



Reactive elastomeric composites: When rubber meets cement

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ABSTRACT

This paper describes a novel reactive composite material comprised of hydrogenated nitrile butadiene rubber (HNBR) compounded with slag cement. The composite initially looks and behaves like rubber, but when exposed to water it simultaneously swells and stiffens due to hydration of the cement component. The material eventually reaches a stiffness that is intermediate between that of HNBR and hydrated cement, while maintaining a relatively large ductility that is more characteristic of rubber. This behavior, which is ideal for sealing applications, differentiates this material from conventional swellable materials that become less stiff upon swelling. The development of this new type of material was motivated by the requirements of oilfield zonal isolation, where alternatives to cement are needed for some challenging sealing applications. A mechanism for the swelling and stiffening of the reactive composite is proposed: water diffuses into the HNBR matrix and is converted to bound water through hydration reactions with the cement, causing the effective solid filler content of the composite to increase. A model is proposed that treats the composite as a cellular solid with a continuous filler phase (hydrated cement). This model is able to reproduce the observed increase in the elastic modulus with time during exposure to water.

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1. Introduction

Zonal isolation, defined as sealing of the wellbore against unwanted movement of fluids, is a significant challenge for safely extracting oil and gas from offshore and deepwater reservoirs, and has become one of the most important environmental concerns for the oilfield industry [4]. In the worst-case scenario, oil or gas moves vertically upward from the reservoir along the borehole and escapes into the surrounding land or seabed. In particular, zonal isolation is a significant challenge for producing shale gas reservoirs due to the stresses generated in the wellbore by hydraulic fracturing, which can damage the isolation material.

The standard approach to zonal isolation is to pump cement slurry into the annular space between the formation and production casing and allow it to harden in place. Ensuring long-term zonal isolation requires a durable material with low permeability and reasonably high compressive strength that completely fills the annular space. Another approach to sealing, widely used in the automotive and aerospace industries and increasingly used in the oilfield, is to utilize gaskets, O-rings and packers made of elasto-

mers. For these applications, the seal provides a localized block against fluid flow. The maximum differential pressure that the seal can sustain is primarily determined by the contact stress between the seal and its confinement, and by the modulus of the seal material [13]. In some cases, the seal relies on its swelling [7,2,3,12]. The ability to seal is crucial to the functioning of diverse components (from a refrigerator or a car to a space shuttle) and sealing failures are responsible for a significant fraction of mechanical breakdowns, leading sometimes to catastrophic results [17]. While predicting seal performance and potential failure are complex tasks [1], improvements in elastomer sealing performance can be achieved, in some conditions, through modulus and strength optimization during service life, i.e., in situ. This was the motivation for the development of the material discussed here.

Swellable elastomer seals are increasingly used to replace cement as elements of zonal isolation under challenging oilwell production conditions. For example, standard oilwell cement provides inconsistent sealing results behind a production casing that is subjected to repeated temperature and pressure cycling. Poor sealing is often related to the tendency for the cement to debond from the casing or rock formation. As a result, over the past decade, there has been growing interest in the use of swellable elastomer seals for downhole applications such as openhole completions, instead of cement. With these seals, no mechanical compression is needed. Instead, a state of compression is developed through the

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swelling of the seal against its confinement. Once in the well, the seal has to sustain a differential pressure that can reach 69 MPa (or 10,000 psi). However, a number of limitations for using such seals have been identified. First, the long-term reliability of these elastomer elements is limited by the tendency for the material to chemically degrade, particularly in the swollen state. Second, the tendency for the mechanical properties to decline as the material swells limits their applicability. In particular, as elastomers swell by imbibing a fluid they lose their stiffness, causing them to deform and extrude under differential pressure. Finally, the inability to control the swelling kinetics is an additional drawback. To summarize, the use of elastomer seals, both to replace cement in the oilfield and to improve the reliability of O-rings, is limited both by the low modulus of the material and the degradation of the physical properties upon fluid exposure.

Here we present a novel category of swellable materials for sealing applications where there is contact with water. These materials consist of a hydrogenated nitrile butadiene rubber (HNBR) matrix compounded with hydraulically active filler particles, such as unhydrated cement and magnesium oxide. These materials have the following important advantages:

- (1) They simultaneously swell and stiffen when in contact with water.
- (2) They maintain ductility in the swollen state.
- (3) They do not degrade over several months of aging.

These materials look and feel like normal rubber, and are initially compliant like rubber. However, after they swell in water, they become much stiffer, due to a chemical reaction of the filler particles that effectively increases the solids loading of the rubber matrix.

Rubber and cement have been combined before. For example, rubber particles have been added to cement to form a self-healing cement system, where the rubber particles can expand on exposure to a particular fluid to close cracks, improving the sealing performances of the cement [6,14]. In addition, hydrophilic polymer gels have been mixed with cementitious materials (hydroxyapatite and calcium phosphate) for bone filler injections [21,16]. However, in the above examples the material transitions from a fluid to a solid as with a traditional cement slurry, while the material described here starts as a solid that becomes much stiffer over time.

The composite of rubber and cement described in this work increases its modulus (stiffness) by a factor of 3.5, reaching 110 MPa, while swelling at the same time by 25%. The conventional swellable rubber material used as a comparison undergoes a modulus decrease of a factor 2, dropping below 2 MPa, when swelling 25%. Despite the increase in stiffness, the ductility of the HNBR-cement material is only slightly reduced. Furthermore, samples do not fully de-swell upon drying, unlike conventional materials, and maintain reasonable mechanical properties after months of fluid exposure. Thus, this material represents a technology platform with the potential to generate a wide variety of applications. It is also worth noting that the ingredients are readily-available materials and that the manufacturing process is relatively simple, making this composite a frugal material [22].

The quality and reliability of these novel, hydraulically active seals result from an optimization between the initial ductility of the elastomer (the seal needs to be able to deform under stress during installation and conform to the groove and gap), the amount of swelling (a state of compression is developed as a result of swelling), and the stiffness of the swollen material (a stiffer material is less likely to extrude, and generates higher contact pressure upon swelling). This study details those results and gives a qualitative analysis of the mechanisms generating swelling and stiffening of the HNBR-cement composites upon water exposure.

2. Experimental

While the swelling/stiffening behavior described above has been demonstrated for a variety of HNBR-cement composites, this paper focuses on a single composition. This composite was made by compounding 39% by volume of cement powder into hydrogenated nitrile butadiene rubber (HNBR), referred to as HNBR-cement. The HNBR has 43 ± 1.5 wt.% acrylonitrile content and 5.5 ± 1.0 wt.% residual double bonds; its Mooney viscosity is 61 ± 7 mooney units (Therban C4367 from Lanxess). The cement used is a mixture of finely ground blast furnace slag (80%) and Portland cement (20%). The slag cement is composed of calcium oxide (42–46%), silicon oxide (30–33%), aluminum oxide (9–11%) and magnesium oxide (5.5–7%). The median diameter is $4 \mu\text{m}$. The composite was manufactured using conventional rubber compounding techniques (internal mixer), with the cement powder added as with any other fillers, along with other typical rubber additives (accelerator, activator, anti-oxidant, antidegradant, processing aids). Sheets were molded and cured at 175°C . The resulting material is illustrated in Fig. 1.

Two additional materials were also studied for comparison purposes. One is a pure HNBR representing the matrix only, and is referred to as HNBR-Ref. This material does not swell in water. The other is a composite consisting of the same HNBR matrix compounded with 7% by volume of poly(acrylic acid) hydrogel (HNBR-hydrogel). The purpose of the hydrogel is to induce water uptake and swelling through osmotic pressure.

Volume changes on exposure to water were determined from buoyancy measurements in pure water. The elastic modulus was measured using a dynamical mechanical analyzer (DMA, model Q800 from TA Instruments) at room temperature, at a frequency of 1 Hz and strain amplitude of 0.1%. In those measurements, the phase angle $\tan\delta$ never exceeded 0.25, so the loss modulus always accounted for less than 6% of the norm of the modulus, and was therefore neglected. Tensile stress–strain curves were obtained using an Instron 5569 testing machine, using samples cut from a die ISO37, die type 3, with a crosshead rate of 20 mm/min. Strain was measured using a video-extensometer SVE from INSTRON.

High-resolution scanning electron microscopy (SEM) images were obtained in backscattered mode using a JEOL JSM-6490LV on the HNBR-cement materials before and after 1 week of hydration. The samples were cut into thin slices, dried, and mounted on carbon tape for better electron conductivity. TEM images were obtained with a JEOL 2010 transmission electron microscope (TEM). In this case the specimens were prepared by cutting thin slices at -160°C using a cryo-microtome apparatus (Leica RM2255) with a liquid nitrogen cooling instrument LN22.

X-ray diffraction was used for a semi-quantitative estimation of the cement hydration kinetics. The spectra were acquired with PANalytical multipurpose diffractometer working in the range $10\text{--}55^\circ 2\theta$, with a step size of $0.017^\circ 2\theta$ and a scan step time of

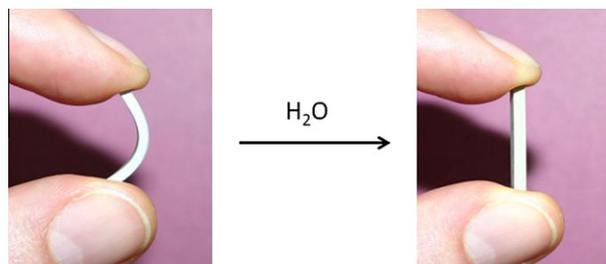


Fig. 1. HNBR-cement composite material before (left) and after (right) exposure to water. The HNBR-cement initially looks and feels like rubber, but the significant stiffening after exposure to water can be experienced by simple finger pressing.

90 s. The spectra were analyzed with PANalytical X'Pert HighScore Plus software.

The phase composition of the samples was investigated by means of thermogravimetry analysis (TGA) performed with a 60 cm³/min nitrogen flow (99.999% purity) and with a dynamic heating ramp (high resolution analysis).

3. Results and discussion

Fig. 2 shows the elastic modulus normalized to the initial value, as a function of swelling for the HNBR-cement and HNBR-hydrogel materials. After swelling by 25% upon exposure to water, the HNBR-hydrogel material loses half of its stiffness, while the HNBR-cement composite increases its stiffness by a factor of three. This property of simultaneous stiffening and swelling is the key advantage of this new type of material.

Fig. 3 shows the kinetics of swelling for all three materials during exposure to pure water at 82 °C. The HNBR-cement sample swells by 25% after 1 month, while the HNBR-hydrogel swells by about 100%. The pure HNBR reference material swells less than 5%, as expected. The 25% volume increase exhibited by the HNBR-cement sample is sufficient for many sealing applications. If higher swelling is required, other hydraulically active fillers can be chosen to match the desired swelling (e.g., Portland cement, magnesium oxide).

It is also important to note the differences in the behavior of the swollen samples on drying. The HNBR-hydrogel material de-swells completely on drying at 82 °C for 24 h; in fact, it reaches a volume that is about 5% lower than the initial unswollen volume (probably due to losses in additives and hydrogel particles). With the same drying treatment, the HNBR-cement material undergoes only partial de-swelling, from 25 ± 1% volume increase down to 11 ± 2%.

The evolution in modulus with time is shown in Fig. 4. The initial stiffness of the HNBR-cement material (32 ± 3 MPa) is significantly higher than that of the HNBR-hydrogel (3.6 ± 0.1 MPa), due to high content of the cement filler particles. After swelling, the final stiffness of the HNBR-cement (107 ± 7 MPa) is almost two orders of magnitude greater than that of the HNBR-hydrogel (1.3 ± 0.1 MPa). The HNBR-ref sample exhibits, as expected, a stable modulus upon exposure to water. The sharp decrease in the modulus of typical hydrophilic materials such as HNBR-hydrogel has a well-identified negative impact on the sealing ability of components made from these materials (O-rings and packers) [5]. Thus

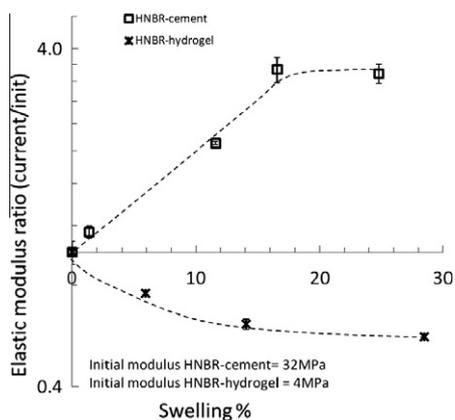


Fig. 2. Elastic modulus ratio (current/initial) as a function of swelling, for HNBR compounded with cement and with hydrogel particles. The HNBR-cement (61–39% by volume, pre-exposure) composite gets three times stiffer, while the HNBR-hydrogel (93–7% by volume, pre-exposure) sample loses half of its stiffness. The error indicated the standard deviation on three samples (HNBR-cement) or two samples (HNBR-hydrogel). The lines are guides to the eye.

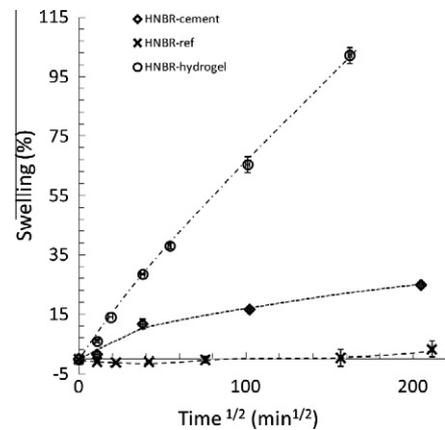


Fig. 3. Kinetics of swelling of all three materials during approximately 1 month of exposure to water at 82 °C. The error indicated the standard deviation on three samples (HNBR-cement) or two samples (HNBR-hydrogel and HNBR-ref). The lines are guides to the eye.

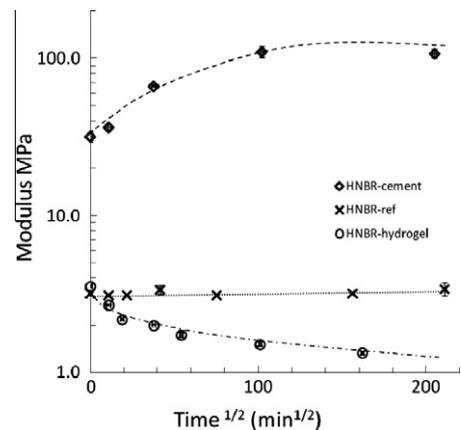


Fig. 4. Evolution of the elastic modulus of all three materials during approximately 1 month of exposure to water at 82 °C. The error bars indicate the standard deviation on three samples (HNBR-cement) or two samples (HNBR-hydrogel and HNBR-ref). The lines are guides to the eye.

it is anticipated that significant improvements in performance will be obtained with HNBR-cement.

It is important to note that despite the significant increase in stiffness of the HNBR-cement, the material ductility is mostly maintained after 1 month of hydration (see Fig. 5). After 7 months of hydration, the ductility of the material is reduced from 410% to 130% engineering strain, indicating possible long-term reaction between cement and rubber.

The increase in modulus with swelling of the HNBR-cement material clearly is qualitatively different from the experimental [15] and predicted [9] behavior based on simple uptake of liquid water. As illustrated in Fig. 6, the hydration and setting of the cement inside the HNBR matrix, which converts liquid water into solid products, is responsible for this difference.

Initially, water diffuses into the rubber driven by osmotic pressure, as with the HNBR-hydrogel material. This process is rather slow even at 82 °C, as can be seen from the swelling kinetics shown in Fig. 3. Once water reaches the cement particles, the hydration reaction is initiated, as with a normal cement paste. The cement particles first dissolve into their ionic constituents, and then these ions precipitate to form cement hydration products, primarily calcium silicate hydrate (C–S–H). (The formation of C–S–H is discussed further below). The hydration products grow primarily at

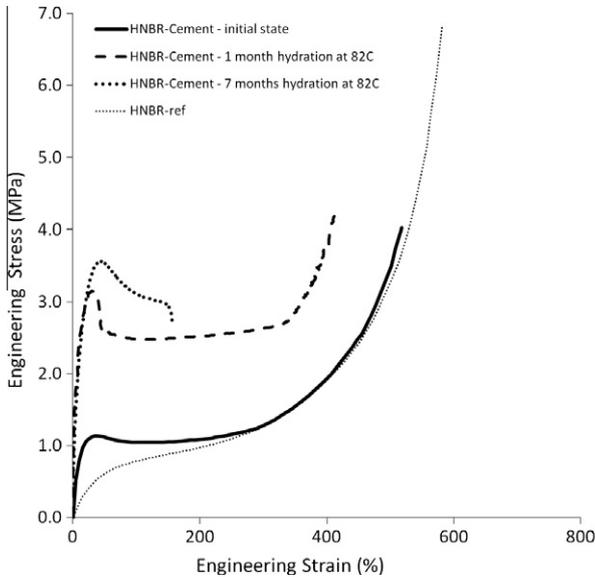


Fig. 5. Tensile stress–strain curves for HNBR-cement (61–39% by volume, pre-exposure) and HNBR-ref (pre-exposure) materials, before swelling and after approximately 1 month and 7 months of exposure to water at 82 °C. The tests were conducted at room temperature using a strain rate of $\sim 0.75 \text{ s}^{-1}$.

the surface of the cement grains, forming a layer. Since these hydration products contain significant amounts of bound water, the hydration process causes the solid filler particles to increase in size, effectively increasing the solid filler content of the composite. As a result, the composite becomes stiffer as it swells.

Fig. 7 shows the SEM images of the microstructure of HNBR-cement, before and after hydration. It is clear that after hydration, the cement particles have expanded significantly, even though many of them have fractured (arrow). Also, instead of having a clear two-phase HNBR-cement composite, it is harder to separate these two phases after hydration, which indicates not only a tighter network of cement particles in the rubber network but also a tighter connection between the particles and the rubber. The decrease in average particle size as well as the tighter network of cement and enhanced bonding to rubber likely contribute to increasing the composite stiffness.

Hydration of slag produces C–S–H with a Ca/Si molar ratio close to one [20,8], while hydration of Portland cement produces a variety of hydration products, with the dominant ones being C–S–H with a higher Ca/Si ratio of about 1.7 and calcium hydroxide (portlandite). Since the main component of the cement filler is the ground slag (80 wt.%), we expect the dominant hydration product to be C–S–H with a low Ca/Si ratio.

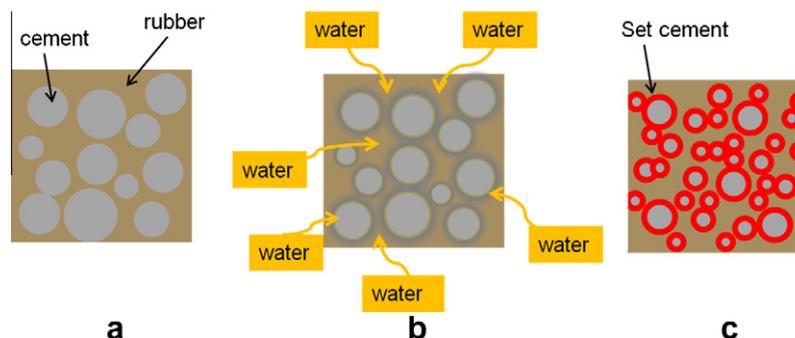


Fig. 6. Schematic of the hydration process occurring inside the HNBR-cement material, which is responsible for the increased stiffness with swelling. (a) Initial composite. (b) Water diffuses and dissolves the cement, and a layer of hydration product precipitates. (c) Layers of hydration product bind together, further increasing the stiffness.

Fig. 8 shows XRD spectra of the HNBR-cement material taken in the unhydrated initial state and after 24 days of swelling in water at 82 °C. The well-defined peaks in the unhydrated material can be associated with Portland cement minerals, such as tricalcium silicate (Ca_3SiO_5), since the slag has a glassy structure that generates no sharp X-ray peaks, and the HNBR matrix also does not generate peaks. In the hydrated composite, well-defined peaks associated with calcium hydroxide and calcium carbonate appear, along with a broader peak that can be associated with the poorly crystalline C–S–H phases [20]. Calcium carbonate is often detected in hydrated cementitious materials in small amounts, resulting from the reaction of calcium hydroxide with carbon dioxide from the air. These XRD results confirm that the volume and modulus gains are associated with the appearance and evolution of hydration products inside the HNBR matrix. In the hydrated composite, the peaks associated with the Portland cement minerals, such as tricalcium silicates, nearly disappear after 24 days, indicating that most of the cement filler has reacted.

The presence of both C–S–H and portlandite in the hydrated HNBR-cement was also confirmed through direct observation by high resolution TEM, as shown in Fig. 9. The C–S–H nanocrystallites display a characteristic layered structure defined by silica-rich interlayers. The lattice spacing determined from the images is $1.15 \pm 0.05 \text{ nm}$, which agrees with published values [19]. Portlandite crystals, which have a characteristic hexagonal shape [20], were also identified by TEM.

The kinetics of the cement hydration process during the early period when hydration is relatively rapid were measured using isothermal calorimetry, which tracks the exothermic heat flow associated with the chemical hydration reactions (see Fig. 10). Both the HNBR-cement composite and pure cement of the same type were measured at 82 °C, and the heat flow in both cases was normalized to the original mass of unhydrated cement. It is clear that the cement hydrates much more slowly when compounded inside the rubber. This can be attributed to the need for water to diffuse into the HNBR matrix before contacting the cement. It can also be attributed to the fact that the hydration products must form within a constricted space.

Integrating the heat flow curves provides the total amount of heat emitted over time (Fig. 10, right), which is proportional to the degree of hydration of the cement. While the pure cement is fully reacted after about 15 h at 82 °C, the HNBR-cement is only about 20% reacted after 48 h. However, this still represents a significant increase of solid volume within the specimen.

4. Model of the stiffening

Here we model the stiffening of the HNBR-cement composite with hydration by calculating the effective increase in filler content

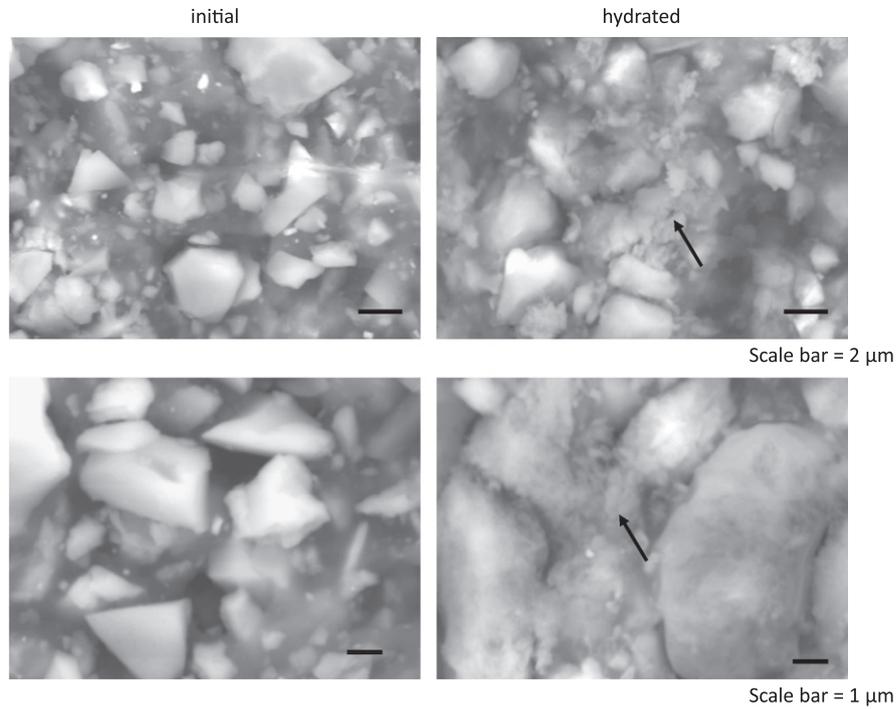


Fig. 7. SEM images of HNBR-cement material before (left) and after (right) hydration. It is shown that after hydration, the hydrated cement particles are expanded, even though many of them broke into small pieces and more particles (arrow) are connected with each other. Both factors contribute to the increase in stiffness.

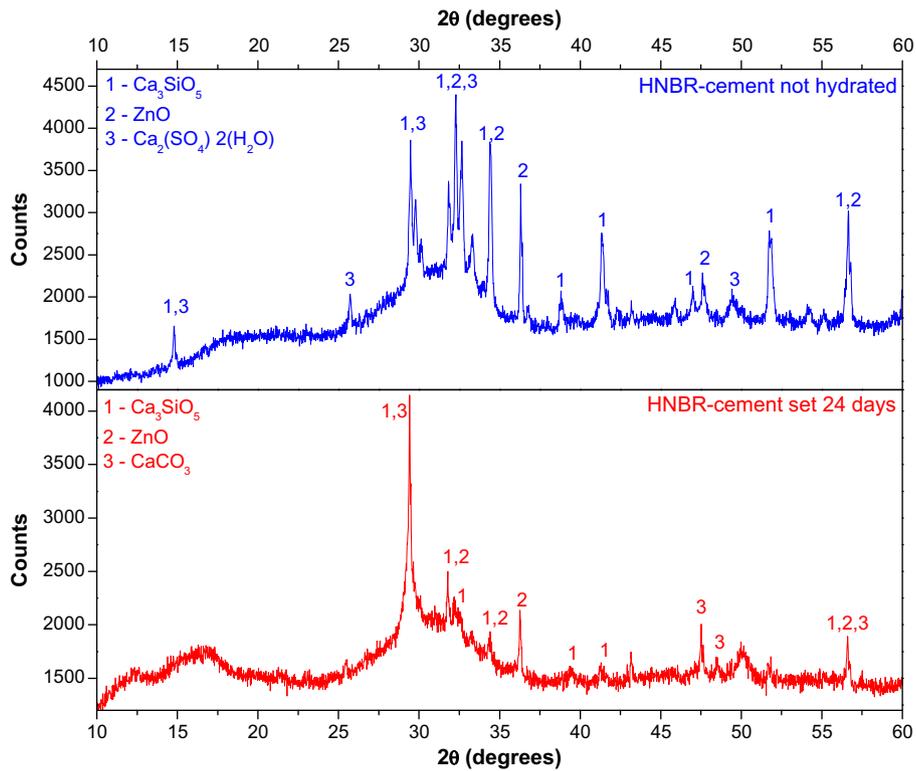


Fig. 8. XRD diffraction spectra of the HNBR-cement composite before and after hydration. The tricalcium silicate (Ca_3SiO_5) peaks prove the presence of un-hydrated Portland cement (top). The calcium hydroxide and calcium carbonate peaks prove the presence of cement hydration products inside the HNBR matrix (bottom).

inside the rubber matrix as liquid water is converted to solid hydration product. This allows us to then predict the change in modulus with hydration using general models for the change in composite modulus with filler content. We consider the matrix

to be unchanged during this process, i.e. we assume the HNBR does not undergo any cross-linking or degradation. For simplicity we also neglect the volume change of the matrix due to the presence of water that is diffusing inward to react with the cement. In other

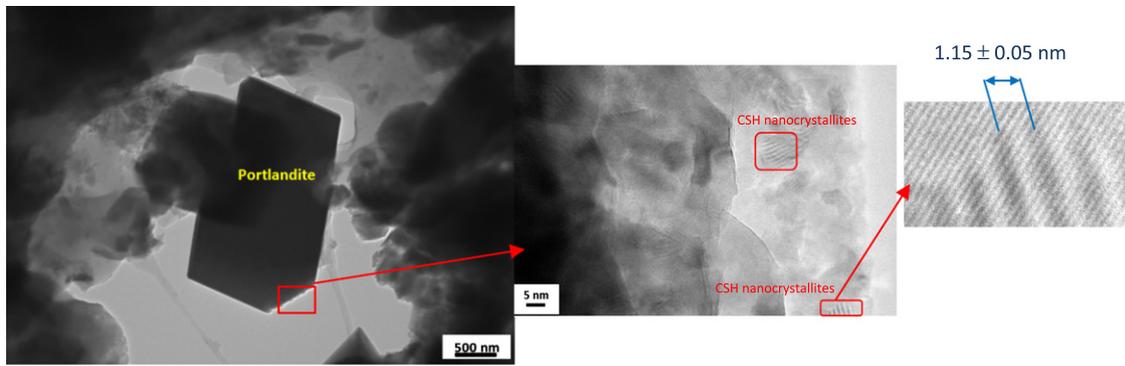


Fig. 9. High resolution TEM images of hydrated HNBR-cement material: Hexagonal portlandite crystal on which nanocrystals of C–S–H are growing (left), C–S–H nanocrystals with a layer spacing of 1.15 ± 0.05 nm (right). The image on the far right has been enhanced and cleaned up by using Fourier Transform filtering (SPIP Image Metrology software).

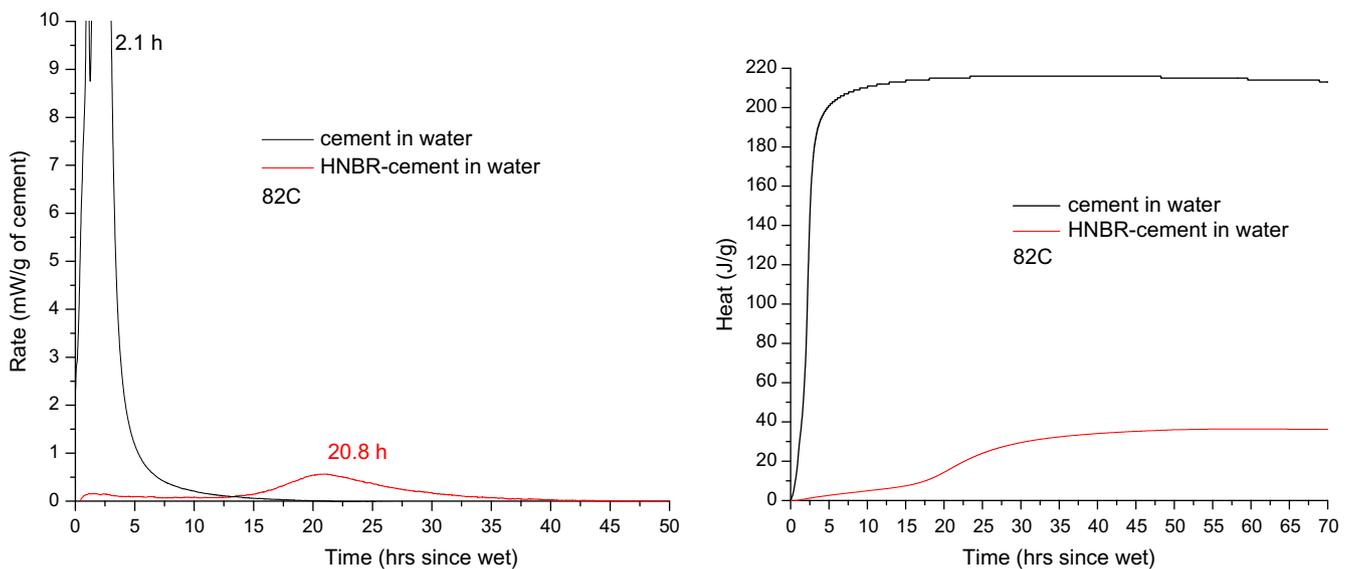


Fig. 10. Hydration kinetics of the HNBR-cement composite and pure cement exposed to water at 82 °C, as measured by isothermal calorimetry: Rate of heat evolution with time (left), total heat evolved with time (right). The cement reacts much more slowly when compounded inside the rubber.

words, we consider all volume changes to take place in the filler phase.

The volume fraction of filler Φ_t in the HNBR-cement at time t is then:

$$\Phi_t = \frac{\Phi_{\text{cement},i} + Q}{1 + Q} \quad (1)$$

where $\Phi_{\text{cement},i}$ is the initial volume fraction of unhydrated cement and Q is the normalized volume change, which was measured experimentally. Fig. 11 shows the evolution of Φ_t calculated from Eq. (1) with time for the HNBR-cement material. The filler volume fraction increases from its initial value of 0.39 to a value of 0.51 after one month of reaction in water.

It is worth noting that the effective filler content significantly exceeds the practical compounding limit of 0.4. Thus we introduce the concept of growing filler in situ to enable reaching otherwise inaccessible high values of filler loading on the reacted material. This allows the composite to reach higher modulus values, and may also decrease its cost, considering that fillers are typically less expensive than rubber.

Because the filler (cement) reaches half the volume of the material, this composite can be seen either as a rubber filled with cement, or as a cellular cement filled with rubber.

In the first case, where rubber is seen as the matrix, the Guth and Gold model [11] is typically used to predict the composite modulus E using a quadratic function of the filler content Φ :

$$E = E_0[1 + 2.5\Phi + 14.1\Phi^2] \quad (2)$$

where E_0 is the modulus of the matrix phase, i.e. the unfilled rubber.

Using $E_0 = 3.3$ MPa (HNBR-ref), and Eq. (1) to calculate Φ the predicted modulus largely underestimates the measured modulus (Fig. 12).

On the other hand, if cement is considered the matrix, the composite can be seen as a random three-dimensional cellular solid where bending arms are made of cement. Using the Gibson-Ashby cellular solid model [10], the composite modulus is predicted to be:

$$E = C.E_s.\Phi^n \quad (3)$$

where C is a parameter that depends on the cell structure, E_s is the modulus of the continuous phase (the hydrating cement in this case), and n is an exponent.

In this case, the exponent n was taken as 3.5 following previous work of [23,18] while $C.E_s$ was varied as a single constant to fit the experimental data. The fitted value of 1.1 GPa is a reasonable

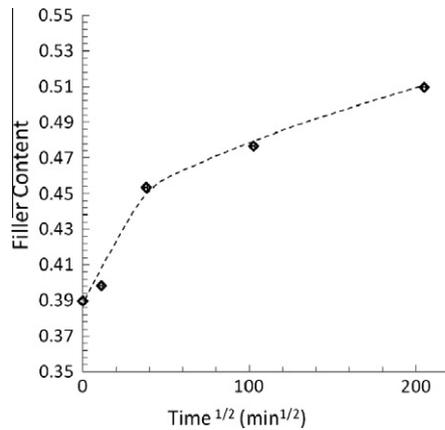


Fig. 11. Effective filler content of the HNBR-cement material resulting from cement hydration, estimated from the measured volume change of the material using Eq. (1). The lines are guides to the eye.

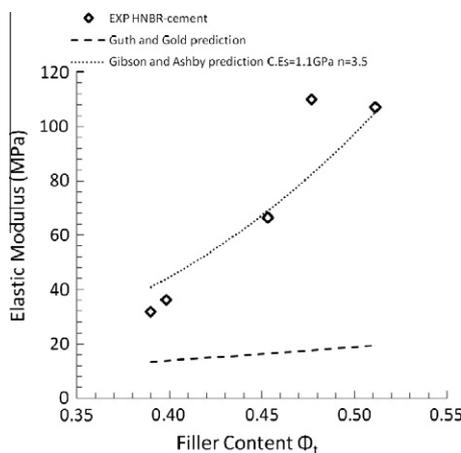


Fig. 12. Elastic modulus of the HNBR-cement as a function of the effective filler content (symbols), along with model predictions (dotted and dashed lines). See text for more details.

match for high porosity slag cement. The Gibson-Ashby model matches the experimental values quite well (Fig. 12).

5. Conclusions

A new type of reactive composite material is described, consisting of HNBR rubber compounded with unhydrated cement particles. On exposure to water, the cement filler undergoes hydration reactions, causing the composite to swell as liquid water diffuses into the matrix and then reacts. Since cement and its hydration products are much stiffer than HNBR, both play the role of sub-micron to micron-sized fillers leading to an overall stiffening of the composite as it swells. At the same time, because the HNBR matrix remains continuous, the stiffening does not compromise the ductility of the composite. The behavior of this material is qualitatively different from that of traditional swellable elastomers that become

less stiff as they absorb liquid water, and is ideal for sealing applications where the sealing component must support a large differential pressure.

Based on the assumption that the hydration reactions produce solid filler inside the matrix, the effective filler content of the composite could be calculated as a function of the measured swelling, and this value increased to levels significantly above the practical compounding limit for HNBR. The Gibson-Ashby cellular solid model was used successfully to model the increase in stiffness with swelling of the HNBR-cement composite material, based on the assumption that the hydrated cement becomes a continuous filler phase.

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