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Stimuli-Responsive Cement-Reinforced Rubber

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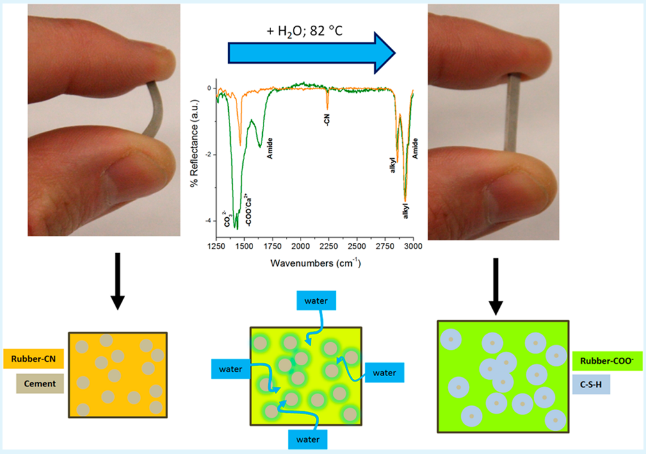
Supporting Information



ABSTRACT: In this work, we report the successful development of a cement–rubber reactive composite with reversible mechanical properties. Initially, the composite behaves like rubber containing inert filler, but when exposed to water, it increases in volume and reaches a stiffness that is intermediate between that of hydrogenated nitrile butadiene rubber (HNBR) and hydrated cement, while maintaining a relatively large ductility characteristic of rubber. After drying, the modulus increases even further up to 400 MPa. Wet/drying cycles prove that the elastic modulus can reversibly change between 150 and 400 MPa. Utilizing attenuated total reflection Fourier transform infrared spectroscopy), we demonstrate that the high pH produced by the hydration of cement triggers the hydrolysis of the rubber nitrile groups into carboxylate anions. Thus, the salt bridges, generated between the carboxylate anions of the elastomer and the cations of the filler, are responsible for the reversible variations in volume and elastic modulus of the composite as a consequence of environmental moisture exposure. These results reveal that cement nanoparticles can successfully be used to accomplish a twofold task: (a) achieve an original postpolymerization modification that allows one to work with carboxylate HNBR (HXNBR) not obtained by direct copolymerization of carboxylate monomers with butadiene, and (b) synthesize a stimuli-responsive polymeric composite. This new type of material, having an ideal behavior for sealing application, could be used as an alternative to cement for oil field zonal isolation applications.

KEYWORDS: *composite, rubber, HNBR, cement, oxides, hydrolysis, stimuli-responsive*

1. INTRODUCTION

Water-swellable elastomers are largely used for applications in numerous fields of technology, from microfluidic valves for flow control[1] to sealing joints for civil engineering.[2] In particular, in the oil field industry, water-swellable polymers are used in swellable packers, a valid alternative to cement for zonal isolation. The swellable packers are placed in the annulus between the casing and the rock formation, and upon absorption of water brine, they increase in volume, consequently sealing the annulus and preventing any fluid leakage that could have catastrophic consequences for the safety of the rig and the environment.[3]

The traditional water-swellable polymers possess the ability to absorb large quantities of water, up to 1000 times their dry weight, through osmosis interactions between water molecules and the long polymer chains (mostly through van der Waals forces and hydrogen bonding). Since no chemical bonding between the solvent and the polymer network exists for these types of swellable materials, two main issues limit the reliability of these elastomers on long-term sealing applications in the oil field industry.[4] First of all, the swelling is reversible when the availability of water changes; moreover, the elastomer modulus decreases due to dilution of the stiff rubber matrix by the water.[5] A conventional swellable rubber typically undergoes a modulus decrease of a factor of 2, dropping below 2 MPa, when swelling 25%.[6] Intrigued by the properties of ionomers,[7,8] a class of copolymers containing up to 15–20% of ionic groups incorporated into the backbone, we decide to try overcoming the aforementioned issues by developing a new mechanically adaptive material for structural applications by using anhydrous cement as reactive filler inside HNBR (hydrogenated nitrile butadiene rubber).[9]

HNBR, an elastomer mostly used for high-temperature applications, shows rather stable mechanical properties, under both wet and dry conditions. Its mechanical properties are

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typically enhanced with the addition of standard inert fillers, such as carbon black or silica fume.[10,11]

Adding filler helps improve the mechanical performances and also reduces the cost of the final composite. In fact, HNBR is an expensive material due to the homogeneous catalytic hydrogenation process employed to remove the double bonds. However, the maximum amount of filler that can be used per unit of rubber is strongly limited by the dispersion/mixing efficiency of the filler particles within the matrix.[12] The addition of fillers also typically reduces the ability of the composite to swell.

In order to achieve adaptable mechanical properties by means of wet modulation, we decided to use microsized cement as reactive filler to convert the ion-free polymer in ionomer-containing carboxylate anions ($-COO^-$), hence enabling the formation of ionic bonds[13,14] between the elastomer backbone and the reactive filler, bonds that can be reversed. We avoided using carboxylate HNBR (HXNBR),[14,15] obtained by direct copolymerization of carboxylate monomers (acrylic or methacrylic acid) with butadiene, because a large number of factors (such as the pH of the polymerization medium, solvent composition, hydrogen bonding generating dimer−monomer equilibrium, etc.) can negatively affect the molecular structure and the properties of the so-produced carboxylate ionomers.[16] As a consequence, by using microsized cement as filler, we developed an original postpolymerization modification that allows us to convert the HNBR's nitrile groups into carboxylate anions through direct interaction of the rubber with the reactive filler.

In this study, we demonstrated that, as the cement gets hydrated inside the rubber, the high pH causes the postpolymerization conversion of the rubber nitrile groups to carboxylate anions. The hydrated cement then produces an ionic cross-linking (salt bridges) network with the carboxylate anions. Hence, after exposure to water, the hydration of the cement, the consequent reaction with rubber, and the elastomeric regions of restricted mobility generated by the salt bridges[13,17] cause an increase of both volume (40% swelling) and stiffness (3 times greater than initial value) never shown by other swellable polymers. The hydration of cement also provokes an increase in the filler content beyond the limit of filler loading currently imposed by the compounding process. Moreover, as shown in wet and dry cycles, upon drying, the HNBR-cement shows a small deswell while it further increases in stiffness.

The remarkable properties of this rubber composite, the use of a frugal material such as cement, and the relative simple manufacturing process make this composite a technological platform with the potential to generate a wide variety of applications.

2. EXPERIMENTAL SECTION

In this study, we used a silica-rich cement having the following composition: CaO 45 wt %, SiO_2 33 wt %, Al_2O_3 10 wt %, Fe_2O_3 2 wt %, MgO 6 wt %, SO_3 3 wt %, other 1 wt %. Typical cement used in downhole applications has a mass median diameter (D_{50}) ≅ 100 μm. However, in order to accelerate the hydration kinetics, the cement has been further ground and sieved to obtain a smaller particle size ($D_{95} \leq 10\ \mu$m, $D_{50} \leq 5\ \mu$m).The composite was made by compounding 39 vol % of cement 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 composite was manufactured using conventional rubber compounding techniques (internal mixer), with the cement powder added as with any other fillers. Sheets were molded and cured at 175 °C. The samples were cut in dogbone shapes, suitable for tensile tests, with dimensions of roughly 2 mm × 4 mm in the narrow central region and a total length of 30 mm.

The mass and volume of each sample were measured. The samples were placed in glass vials, where they were submerged with water. The vials were sealed and placed in an oven at 82 °C for the hydrothermal treatment. This temperature was chosen to reproduce a typical downhole temperature faced during sealing applications in the oil field. At intervals of 0 h, 2 h, 1 day, 7 days, and 24 days, a set of samples was removed from the water bath. After measuring the change in mass and volume, the samples were placed into an 82 °C oven in order to evaporate all the free water. After drying, the mass and volume of the samples were measured again.

Volume changes on exposure to water were determined from buoyancy measurements in pure water.

The elastic modulus of each HNBR-cement composite sample was measured using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) at room temperature using parallelepiped samples under uniaxial tensile cyclic loading at 1 Hz. A 0.1% oscillating strain amplitude was applied to the sample at a frequency of 1 Hz. Both storage modulus, or elastic modulus, E', and loss modulus E'', were recorded; this study focuses on the elastic modulus E', which can be approximated as equal to the Young's modulus. Indeed, the loss factor ($\tan\ \delta = E''/E'$) was never greater than 0.25. The loss modulus accounts for less than a 16th of the norm of the complex modulus and was neglected in this work.

TEM images were obtained with a JEOL 2010 transmission electron microscope (TEM). The samples were cut at −160 °C using a cryo-microtome apparatus (Leica RM2255) with a liquid nitrogen cooling instrument LN22, and then they were mounted on a copper grid for TEM.

X-ray diffraction was used for a semiquantitative estimation of the cement hydration kinetics. The spectra were acquired with a PANalytical multipurpose diffractometer working in the range of 10−55° 2θ, with a step size of 0.017° 2θ and a scan step time of 90 s. The spectra were analyzed with PANalytical X'Pert HighScore Plus software.

The infrared spectra between 4000 and 650 cm^{-1} were recorded for the composites, both before and after hydrothermal treatment, by means of the attenuated total reflection Fourier transform infrared (ATR) technique with a Thermo Nicolet spectrophotometer (model 6700 FTIR) equipped with a Ge crystal. The spectra were obtained collecting 128 scans with a resolution of 4 cm^{-1}.

A differential scanning calorimeter (MC-DSC, TA Instruments, Lindon, UT) was used to monitor the rate of heat output under isothermal conditions at 82 °C for the cement, both standing alone and inside the rubber. Results for cumulative heat are reported per gram of cement powder.

3. RESULTS AND DISCUSSION

As shown in Figure 1, before hydrothermal treatment, the composite looks and behaves like rubber filled with inert filler. When a small sample gets pressed between two fingers, it easily bends. However, the composite's behavior dramatically changes after water exposure. The stiffness significantly increases at the point that the same sample cannot be bent anymore when applying an equal or greater pressure between two fingers (Figure 1, right).

When the rubber cement composite is first exposed to water at 82 °C, the water molecules diffuse through the rubber matrix driven by osmotic pressure. While the water diffuses inside the rubber, it gets in contact with the cement particles, hence triggering several reactions, of which the first one is the cement hydration. However, we have to underline that, as shown in Figure 2, the slow water diffusion into the rubber controls both the mass intake and the kinetics of hydration of the cement. In

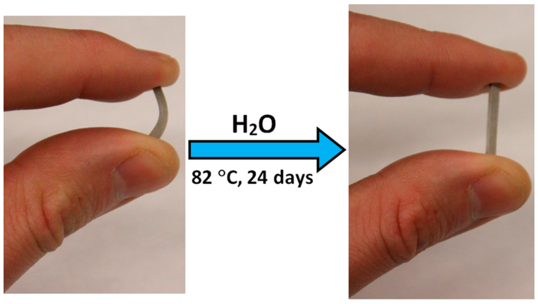

Figure 1. Comparison of HNBR-cement ($D_{50} \leq 5$ μm) stiffness before (left) and after (right) water exposure.

particular, as can be seen from the isothermal calorimetry results in Figure 2 (right), the hydration of the cement, whether it is the microsized one, is significantly slowed down when it occurs inside the rubber (in every case, the cumulative heat has been normalized to the original mass of unhydrated cement). During cement hydration, the tricalcium silicate (C_3S), and, much more slowly, the dicalcium silicate (C_2S), reacts to release a large amount of heat and hydroxide ions, which, in turn, combine with calcium ions to form calcium hydroxide ($Ca(OH)_2$).[18] At the same time, silicate material enters the liquid phase and the dissolved components combine to form the calcium silicate hydrate (C-S-H) gel, an amorphous two-component solid solution composed of $Ca(OH)_2$ and calcium silicate hydrate. After few minutes, the initial hydrolysis decelerates down and the reaction slowly continues, producing calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize; consequently, the ions precipitate out of solution, accelerating the reaction of tricalcium silicate to calcium and hydroxide ions. The formation of the calcium hydroxide and calcium silicate hydrate crystals provide "seeds" upon which more calcium silicate hydrate can form. The calcium silicate hydrate crystals grow thicker, making it more difficult for water molecules to reach the unhydrated tricalcium silicate. The speed of the reaction is now controlled by the rate at which water molecules diffuse through the calcium silicate hydrate coating. This coating thickens over time, causing the production of calcium silicate hydrate to become slower and slower.[19,20] The formation of C-S-H in the hydrated composite was confirmed through direct observation by high-resolution TEM, as shown in Figure 3. These cement hydrates display a characteristic layered structure (Figure 3, right) defined by silica-rich interlayers.[21]

Since the hydration products contain a significant amount of bound water, the hydration process causes the filler to increase in size and mass, effectively producing a 40% swelling and an increase of filler content estimated from 39 to 51 vol % after 24 days hydration (Figure 5a). It is worthwhile underlining that 51 vol % filler, estimated after the composite was dried, is beyond the limit of filler loading currently imposed by the compounding process (the limit is actually close to the initial content of 39 vol % in the present case).

The alkaline environment (pH ≅ 12.8), generated by the hydroxide release during the hydration of the cement, significantly changes the chemical properties of the rubber by inducing the hydrolysis of nitrile groups to carboxylate anions,[22] as shown in Figure 4.

The so-formed anionic species interacts with the metallic cations (mainly free Ca^{2+} or $-Ca^{+}$ contained on the surface of C-S-H) through the formation of ionic bonds (salt bridges).[23]

Since ions get shielded in the presence of water, with a consequent decrease in the intensity of the electrostatic forces, the ionic bonds generate regions of restricted mobility that are responsive to water stimulus.[13,17] As shown in Figure 5a, after 24 day hydrothermal treatment, the HNBR-cement composite (still wet) shows an increase in the elastic modulus from 32 MPa (pristine unhydrated composite) up to 100 MPa. When the composite is dried to remove the excess of absorbed water, the elastic modulus further increases up to 400 MPa. On the other hand, when the dry composite is re-exposed to water, the elastic modulus decreases to about 150 MPa. Then, as shown in Figure 5a, by running a cycle of wet/dry test on the composite, a reversible change of the elastic modulus is evident. Such behavior is explained with the different strength of the ionic bonds depending on the presence of free water molecules. When the free water molecules are removed from the composite, the opposed ions of the matrix and filler strongly attract each other in a firmly bonded structure (Figure 6, left), with a consequent increase in stiffness. On the other hand, when the dry composite is re-exposed to the aqueous environment, the water molecules percolating through the matrix interact with the ions and create a hydration shell that

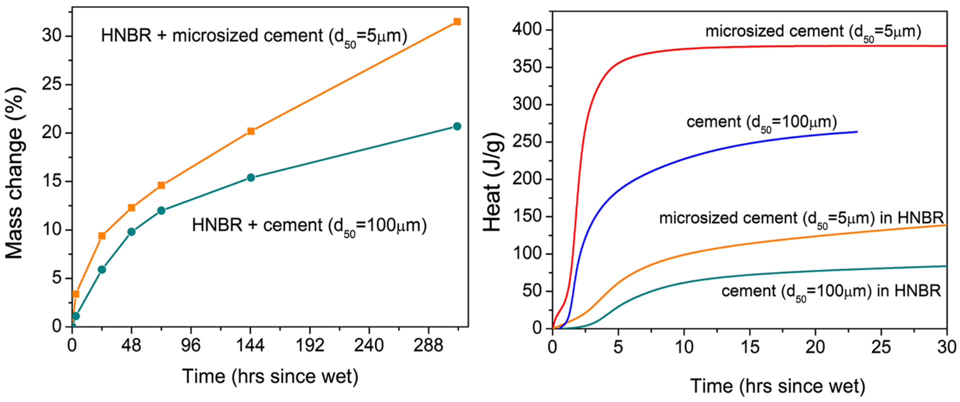

Figure 2. On the left, the comparison of the mass intake of the composite absorbing water (at 82 °C) when filled with cement with different particle sizes. On the right, the cumulative heat evolution during the hydration of cement with different particle sizes, in water at 82 °C, both in HNBR and standing alone. The finer particle size causes a faster hydration. When the cement is embedded in the rubber, the hydration kinetics is strongly affected by the water diffusion in the rubber matrix.

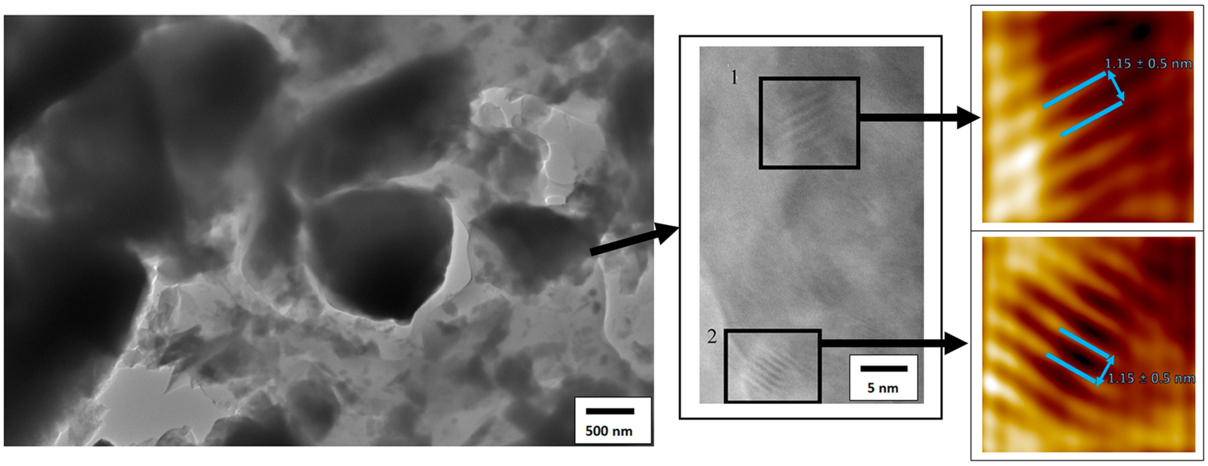

Figure 3. High-resolution TEM pictures of hydrated cement particles embedded in the rubber matrix (sample containing microsized particles of cement, exposed to water at 82 °C for 24 days). On the right, a detail of nanocrystals of C-S-H with a layer spacing of 1.15 ± 0.05 nm is shown (right). The image on the far right has been enhanced and cleaned up by using Fourier transform filtering (SPIP image analysis software, Image Metrology, Denmark).

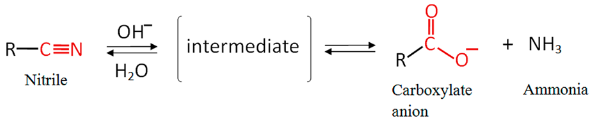

Figure 4. Schematic representation of the hydrolysis reaction occurring to nitrile groups in basic solution.

shields the charges, weakening the ionic cross-linking (Figure 6, right), hence reducing the composite's stiffness.

For what concerns the change in volume of the composite, as mentioned before, after 24 days hydration, the wet composite shows a 40% swelling, which corresponds to about 34% mass intake (Figure 5b). After the sample is dried to remove the excess of free water, the material partially deswells down to 23% (residual swelling), which corresponds to a residual absorbed mass of ca. 3−5%. This 17% deswelling during drying is caused by the fact that the structural collapse caused by the water removal is counterbalanced by the increased stiffness of the system. Therefore, we assume that the water removal creates a porous structure in the filler and at the interface between filler and rubber.

On the other hand, in the following wet/dry cycles, between the wet and the dry material, a small variation in volume (from 22% to 16%) is visible, while the mass change is more significant (from 21% to 3%). It has to be noted that, in these cycles, the exposure to water has been performed for 5 days while the drying lasted 1 day. The times were chosen to reach the plateau value in each case. We believe that the increased stiffness and the intrinsic porosity of the hydrated filler are responsible for such behavior. During the successive hydrothermal treatments, the water molecules keep being abundantly absorbed due to osmotic pressure (thus, the significant mass intake), but the water molecules get mostly absorbed in the pores and voids with little swelling for the composite.

The ATR-FTIR spectra recorded on pure HNBR and on the composites (Figure 7) exhibit important differences in the features, proving that the conversion of the nitrile groups to carboxylate anions occurs due to hydrolysis reaction, catalyzed in the aqueous medium at elevated temperature and pH greater than 11. The FTIR spectrum of pure HNBR reveals very distinctive features, such as the peak at 1465 cm^{-1}, characteristic of in-plane deformation of the methylene group, and the

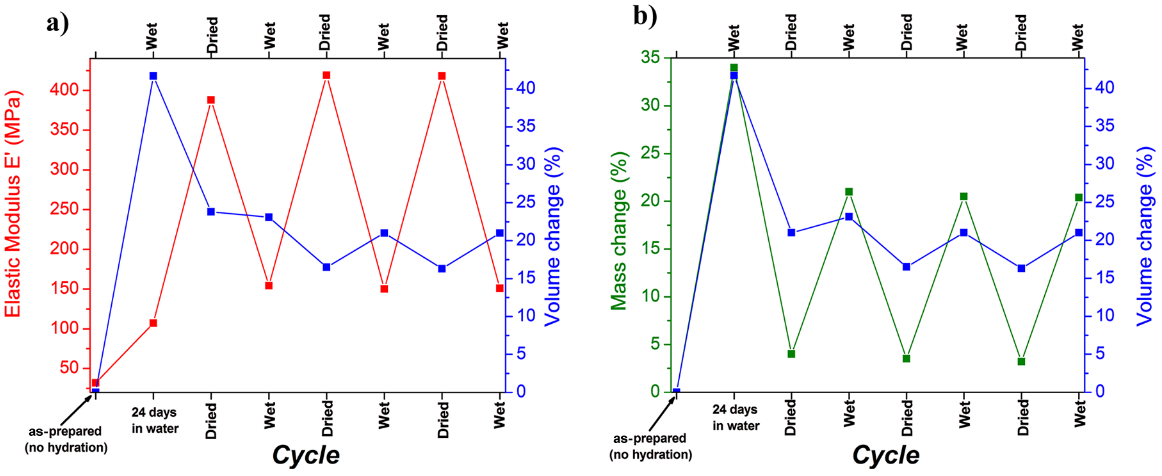

Figure 5. Reversible changes of volume (blue) and elastic modulus (red) of the composite upon wet−dry condition exposure (left). Reversible changes of volume (blue) and mass (green) of the composite upon wet−dry condition exposure (right).

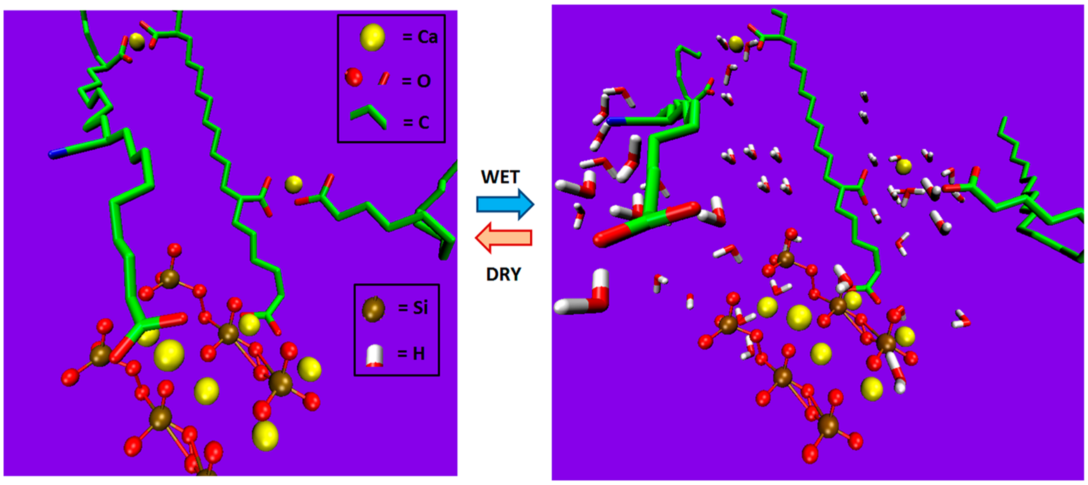

Figure 6. Ionic interaction between polymeric carboxylate anions and inorganic cations (either isolated Ca^{2+} or calcium monovalent cations bonded on the surface of C-S-H particles) can be switched on and off depending on the presence of water molecules. In fact, the presence of free water molecules reduces the strength of the ionic cross-link (through solvation mechanism) between the rubber chains and the filler.

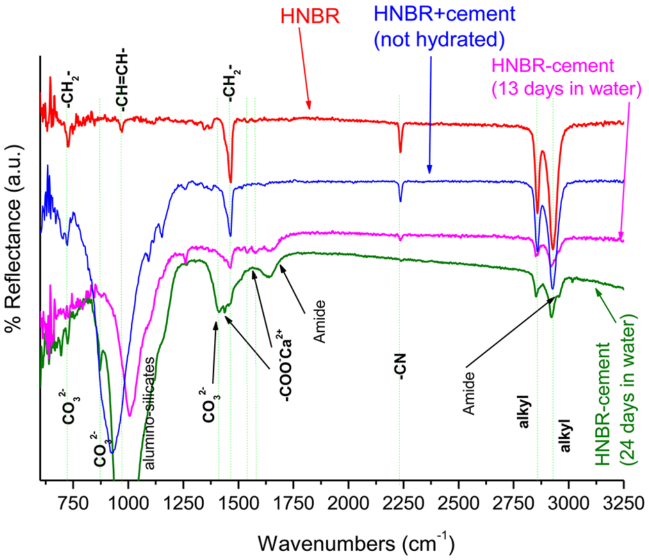

Figure 7. ATR-FTIR study of the chemical reaction occurring to the HNBR as a consequence of cement hydration (microsized cement particles).

signals at 2860 and 2930 cm^{-1} are assigned to symmetric and asymmetric stretching modes of alkyl groups ($-CH_2$, $-CH_3$), respectively.

The band at 970 cm^{-1} is assigned to the out-of-plane deformation of the trans double bond ($-CH{=}CH-$), while the band at 726 cm^{-1} is assigned to the methylene rocking vibration (when the number of consecutive $-CH_2-$ groups is more than 4). In addition, the absorption at 2236 cm^{-1} is distinctive of the stretching mode of the carbon/nitrogen triple bond contained in the nitrile group ($-C{\equiv}N$).[14,24,25] The HNBR-cement composite, both before and after hydrothermal treatment, shows the presence of a strong band at 960−1006 cm^{-1}, indicating the presence of alumino-silicates.

However, the major spectral changes occur only when the composite is set in water for 24 days. The spectra exhibit new peaks at 712 and 878 cm^{-1} (O−C−O bending) and at 1412 cm^{-1} (CO_3^{2-} stretching), indicating the formation of calcium carbonate ($CaCO_3$).[26]

In addition, the formation of calcium carboxylate ($-COO^-Ca^{2+}$) is revealed by the appearance of new bands at 1420 cm^{-1}, attributed to the overlapping of the symmetric carbonyl stretching of calcium carboxylate with the peak due to the formation of calcium carbonate, and in the 1510−1580 cm^{-1} range, as a consequence of the asymmetric carbonyl stretching of calcium carboxylate.[25,27] The appearance of these modes along with the diminished intensity of the nitrile peak proves that a significant amount of nitrile groups was converted to carboxylate groups ($-COO^-$).

Furthermore, the sample treated for 24 days shows extra features (871, 1640, and 3016 cm^{-1}) due to traces of amide groups produced as intermediates during the hydrolysis process.[22,24]

We monitored the chemical change occurring to the nitrile group by measuring the ratio between the intensity of the nitrile peak and the intensity of both the symmetric (I_{CN}/I_{sym}) and the asymmetric (I_{CN}/I_{asym}) stretching modes of alkyl groups. The evolution of the intensity ratios plotted as a function of treatment time proves that the nitrile groups, originally present in the anhydrous composite, were gradually converted to carboxylate anions as the treatment time increased (Figure 8).

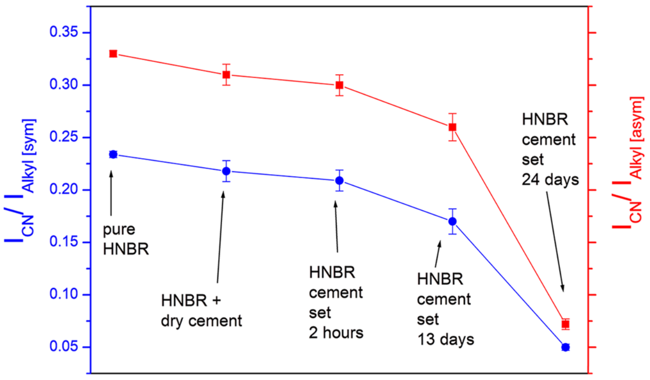

Figure 8. Plot showing the evolution of the ratio between the intensity of the nitrile peak and the intensity of either the symmetric (I_{CN}/I_{sym}) or the asymmetric (I_{CN}/I_{asym}) stretching modes of alkyl groups.

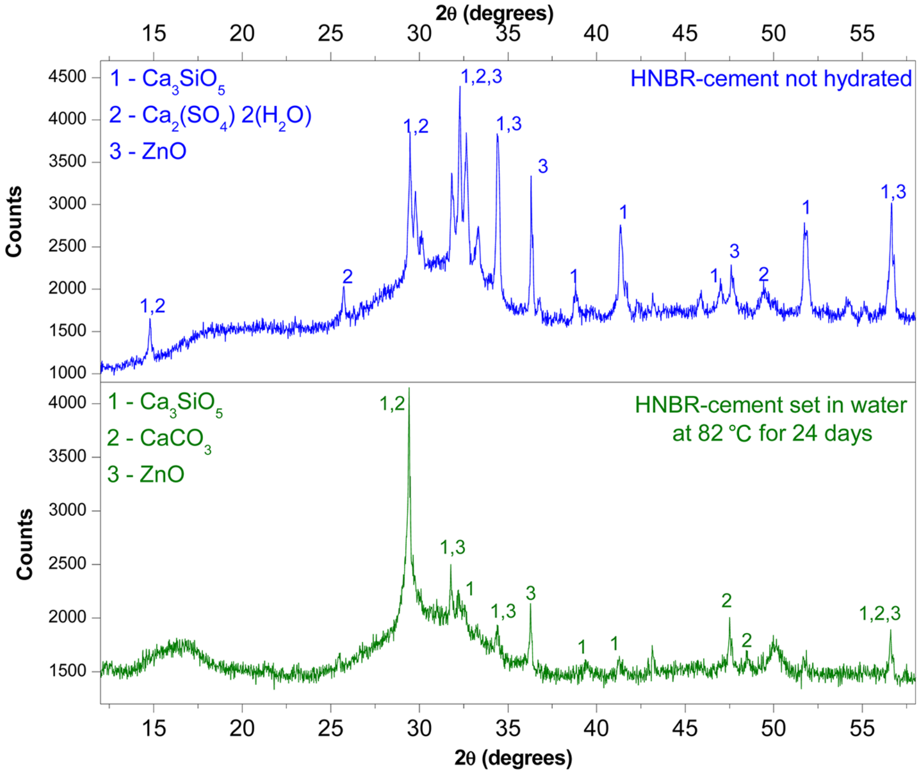

Figure 9. XRD diffraction spectra of the composite containing microsized cement before and after hydration. The tricalcium silicate (Ca_3SiO_5) peaks prove the presence of unhydrated Portland cement (top). The calcium hydroxide and calcium carbonate peaks prove the presence of cement hydration products inside the HNBR matrix (bottom).

We also found a small change comparing the intensity ratios of the pure HNBR with the composite filled with anhydrous cement. This negligible change may be due to the prolonged exposition of the as-produced composite to the ambient moisture with resulting hydration of a not negligible amount of cement particles.

The X-ray diffraction (XRD) spectra, collected on both the as-prepared and post-treatment composite (Figure 9), allowed us to qualitatively estimate the hydration kinetic of cement particles.

In fact, by fitting the diffraction patterns, we were able to evaluate the changes in the cement phase composition due to the conversion of the crystalline phase (clinker phase) to the amorphous phase (C-S-H). Our analysis confirmed that, even though the hydration process started within 2 h, the reaction was not yet concluded after 24 days of water exposure (the peaks associated with the Portland cement minerals, such as tricalcium silicates, did not completely disappear). The incomplete hydration can be explained by a combination of two mechanisms: (i) the hydration products create a diffusion barrier on the surface of the anhydrous core, hence hampering the water molecules from interacting with the core; and (ii) the particles are composed of different phases with different hydration kinetics.

4. CONCLUSIONS

In conclusion, we demonstrated the emergence of two peculiar and useful properties due to the application of cement as reactive filler in HNBR. When the composite is exposed to water, the cement particles get hydrated, with a consequent increase in mass and volume of filler (above the limit of filler loading currently imposed by the compounding process). The cement hydration also generates an increase in the composite volume and an increase in the pH. As proved by infrared spectroscopy, the high pH enables a novel postpolymerization conversion of nitrile groups to carboxylate anions. The ionic cross-linking (salt bridges) generated between cement cations and the anions (carboxylate) of the elastomer network is responsible for the reversible change of the elastic modulus upon wet and dry conditions. This new type of material shows a qualitatively improved behavior from that of traditional swellable elastomers that become less stiff as they absorb liquid water, making it an ideal candidate for sealing application as an alternative to cement for oil field zonal isolation applications. Furthermore, the reversible mechanical responsiveness to the wet/dry environment, enabled by the salt bridges, is very interesting for other applications such as car tires with variable tread to suit driving in dry or wet conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Nanoindentation analysis, cement particle size distribution, and details of ATR-FTIR spectral changes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) Beebe, D. J.; Moore, J. S.; Bauer, J. M.; Yu, Q.; Liu, R. H.; Devadoss, C.; Jo, B.-H. Functional Hydrogel Structures for Autonomous Flow Control inside Microfluidics Channels. *Nature* **2000**, *404*, 588−590.

(2) Wack, H.; Bertling, J. Water-Swellable Materials – Application in Self-Healing Sealing Systems. In *Proceedings of the First International Conference on Self Healing Materials*, Noordwijk aan Zee, The Netherlands, April 18−20, 2007; Springer: Dordrecht, The Netherlands, 2007; pp 1−9.

(3) McElfresh, P.; Guo, L. Studies of Water Swellable NBR for Downhole Sealing Applications. *Rubber World* **2008**, *238*, 41−44.

(4) Boesch, D. Deep-Water Drilling Remains a Risky Business. *Nature* **2012**, *484*, 289.

(5) Rubinstein, M.; Colby, R. H.; Dobrynin, A. V.; Joanny, J.-F. Elastic Modulus and Equilibrium Swelling of Polyelectrolyte Gel. *Macromolecules* **1996**, *29*, 398−406.

(6) Robisson, A.; Maheshwari, S.; Musso, S.; Thomas, J. J.; Auzerais, F. M.; Han, D.; Qu, M.; Ulm, F.-J. Reactive Elastomeric Composites: When Rubber Meets Cement. *Compos. Sci. Technol.* **2013**, *75*, 77−83.

(7) Longworth, R.; Vaughan, D. J. Physical Structure of Ionomers. *Nature* **1968**, *218*, 85−87.

(8) Weiss, R.; Izzo, E.; Mandelbaum, S. New Design of Shape Memory Polymers: Mixtures of an Elastomeric Ionomer and Low Molar Mass Fatty Acids and Their Salts. *Macromolecules* **2008**, *41*, 2978−2980.

(9) Thavamani, P.; Bhowmick, A. K. Influence of Compositional Variables and Testing Temperature on the Wear of Hydrogenated Nitrile Rubber. *J. Mater. Sci.* **1993**, *28*, 1351−1359.

(10) Xu, D.; Karger-Kocsis, J.; Schlarb, A. K. Friction and Wear of HNBR with Different Fillers under Dry Rolling and Sliding Conditions. *eXPRESS Polym. Lett.* **2009**, *3*, 126−136.

(11) Gatos, K. G.; Sawanis, N. S.; Apostolov, A. A.; Thomann, R.; Karger-Kocsis, J. Nanocomposite Formation in Hydrogenated Nitrile Rubber (HNBR)/Organo-Montmorillonite as a Function of the Intercalant Type. *Macromol. Mater. Eng.* **2004**, *289*, 1079−1086.

(12) Thomas, S., Chan, C. H., Pothen, L., Joy, J., Maria, H., et al., Eds. *Natural Rubber Materials*; Composites and Nanocomposites; The Royal Society of Chemistry: Cambridge, U.K., 2013; Vol. 2.

(13) Hird, B.; Eisenberg, A. Sizes and Stabilities of Multiplets and Clusters in Carboxylated and Sulfonated Styrene Ionomers. *Macromolecules* **1992**, *25*, 6466−6474.

(14) Ibarra, L.; Rodriguez, A.; Moras-Barrantes, I. Crosslinking of Carboxylated Nitrile Rubber (XNBR) Induced by Coordination with Anhydrous Copper Sulfate. *Polym. Int.* **2009**, *58*, 218−226.

(15) Guo, S. X.; von Hellens, W. Physical Properties of Peroxide Cured HXNBR Based Compounds. *Rubber World* **2002**, *225*, 51−55.

(16) Tant, M. R.; Mauritz, K. A.; Wilkes, G. L. *Ionomers: Synthesis, Structure, Properties, And Applications*, 1st ed.; Blackie Academic & Professional Publications: London, 1997.

(17) Eisenberg, A.; Hird, B.; Moore, R. B. A New Multiplet-Cluster Model for the Morphology of Random Ionomers. *Macromolecules* **1990**, *23*, 4098−4107.

(18) Taylor, H. F. *Cement Chemistry*, 2nd ed.; Thomas Telford Publishing: London, 1997.

(19) Sugama, T.; Kukacka, L. E.; Horn, W. Hydraulilc Cement-type Fillers For Hydrothermally Stable Polymer Concretes. *J. Mater. Sci.* **1980**, *15*, 1498−1508.

(20) MacLaren, D. C.; White, M. A. Cement: Its Chemistry and Properties. *J. Chem. Educ.* **2003**, *80*, 623−635.

(21) Pellenq, R.M-J.; Kushima, A.; Shahsavari, R.; Van Vliet, K. J.; Buehler, M. J.; Yip, S.; Ulm, F. J. A Realistic Molecular Model of Cement Hydrates. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 16102−16107.

(22) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part A: Structure and Mechanisms*, 5th ed.; Springer Publications: New York, 2007.

(23) Boutti, S.; Urvoy, M.; Dubois-Brugger, I.; Graillat, C.; Bourgeat-Lami, E.; Spitz, R. Influence of Low Fractions of Styrene/Butyl Acrylate Polymer Latexes on Some Properties of Ordinary Portland Cement Mortars. *Macromol. Mater. Eng.* **2007**, *292*, 33−45.

(24) Vega-Cantù, Y.; Hauge, R.; Norman, L.; Billups, W. E. $ZnBr_2$-Catalyzed Chemical Effects in Poly(Acrylonitrile-*co*-Butadiene). *J. Appl. Polym. Sci.* **2003**, *89*, 1250−1257.

(25) Mandal, U. K. Ionic Elastomer Based on Carboxylated Nitrile Rubber: Infrared Spectral Analysis. *Polym. Int.* **2000**, *49*, 1653−1657.

(26) Xie, A. J.; Zhang, C.-Y.; Shen, Y.-H.; Qiu, L.-G.; Xiao, P.-P.; Hu, Z.-Y. Morphologies of Calcium Carbonate Crystallites Grown from Aqueous Solutions Containing Polyethylene Glycol. *Cryst. Res. Technol.* **2006**, *41*, 967−971.

(27) Brozoski, B. A.; Coleman, M. M.; Painter, P. C. Local Structures in Ionomer Multiplets. A Vibrational Spectroscopic Analysis. *Macromolecules* **1984**, *17*, 230−234.