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Novel Reactive Elastomer-Metal Oxide Composite: Effect of Filler Size and Content on Swelling and Reinforcement

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Abstract. A novel elastomer-metal oxide composite that swells and stiffens upon hydration will be presented. Conventional water-swellaable elastomers filled with hydrogels absorb water and swell upon hydration but their modulus decreases as a result of fluid water diluting the rubber matrix. Reduced stiffness compromise the reliability of swellaable elastomers used in sealing applications. One major application of swellaable elastomers is fluid containment seals for zonal isolation in the oilfield. For effective sealing, the contact pressure between the seal and the surrounding wall should be high while deformation should be limited when a differential pressure is applied. Both conditions can be achieved by means of swelling and stiffening of the seal; hence, the new reactive elastomer-metal oxide composite is developed such that after it is exposed to water, the composite swells and stiffens simultaneously. Composites filled with different amounts of oxide were studied and it was observed that swelling up to almost 100% with an increase in modulus of about 200% could be achieved for the best performing compound. Composites filled with different sizes of the metal oxide were also studied. The finest filler was found to impart the greatest modulus, both before and after hydration, to the composite although swelling was slightly reduced compared with the larger particles. Another advantage of the composite for sealing purposes is that the swelling is largely retained even after complete removal of the solvent; i.e., drying.

Keywords: Composite, elastomer, rubber, filler, modulus, swelling

PACS: 83.80.Wx, 88.10.gp

INTRODUCTION

In the oilfield, different geographical layers of the well may produce different fluids or fluids at different pressures. Zonal isolation refers to the prevention of the unwanted movement of these fluids across the different zones by means of sealing the annular space between the formation and production casing (Fig. 1a). When zonal isolation fails, the well production is degraded and in the worst scenario, hydrocarbon fluids may escape from the reservoir onto the surface, invoking great safety and environmental concerns. Hence, reliable sealing capability for zonal isolation is very critical. Traditionally, sealing of the different zones is achieved using cement. However, one common problem encountered as a result of temperature and pressure cycling is the de-bonding of cement from the casing, leading to the creation of a micro-annulus [1, 2]. Significant operating costs in terms of time and money are incurred to remedy the leakage. As a result, swellaable elastomers, which are compliant and hence react and conform to changes in formation and casing, are becoming more common in recent years for sealing in downhole applications [2, 3].

Swellaable elastomers are cross-linked polymers that exhibit an increase in volume by imbibing large volumes of oil or water and their elasticity is retained even after swelling. Seal quality of swellaable elastomers depends on the contact pressure exerted by the seal on its surrounding walls and also the modulus of the seal material [4]. For most conventional water- and oil- swelling elastomers, their modulus decreases as they swell due to the dilution of the stiff rubber matrix by the solvent [5, 6]. This modulus decrease limits the reliability of these elastomers on long-term sealing applications in the oil field. On the contrary, the novel composite introduced in this paper swells and exhibits an increase in stiffness upon hydration. Figure 1b shows the decrease in the modulus of a common water swellaable elastomer, made by compounding rubber with superabsorbent polymers (SAPs), and the increase in the modulus of the elastomer-metal oxide composite as they absorb water and swell with time.

To better understand and explore the potential of the reactive composites, composites filled with various filler sizes and content were studied.

FIGURE 1. (a) Deployment of swellable packers for zonal isolation (b) Change in modulus of pure rubber, conventional water swellable elastomer and elastomer-metal oxide composite after immersion in de-ionized water

EXPERIMENTAL METHODS

Hydrogenated acrylonitrile butadiene rubber (HNBR) was chosen as the rubber matrix. The metal oxide was purchased from Schlumberger and its purity was measured to be approximately 80% using X-ray fluorescence spectrometry (SPECTRO XEPOS).

The rubber was compounded with 2 μm metal oxide at different concentrations (0%, 14%, 28% and 40% by volume) to study the effect the filler content had on swelling and reinforcements. To investigate the effect of filler size on swelling and reinforcement, the rubber was compounded with 40 vol% of metal oxide of different sizes (2 μm , 5 μm and 10 μm). Cuboidal coupon samples measuring 20 mm x 4 mm x 2 mm were used for water exposure tests at 82°C. After immersion in water, the coupon samples were dried in oven at 82°C for a week, and no additional loss in mass was observed. The mass, volume and storage modulus changes of the samples were measured at various time intervals until a plateau was observed.

The storage modulus of the samples were tested under uniaxial tension using a dynamic mechanical analyzer (DMA Q800, TA instruments) set at 0.1% strain amplitude and 125% force track. The loss modulus is small and so the storage modulus alone represents the Young's modulus well.

RESULTS

Figure 2 shows the change in modulus and volume of the HNBR-metal oxide composite before hydration, after hydration (in the wet state) and after hydration and subsequent drying (in the dried state). The composite exhibits an increase in modulus with swelling and the extent of modulus and volume change increases with increasing filler content. As shown in Fig. 2a, the modulus of the composite before hydration increases by about a factor of 10 when the filler content increased from 0% to 40%. After hydration, the modulus increases by almost 30 times to 80 MPa as the filler content increased. Figure 2b shows that a maximum of 100% increase in volume can be attained and even after drying the solvent completely, the volume increase is largely retained.

FIGURE 2. Effect of filler content on (a) modulus and (b) swelling of HNBR-metal oxide composite

Figure 3 presents the change in modulus increase and swelling of the composite as a function of filler size. As the filler size increased 5-folds from 2 μm to 10 μm , the modulus before hydration was reduced by approximately one half from 27 to 13 MPa (Fig. 3a). After hydration, the reduction in modulus was even more pronounced at roughly 8 times. In fact, modulus of the composite filled with 10 μm fillers does not change significantly after hydration. Although the larger size filler does not provide much reinforcement, swelling of composites filled with 10 μm fillers was observed to be slightly higher than that for the 2 μm fillers (Fig. 3b).

Figure 3. Effect of filler size on (a) modulus and (b) swelling of HNBR-metal oxide composite

DISCUSSION

The swelling observed is mainly due to the water that is chemically bonded to metal oxide, as shown in Equation 1, to form solid metal hydroxide. This explains why most of the observed swelling is retained even after oven-drying. Some additional swelling is contributed by the free unbounded water present in the composite in the wet state.

The increase in swelling of the composites with increasing filler content can be explained by the increased amount of water chemically bonded to the metal oxide. This increase in volume of fillers after hydration leads to the

higher filled composites having a higher modulus after hydration. More information can be found in earlier work by Han et al. [7] where it was postulated that the modulus increase after hydration is due to both an increase in filler content and also an increase in specific surface area of the fillers after hydration, giving rise to an increased area of interaction at the matrix-filler interface.

Poorer reinforcement offered by the larger fillers compared to the finer fillers is likely due to the reduction in effective contact area between the filler and the matrix. With decreased interaction, the transfer of stress between the matrix and the fillers becomes less effective. After hydration, the disparity in the modulus of the composites filled with different size fillers increased. This may be a result of the finer particles being able to better redistribute themselves with small-scale diffusion after hydration while the hydrated particles of larger particles, particularly at their cores, are more likely to agglomerate around the parent particles or hydrated particles at the surface, forming larger secondary structures. Although the primary structure of metal hydroxide formed from precipitation may be finer than the original metal oxide, large agglomerates may cause the reinforcement to be less effective. Nonetheless, there is no significant loss in modulus even though composite swelling on the order of 100% increase in volume was observed (see Fig. 3) for the compound filled with the largest 10 μm fillers. Greatest swelling observed for the composite filled with largest fillers might be related to its lowest stiffness.

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