EPDM; 16$(J/cm^3)^{0.5}$) will dissolve in oil and upon cross-linking will swell. Notably, the cross-link density of the rubber product determines not only the physical and elastic properties, but also the degree of oil swell. Since the crude oil in an oil field can be quite hot (up to 200°C) and the hybrid swell packers have to function for prolonged period of time, the elastomer to be used should not only swell in oil, but should also have an excellent heat resistance. NR and BR are both polydiene rubbers with very high levels of unsaturation in the polymer backbone and thus, have poor heat resistance. EPDM rubber with its saturated eth-ylene-propylene backbone and only a small amount of residual unsaturation in side groups gives excellent heat resistance and consequently, is the polymer of choice for hybrid swell packers. [8]

Thereafter, for the development of a hybrid swelling EPDM-based packer compound, the right WA has to be chosen. Water swellable elastomers (WSE) are typically based on mixtures of rubber and WA, produced via blending or graft polymerization to allow for a homogeneous dispersion of the polar WA in the nonpolar rubber matrix. [9,10]

WAs typically used for WSEs are able to absorb huge quantities of water up to several (hundred) times their initial weight. [11–13] Recent examples of WSEs includes materials based on natural rubbers composites with starch-g-polyacrylamide superabsorbent [14]

and nitrile-butadiene rubber modified with interpenetrating networks of cross-linked poly(acrylic acid-co-butyl acrylate). [15]

The presence of charges in ionic WAs (for example, neutralized homo- and co-polymers of (meth)acrylic acid) provides a clear advantage in terms of swelling performance over neutral WAs (such as polyvinylalcohol or polysaccharide based). [16] The most popular examples of such charged absorbents are based on (meth)acrylic copolymers. [17,18] There is a fair correlation between the WA content and the WSE swelling performance in water. [9] The cross-link density of the rubber matrix will also affect the swelling of the dispersed WSE in water.

Obviously, the development of a hybrid EPDM/WA compound with good physical and elastic properties and good swelling performance in both water and oil is rather complex, since the WA type and amount and the crosslink density of the EPDM rubber have to be optimized. The purpose of this study is to identify the optimum (combination of) WA(s) for a given EPDM compound for hybrid swell applications. The main aim is to achieve high and fast swelling, both in oil and in water, by screening various WAs, alone or in combination. To our knowledge, such a systematic study of hybrid swelling elastomers constitutes a novelty in the open literature. To achieve this goal, first an EPDM masterbatch (MB) was mixed with carbon black, plasticizers and part of a sulfur curative package (sulfur, zinc oxide, and stearic acid) (Table 1) on a large scale. The EPDM MB was based on Keltan 4450S, an EPDM with (a) a low Mooney viscosity to enable good processing of the rubber compound with WA and carbon black filler, (b) a medium 5-ethylidene-2norbornene content for sulfur vulcanization, and (c) a low ethylene content to ensure amorphous behavior and no effects of crystallinity on properties. Then, compounds of this EPDM MB were mixed with various WA on a small scale. After a third mixing step of these EPDM/WA compounds with the sulfur vulcanization accelerators, the compounds were first vulcanized in a rheometer to assess the vulcanization kinetics and the final state of cure. Finally, the EPDM/WA compounds were vulcanized by compression molding into test samples for swelling.

Samples of EPDM/WA vulcanizates were swollen at room temperature in decahydronaphthalene (decalin) as a well-defined, high-boiling model for hydrocarbon oil that still allows evaporation after swelling and thus, also allows assessment of the rubber gel content. The final degree of swelling in decalin and the rubber gel content can be viewed as a measurement of the cross-link density

TABLE 1 Composition of EPDM masterbatch and final EPDM compound

Ingredient	Amount (phr)	Chemical composition and/or function
EPDM masterbatch		
Keltan 4450S	100	EPDM rubber with 52% ethylene and 4.3% ENB
N772	50	Carbon black as reinforcing filler
Sunpar 2,280	25	Mineral oil as plasticizer

Aflux 42	1.0	Mixture of fatty alcohols/acid esters as dispersing agent
PEG	3.0	Polyethylene glycol
Sulfur 80	0.7	Vulcanization agent
Zinc oxide	3.0	Vulcanization activator
Stearic acid	1.0	Vulcanization activator
Total masterbatch	183.7	
Water absorbent (or reference)	75	See Table 2
Vulcanization accelerators		
ZBEC	0.6	Zinc dibenzyl dithiocarbamate
ZDTP	2.0	Zinc dialkyl dithiophosphate
Total compound	262	

Abbreviation: EPDM, ethylene/propylene/diene monomer.

of the EPDM vulcanizate [19,20] and will be correlated with the rheometer maximum torque values. Samples were also swollen in demineralized water and in an aqueous solution of sodium chloride as "synthetic" seawater. Since water has to diffuse through the nonpolar EPDM rubber matrix to the dispersed WA, the swelling will be slow. Thus, the water swelling experiments were performed at an elevated temperature (80°C) to speed up the swelling. The WAs used in this study include modified polysaccharide-based products, but also synthetic polymers and inorganic materials (Table 2). Talc was used as a nonwater absorbent reference filler. In a first screening single WAs were investigated. In a second step mixtures of optimum WAs were explored in order to identify possible synergistic effects, as were previously identified for the use of synthetic WA together with silica. [21,22] During the swelling experiments, samples were collected as a function of time to assess the swelling kinetics and the final degree of swelling.

2 | EXPERIMENTAL

1 | Materials

The EPDM rubber MB (Table 1 top, prepared in a 1.5 L internal mixer with a set temperature of 50°C), samples of talc, bentonite, six different polymeric WAs, (Table 2) and three sulfur vulcanization accelerators (Table 1 bottom) were kindly provided by ARLANXEO, Geleen, Netherlands. Silica and decalin were purchased from Sigma-Aldrich, Zwijndrecht, Netherlands. The amounts of the various ingredients in Table 1 are expressed in parts per 100 parts rubber by weight (phr).

2 | Preparation of the unvulcanized, hybrid swelling rubber compounds

The compounds were prepared in a 50 ml Brabender Plasti-Corder PL2000 mixer equipped with counterrotating rotors. A constant degree of filling of 23 g (75% filling factor) was used for all the compounds, the rotor speed was set at 50 rpm and the body temperature was set to 75°C. The rubber MB (Table 1) was added to the mixer first for warming up and homogenization, followed by the addition of WA after 2 min . After a further 2 min of additional mixing, the three vulcanization accelerators were added and the mixing continued for another 2 min for final homogenization (total mixing time of 6 min).

3 | Vulcanization of the rubber compounds

Curing tests were performed for all of the compounds using an Oscillating Disk Rheometer (ODR; Monsanto 2000) according to the ISO 3417 standard for 30 to 40 min at 160°C in order to determine the full curing kinetics characteristics, including the optimum cure time and the final degree of cross-linking. The scorch time (ts2), which is the time for the onset of vulcanization, and the optimum cure time (t90), which is the time needed to obtain 90% of curing, were determined from each cure curve obtained. The final degree of crosslinking was determined as the difference between the maximum and minimum torque values of the cure curve ($\Delta S = MH - ML$).

For the swelling tests, the vulcanizates were cured into disks (diameter of 13 mm , thickness of 2 mm) via compression molding at 160°C and 100 bar for 1.1 times t90, as determined from the rheometer test. The mold plates were bumped (meaning that pressure was applied

TABLE 2 Water absorbents screened

Commercial name	Chemical composition	Supplier	Abbreviation
Nanoclay	Hydrophilic bentonite	Sigma-Aldrich	Bentonite
Creabloc SIS	Poly(acrylamide-co-acrylic acid)	Evonik	CS
Creabloc E4080 (developmental)	Copolymer of carboxyl- and sulfur-groupscontaining monomers	Evonik	CE
Creabloc T5066F	Partially sodium neutralized polysodium acrylate	Evonik	CT
Tylose H6000 YP2	Hydroxyethyl cellulose	ShinEtsu	TH

Tylose MM 10008 P4	Methyl hydroxyethyl cellulose	ShinEtsu	TM
Walocel CRT 50000 PA07	Sodium salt of carboxymethylcellulose	DOW	WC
Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$	Sigma-Aldrich	Talc
Silica	SiO_2	Sigma-Aldrich	Silica

and then released) a few times in order to remove porosity.

All the experiments were performed without refreshing the swelling medium. The degree of swelling is calculated as in Equation (1):

$$\text{degree of swelling (\%)} = \frac{\text{weight of swollen rubber} - \text{initial weight}}{\text{initial weight}} \times 100. \quad (1)$$

Note that if no swelling occurs, the degree of swelling is 0%. After the degree of swelling had been determined, the swollen rubber samples were dried at 85°C in a vacuum oven until a constant weight was achieved. From the decalin swelling experiment, the rubber gel content is calculated as in Equation (2):

4 | Swelling tests

The swelling tests with the vulcanized rubber disks were performed in three different environments: (a) decalin, as a model for oil, (b) demineralized water, and (c) a 3.5 wt % of NaCl solution in water, which will hitherto be referred to as "saline water". The decalin swelling was performed using duplicate test pieces at room temperature for 3 days. The swelling in water and saline water was performed at 80°C to speed up the swelling rate, enabling the approach of swelling equilibrium in these

$$\text{rubber gel content (\%)} = \frac{\text{swollen rubber after drying} - \text{content of carbon black and WA}}{\text{initial weight} - \text{content of carbon black, oil and WA}} \times 100. \quad (2)$$

media within 35 days. At various time intervals, the swollen rubber disks were weighted after removing adherent liquid by carefully drying the surface with a paper tissue.

For water and saline water swelling, the amount of WA leached out of the rubber sample is calculated as in Equation (3):

$$\text{WA leaching (\%)} = \frac{\text{swollen rubber after drying} - \text{weight of EPDM, oil, and carbon black}}{\text{initial weight of disk} - \text{weight of EPDM, oil, and carbon black}} \times 100. \quad (3)$$

As one referee of this work pointed out, the swelling should be rather expressed in volume. As the materials possess different densities, the relative values of swelling expressed in volume would be slightly different. In fact, the EPDM MB has a density of 1.02 g/ml, while

for the binary mixtures values vary from 0.92 (MB + hydroxyethyl cellulose) to 1.26 g/ml (MB + bentonite). We preferred to express swelling in weight rather than volume %, as the weight is the quantity directly and more easily measured in our experiments. This does not affect the discussion and conclusions.

3 | RESULTS AND DISCUSSION

1 | EPDM vulcanizates with single water absorbent

The first part of this work involved the evaluation of the performance of the six polymeric WAs plus bentonite and talc as references. This was accomplished by preparing mixtures of the EPDM MB with a fixed amount of each WA (75 phr), vulcanizing the obtained compounds, and performing the swelling experiments with the vulcanized rubber disks.

1 | Mixing

Figure 1 shows a typical torque curve obtained during mixing. Warming and homogenization of the premixed EPDM/carbon black MB occurs during the first 120 sec . A strong increase of the torque is observed when the WA is added to the EPDM MB. After 240 sec , the vulcanization accelerators are added. During mixing, the temperature also rises, due to viscous dissipation, but it remains below 120°C, so scorch of the rubber compound will not occur. After 360 sec of mixing, stable torque and temperature are reached. It can be concluded that mixing WA in the EPDM MB at 75 phr does not pose any problem and yields a coherent, homogeneous rubber compound. The high shear generated during the mixing of the highly viscous rubber matrix, provides enough energy to disperse WAs particles.

2 | Cure tests and decalin swelling

To establish the proper vulcanization conditions, cure tests were conducted on all the EPDM/WA compounds in an ODR rheometer at 160°C. Table 3 shows ts2 (scorch time) and t90 (optimum vulcanization time) and the difference between the final and initial torque (ΔS), as an indication for the cross-link density. ts2 of the EPDM compound is not affected by the addition of WA, with the exception of Tylose MM 10008 P4 (TM) (somewhat slower). It is hard to explain why t90 is similar, larger, or smaller compared to the EPDM MB, depending on the particular choice of the WA type. The ΔS values obtained for the compounds with polymeric WAs and silica are all lower compared to the EPDM MB as such, indicating that these polymeric WAs interfere with sulfur vulcanization, though not to a dramatic extent. This is not simply due to dilution, since ΔS is not affected by the inert bentonite and talc minerals. Although the materials are inert, they might interfere with the curing process. As the sulfur vulcanization accelerators are polar as the WAs, while the EPDM matrix is non-polar,

FIGURE 1 Torque (black line) and temperature (red line) profiles during mixing of the ethylene/propylene/diene monomer (EPDM) rubber masterbatch with first Creabloc water absorbent (WA) and finally vulcanization accelerators

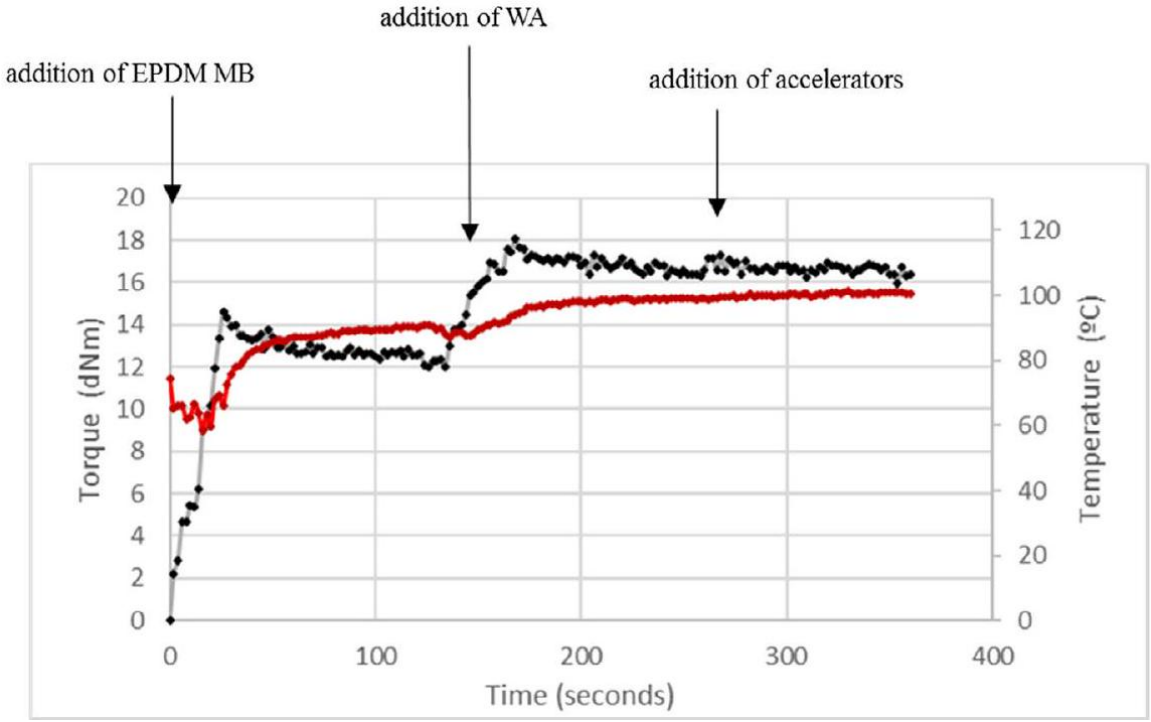


TABLE 3 Results of vulcanization tests and swelling experiments in decalin, demineralized, and saline water for EPDM compounds with single WA

Water absorbent	ts2 [a] (min)	t90 [b] (min)	ΔS^c(dNm)	Rubber gel content (decalin) (%)	Decalin swelling (%)	WA leached in water (%)	WA leached in saline water (%)
-	1.4	9.2	56.4	100.0	265	Blank	Blank
CS	1.4	11.3	49.5	95.8	259	42.5	20.1
CE	1.4	8.8	48.5	93.9	242	52.0	37.8
CT	1.4	7.2	50.5	96.9	239	78.7	60.3
TH	1.4	12.0	44.0	94.5	260	48.7	60.4
TM	1.6	7.9	40.5	98.6	243	12.4	31.4
WC	1.3	11.7	53.3	88.5	250	82.1	32.4
Bentonite	1.3	12.5	55.2	95.0	215	9.3	8.1

Talc	1.4	10.5	52.7	100.0	193	0.1	1.7
Silica	1.4	19.5	47.3	95.7	210	6.2	4.4

[a] Scorch time (2 units above ML).
[b] Optimum vulcanization time (90% of MH).
[c] Difference between final and initial torque, MH-ML.
Abbreviations: CE, Creabloc E4080; CS, Creabloc SIS; CT, Creabloc T5066F; EPDM, ethylene/propylene/diene monomer; TH, Tylose H6000 YP2; TM, Tylose MM 10008 P4; WA, water absorbent; WC, Walocel CRT 50000 PA07.

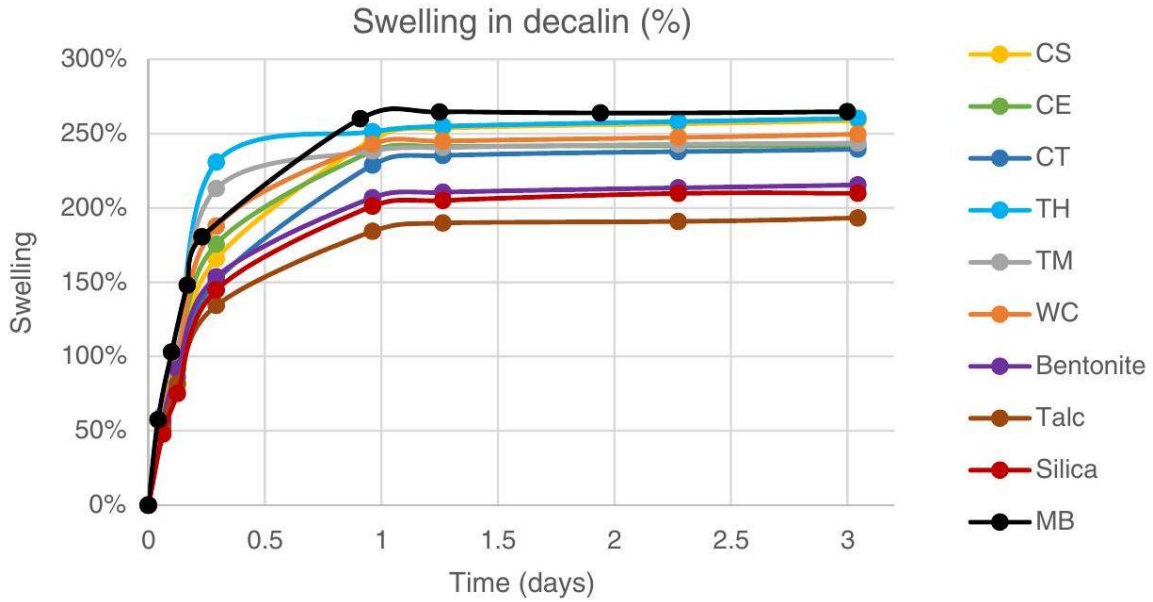


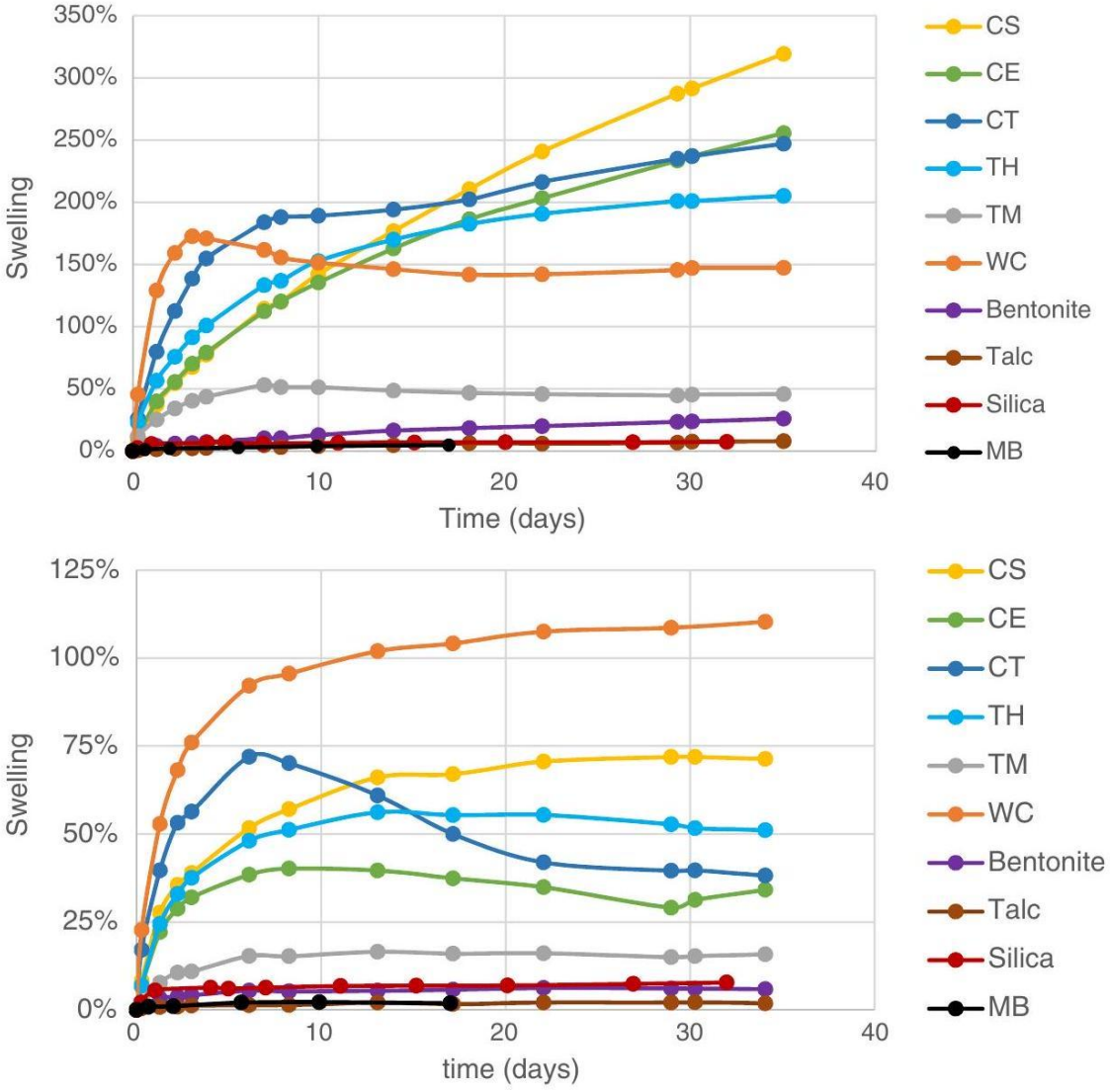
FIGURE 2 Effect of type of water absorbent on swelling of vulcanized ethylene/propylene/diene monomer rubber disks in decalin at room temperature. CE, Creabloc E4080; CS, Creabloc SIS; CT, Creabloc T5066F; TH, Tylose H6000 YP2; TM, Tylose MM 10008 P4; WC, Walocel CRT 50000 PA07 it is possible that they adsorbs on the WAs, being subtracted from the rubber matrix, and therefore hindering the vulcanization.

The data of t90 listed in Table 3 have been used to determine the proper compression molding times (1.1 times t90) to ensure complete vulcanization of the rubber disks to be used for swelling.

The swelling of the vulcanized rubber disks in decalin was determined over a range of times, resulting in "parallel" concave swelling curves (Figure 2). In all cases, a constant weight, indicating equilibrium swelling, was reached within 1.5 days. The final values, taken after 3 days, are reported in Table 3. Most EPDM/WA samples can swell in decalin more than twice their original weight. In all cases, the addition of the WA to the EPDM compound results in a reduction of the decalin swelling (265% → 193 to 260%), simply because the amount of swellable rubber is "diluted" by the WA, which will not swell in decalin when mixed into the EPDM/WA compound. It is worth noticing that the plasticizer oil is probably extracted during decalin swelling. This is taken into

account in our calculations. The rubber gel contents, determined after the swelling experiment (Table 3), are very high and close to 100% in all samples (>93%; except for Walocel), confirming a satisfactory degree of crosslinking. These data suggest that the addition of WAs does

FIGURE 3 Effect of type of water absorbent on degree of swelling of vulcanized ethylene/ propylene/diene monomer rubber disks in demineralized water (top) and saline water (bottom) at 80°C. CE, Creabloc E4080; CS, Creabloc SIS; CT, Creabloc T5066F; TH, Tylose H6000 YP2; TM, Tylose MM 10008 P4; WC, Walocel CRT 50000 PA07 .



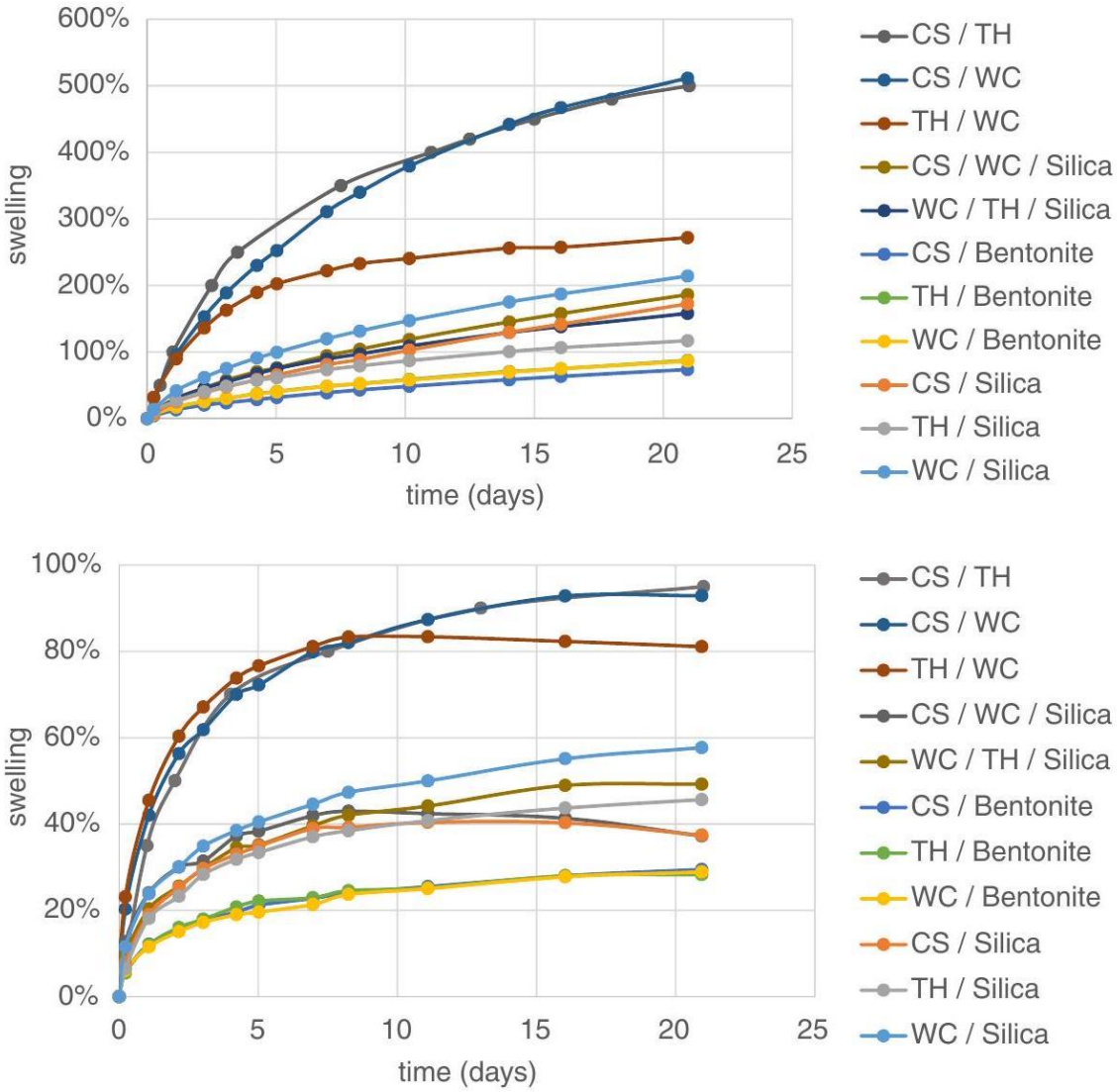
not affect significantly the cross-linking density, which is a good indicator of mechanical performance of rubbers (in particular elasticity). Therefore, the mechanical properties of the prepared samples should be satisfactory. However, a full characterization of mechanical properties was outside the scope of this work.

According to the Flory-Rehner theory, [23,24] the equilibrium swelling of a cross-linked rubber in a good solvent correlates with the cross-link density. The rubber gel content and the rheometer ΔS are also measures for the cross-link density. Surprisingly, plots of these three quantities did not show simple correlations, but actually show quite some scatter (plots not shown), indicating that the cross-link density is not the only relevant parameter affecting the swell in decalin. Apparently, other parameters also play a role, such as possibly the type and dispersion of the WA.

3 | Swelling in demineralized and saline water

The vulcanized rubber disks were swollen in demineralized and saline water, and the change of swelling over time (Figure 3) as well as the final amount of WA that leached out of the test pieces (Table 3) were determined.

The studied WAs show quite different water absorption rates and final levels of swelling. In demineralized water, the swelling is typically more pronounced than in saline water for all WAs. This is probably due to osmotic effects that have already been observed in the case of poly (acrylic acid)-based copolymers. [25] Due to the polyelectrolytic nature of the WA (charged repeating unit), the macromolecular chains stretch in demineralized water to compensate for the charge gradient generated by the polymers. In contrast, in high salinity water this effect does not occur and the polymer chains assume a random coil conformation. [25] Also, leaching of the WAs in water is generally more extensive than in saline water, except for the two Tylose products. Considering the swelling graphs in Figure 3, four different types of swelling behavior can be distinguished: (a) no or little swelling in demineralized and saline water, (b) significant swelling in demineralized and saline water until an equilibrium is reached, (c) continuous swelling without reaching an equilibrium even after 35 days, and (d) significant swelling with the degree of swelling going through a



maximum. For (b), (c), and (d), the swelling in demineralized and saline water shows dissimilar trends as a function of WA type. For these three groups, the swelling in demineralized and saline water takes much more time, despite being performed at 80°C, than the equilibrium swelling in decalin at room temperature. This is most probably due to the fact that the nonpolar EPDM rubber forms a continuous matrix of the compounds and thus, is easily accessible for decalin, whereas the polar water has to diffuse through the nonpolar EPDM matrix before swelling the hydrophilic WA dispersion.

It is clearly noted that the EPDM vulcanizates with the inorganic WA bentonite and the inert mineral filler references, that is, silica and talc, have negligible swelling in both demineralized and saline water. The swelling results are similar to those of the EPDM MB without WA, which obviously will not swell at all in water. Leaching of these inorganic materials to water is also limited ($< 10\%$). The EPDM vulcanizate with TM also has a poor swelling performance in water compared to those with the other WAs and also shows relatively low leaching values. The correlation between low saline water swelling and low

values of leaching in both media points simply to a poor affinity of the WAs/fillers of this first group toward water.

FIGURE 4 Effect of mixtures of water absorbents on swelling of ethylene/propylene/diene monomer rubber disks in water (top) and saline water (bottom) at 80°C. CE, Creabloc E4080; CS, Creabloc SIS; CT, Creabloc T5066F; TH, Tylose H6000 YP2; TM, Tylose MM 10008 P4; WC, Walocel CRT 50000 PA07 Group (b): some EPDM/WA vulcanizates indicate significant swelling in demineralized and/or saline water with time and reach a swelling plateau within 35 days (Figure 2), viz. the vulcanizates with Tylose H6000 YP2 (TH) in demineralized water (200%) and the vulcanizates with Creabloc E4080 (CE), TH, Creabloc SIS (CS), and Walocel CRT 50000 PA07 (WC) in saline water (30 to 110%). This is the expected and, in a way, the desired behavior.

Group (c): some EPDM/WA vulcanizates also evidence significant swelling in demineralized water, but do not reach a swelling plateau even after 35 days of swelling at 80°C. The vulcanizates with CE, Creabloc T5066F (CT), and CS show this behavior in demineralized water and so the final degrees of swelling will be above the observed 225 to 300%. Interestingly, the vulcanizates with CE, CT, and CS do not show this behavior in saline water, where the vulcanizates with CE and CS reach equilibrium levels of 70 and 120%, respectively, within 20 days.

Group (d): the vulcanizate with WC actually displays a peak in its degree of swelling in demineralized water and similar effect is observed with CT in saline water. In both cases, this results in swelling curves that cross back over some of the other, fully concaved, swelling curves.

TABLE 4 Results of vulcanization tests and swelling experiments in decalin and water for EPDM vulcanizates with mixtures of water absorbents

Water absorbent combination	t90 (min)	ΔS (dNm)	Decalin swelling (%)
CS/WC	10.4	52.7	223
CS/WC/silica	12.0	55.5	238
TH/WC	11.2	49.7	247
TH/WC/silica	11.7	54.1	227
CS/bentonite	11.3	50.4	246
TH/bentonite	12.0	49.7	248
WC/bentonite	10.1	51.7	228
CS/silica	13.2	50.5	256
TH/silica	14.6	53.3	246
WC/silica	10.5	57.9	240

Abbreviations: CE, Creabloc E4080; CS, Creabloc SIS; CT, Creabloc T5066F; TH, Tylose H6000 YP2; TM, Tylose MM 10008 P4; WC, Walocel CRT 50000 PA07.

The observation of a swelling maximum is accompanied with very high levels of leaching of the WA out of the EPDM/WA vulcanizates (Table 3:82 and 60%, respectively). Apparently, the diffusion of the water into these EPDM/WA vulcanizates proceeds faster than the leaching out of the very high molecular weight WAs, which then shows up as a maximum in the degree of water swelling.

It was actually observed that all WAs show significant leaching behavior with CT in demineralized water and TH in saline water also, reaching values as high as 79 and 60%, respectively. Therefore, the simple smooth swelling curves for groups (b) and (c) observed in Figure 3 are also the net result of water swelling and WA leaching, but with the rate of leaching being in the same order of magnitude or faster as that of the water swelling. The swelling of the vulcanizate with CT in water shows an inflection at around 15 days, which is probably also related to the different kinetics of swelling and leaching.

Finally, note that for those vulcanizates with a WA that do show swelling in water, the cross-link density of the rubber matrix is comparable (Table 3) and thus, the differences in water swelling are only due to the type (and dispersion) of the WA. Unfortunately, we have insufficient information on the chemical and physical structure of the WAs screened in this study to enable further explanations on their different performance. From a practical perspective, the ideal WA should provide a fast and high level of swelling of the EPDM/WA vulcanizate in water combined with a minimum of loss due to leaching out.

Some simple models for the swelling kinetics of WSEs have been presented in the literature, [9] especially regarding their swelling in water. According to these models, the swelling is considered to be influenced by two factors: (a) the water diffusion into the rubber and (b) the rubber relaxation followed by a network expansion. Considering only the first process governed by Fickian diffusion of the water molecules into the rubber, the following Equation (4) is applicable if water swelling is fast enough: [9]

$$\frac{W_t}{W_e} = \left(\frac{4}{\sqrt{\pi}}\right) \cdot \left(\frac{Dt}{h^2}\right)^{1/2}, \tag{4}$$

where W_t and W_e are the mass of adsorbed water at time t and at equilibrium, respectively, D is the diffusion coefficient and h the thickness of the sample. Unfortunately, the data obtained in our investigation do not provide linear fits when W_t/W_e is plotted versus square root of time (data not shown), suggesting that this model is too simplistic.

2 | EPDM vulcanizates with mixtures of water absorbents

After this first screening of EPDM vulcanizates with a single WA at 75 phr , EPDM vulcanizates with a combination of two or three WAs, in equal amounts but still totaling a sum of 75 phr (37.5 phr for each WA in binary mixtures and 25 phr for each component in ternary mixtures), were then investigated in order to optimize the swelling performance. For this purpose the following three WAs were selected: (a) CS because it shows the highest water swelling and fairly high saline water swelling; (b) WC because it shows the highest saline water swelling and a very fast swelling in both water media; and (c) TH because it shows fair swelling in both water media. In addition to mixtures of

the selected polymeric WAs, also mixtures of these polymeric WA with inorganic bentonite and silica were explored for possible synergistic effects. [22]

The t90 values for all EPDM compounds with WA combinations are now longer than that of the EPDM MB: 10 to 15 min versus 9.2 min , indicating a slower cure rate. The values for ΔS and equilibrium swelling in decalin for the EPDM vulcanizates with WA mixtures (Table 4) are similar to those obtained with single WAs, showing that the vulcanization process, though slower, also proceeds without problems for these vulcanizates. The ΔS and decalin swell values for the EPDM vulcanizates with both single and multi-WA combinations are lower than those obtained for EPDM MB without WA, although the decalin uptake is still substantial, 220 to 260%.

All the EPDM vulcanizates with WA mixtures presented similar swelling behavior in decalin with the swelling equilibrium reached after 1 day (curves not shown, but similar to Figure 2) and the final swelling ranging from 210 to 250% (Table 4). This is very similar to what was observed for the EPDM vulcanizates with a single WA. The swelling curves of the EPDM vulcanizates with WA combinations in demineralized water are all concaved, do not cross over and do not reach an equilibrium in 20 days (in hindsight, a somewhat short experimental time compared to the vulcanizates with a single WA), as shown in Figure 4. The EPDM vulcanizate with the TH/ WC combination is an exception, since it initially swells fast but then the swelling rate levels off. With the exception of the vulcanizates with the CS/WC and CS/TH combinations, the "final" degrees of swelling are typically below 250% after 20 days. This is similar to the performance of the EPDM vulcanizates with single WA (Figure 3) and indicates the absence of synergy for almost all WA combinations including those consisting of a polymeric and an inorganic WA. However, the EPDM vulcanizates with the CS/WC and CS/TH combinations have water swell values above 500% after 20 days without having reached a plateau. These are true examples of synergy. In saline water, most EPDM vulcanizates with WA combinations reach a swelling equilibrium within 20 days. Vulcanizates with the CS/silica, TH/WC, and CS/WC/silica combinations showed a slight decrease of swelling at longer times. The final degree of swelling in saline water is similar to that of the vulcanizates with a single WA, indicating the absence of any synergy. As for the EPDM vulcanizates with a single WA, the swelling in demineralized water is more pronounced than in saline water.

EPDM vulcanizates with the combination of CS with either WC or TH show rather promising results both in demineralized and saline water. The swelling in demineralized water is greatly enhanced, while the swelling in saline water remains comparable to that of single WAs.

4 | CONCLUSIONS

EPDM vulcanizates with (mixtures of) WAs have been investigated in an effort to optimize the compound compositions for hybrid swell packer applications. Mixing of the various WAs in an EPDM/carbon black MB at 75 phr does not pose any problems, although the WAs do affect the sulfur vulcanization. Decalin swelling of the EPDM/ WA vulcanizates at room temperature is very fast, reaching equilibrium within 1.5 days, with substantial levels of swelling (200 to 300%). Swelling in demineralized and saline water is much slower, despite being performed at 80°C, with up to 300% swelling in water and up to 100% swelling in saline water. Equilibrium swelling in saline water is reached within 20 days for all WAs, but it takes beyond 30 days in water for some of the WAs. The inorganic

bentonite, silica, and talc fillers do not facilitate any water absorption. Significant leaching of the organic WAs from the EPDM vulcanizates to the water phase occurs, which explains the observation of some swelling curves reaching a peak followed by a loss of the degree of swell. Some combinations of WAs do show synergetic effects for swelling in water, reaching degrees of swelling up to 500%, but synergy is absent for saline water.

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