

Antiswelling and Frost-resistant Properties of a Zeolite-modified Rubber Mechanical Seal at Low Temperature

N. N. Petrova,^{†,‡,*} Jungkeun Lee,[§] V. V. Portnyagina,^{†,‡} Dae-Yong Jeong,[§] and Jin-Ho Cho^{†,¶,*}

[†]Department of Chemistry, North-Eastern Federal University, Yakutsk 677000, Russia.

*E-mail: pnn2002@mail.ru

[‡]Arctic Innovation Center, North-Eastern Federal University, Yakutsk 677000, Russia

[§]Department of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

[¶]Department of Energy and Biotechnology, Myongji University, Kyunggido 449-728, Korea

*E-mail: jinhcho@mju.ac.kr

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The blending of an activated zeolite with a butadiene nitrile-based rubber was investigated as a potential means of achieving mechanical seals suitable for low-temperature operation. Through this, it was discovered that zeolite addition increases the oil and frost resistance of the rubber, as well as improves the climatic stability of the elastomer in a hydrocarbon medium. These improvements are attributed to both physical and chemical interactions, with the presence of zeolite inducing strong crosslinking during vulcanization and increasing the absorption of additives such as plasticizers. Rubber modified in this way is therefore recommended for use with hydrocarbon liquids exposed to cold climates. Swelling test was conducted over 2 years in the ambient atmosphere. Zeolites induced the strong crosslinking during vulcanization of rubbers and the adsorption of plasticizers or other ingredients of rubber blends onto zeolites were also strengthened.

Keywords: Zeolite, Butadiene nitrile-based rubber, Mechanical seal, Swelling, Frost resistance, Low temperature environment

Introduction

The unique properties of rubber in terms of its high elasticity, durability over multiple deformations, chemical and physical stability, and relative ease of manufacturing have seen it become an irreplaceable material in the production of a range of different sealing devices. However, the exposure of such parts to the impact of pressure oscillations, impulse loads, various process media, and climatic factors also creates a need for rubber materials to be capable of maintaining specific strength properties, an ability to withstand elastic recovery after unloading and frost resistance.¹ These requirements are of particular importance when the rubber is exposed to severe climatic conditions, much like those encountered in Siberia, the Republic of Sakha (Yakutia).²

In Yakutia, not only does the ambient temperature in winter regularly drop to -65°C , but there is also a sharp oscillation in temperature above/below 0°C in spring and autumn. When these climatic conditions are combined with an aggressive medium, it can have a serious detrimental effect on the properties of rubber.³ A further problem, which is seldom taken into consideration while choosing the material for a seal, is the interaction it has with the working media.⁴ For example, rubber seals are commonly exposed to oils, lubricants, and/or hydrocarbon fuels, all of which have a very similar chemical nature to that of rubber. As a result, these hydrocarbons not only can cause reversible physical changes with little damage to the chemical chains, but can also cause a weakening of

intermolecular interaction and a degradation of strength in the rubber through swelling. It is also possible for some ingredients of the rubber to be dissolved in the hydrocarbon media, thereby creating further degradation.⁴

Plasticizers, materials added to a rubber to increase its frost resistance,³ are particularly susceptible to being washed out from rubber when exposed to a hydrocarbon media. This results in shrinkage of the rubber, making it more rigid and ultimately preventing it from functioning effectively as a mechanical seal.¹ Thus, in order to manufacture a reliable seal, it is crucial to find a means of slowing the diffusion of plasticizers from the polymer matrix into a contacting hydrocarbon liquid.

This study therefore explores the possibility of using natural zeolites^{5,6} to regulate the velocity of ingredient wash out from rubber mixtures.⁷ This is based on the notion that both natural and synthetic zeolites have widely been used to improve the properties of various different classes of polymeric materials,^{8–13} with previous investigations suggesting that the addition of relatively small amounts of natural zeolites into butadiene nitrile rubber (BNR)-18 can significantly improve its stability in oil and its low-temperature wear resistance through an increase in the crosslink density of the rubber.¹⁰

Experimental

The natural zeolite used in this study was sourced from the Hon-gurou deposit in the Republic of Sakha, Russian Federation. After being calcinated in oven at 450°C for 1 h, this zeolite

Table 1. Physical properties of zeolite.

Physical properties	Before activation	After activation
Specific pore volume (cm ³ /g)	0.033	0.044
Specific geometric surface area (m ² /g)	11.0	16.9
Average pore size (nm)	4.1	3.5

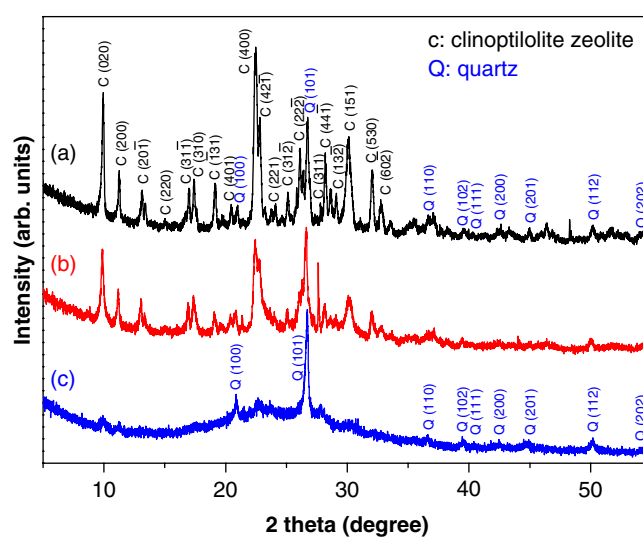
powder was activated by grinding for 3 min in a planetary mill activator (AGO-2S) that was originally developed by the Institute of Chemistry of Solid and Mechanical Chemistry of the Siberian Branch of the Russian Academy of Science (Novosibirsk, Russia).¹⁴ FT-IR spectrometer (FT/IR 4100; Jasco Inc., Tokyo, Japan) and X-ray diffractometry (XRD; Rigaku Co., DMAX-2500, Tokyo, Japan) were used to analyze the resulting zeolite powder, and its physical properties before and after activation are summarized in Table 1. The IR samples were prepared by the quick press pellet kit with the 3.0 wt% in KBr. All IR spectra in Figure 2 were corrected by removing CO₂ and water peaks. The structure of zeolite–rubber composite was investigated using a transmission electron microscope (TEM; CM200/Philips, Eindhoven, The Netherlands).

The activated zeolite was then blended with a BNR-18 at 40 °C for 7 min using a plasticorder (Brabender PL-2200-3, Duisburg, Germany) to give a final zeolite content of 15 mass%. This mixture was then cured at 150 °C for 30 min. A BNR-18 was selected on the basis that it is a serial rubber widely used in low-temperature seals, and consists of a nitrile-butadiene rubber mixed with various activators, vulcanization accelerators, antioxidants, carbon black, sulfur as a vulcanizing agent, and a dibutyl phthalate (DBP) plasticizer.

To best assess the climatic stability of the zeolite-modified elastomer against an unmodified control, full-scale exposure to real-world cold climate conditions was used. The effectiveness of each seal when exposed to a hydrocarbon was quantified by Russian Standard methods for determining the frost-resistant coefficient at elongation (GOST 408-78),¹⁵ degree of swelling in a hydrocarbon medium (GOST 9.030-74),¹⁶ residual compression deformation (GOST 9.024-74),¹⁷ and the mechanical properties of a rubber (GOST 270-84).¹⁸ For this, the samples were immersed in Talakan oil¹⁹ for a period of 2 years under ambient conditions, being only removed periodically for testing. The amount of plasticizer remaining in each rubber sample was extracted with chloroform and analyzed by the IR spectrometry (Paragon-1000; Perkin Elmer, USA). This allowed the complex characteristics of each material to be evaluated in relation to the degradation caused by both climatic factors and the aggressive medium.

Results and Discussion

In the XRD patterns obtained from the zeolites (Figure 1), most of the peaks are indexed as crystalline clinoptilolite, although some peaks were identified as crystalline quartz. From this, we find out that although calcination does not significantly affect the crystalline structure, subsequent

**Figure 1.** X-ray patterns of natural zeolite powder: (a) original, (b) calcinated at 450 °C for 1 h, and (c) calcinated and activated.

activation does induce a considerable change. Specifically, most of the crystalline structures are changed to an amorphous phase that corresponds to the broad peak at around 25°, with SiO₂ being the only remaining crystalline phase.

To investigate the structure of the zeolites in more detail, their IR spectra (Figure 2) were measured and compared against data in the literature.⁵ The absorption is attributed to asymmetric oscillation of Si–O–Si framework bonds in zeolite within the 800–1200 cm⁻¹ range and symmetric oscillation in the 600–800 cm⁻¹ range. The change in the finger print region peaks at 604 and 804 cm⁻¹ evident in Figure 2 may therefore result from deformation oscillations introduced by a loosening of the crystalline structure of zeolite by calcination and activation. Furthermore, the strong decline at 804 cm⁻¹ that is found in the activated zeolites, and the fact that the absorption peaks remain at nearly at the same wave number, indicates that the difference in the XRD patterns of the functional groups is not changed by calcination and activation. Furthermore, the strong intensity difference in the IR spectra indicates that there is a significant difference in the crystallinity of the activated zeolites.

Figure 3 shows the TEM images of the zeolite–rubber composites. Zeolite particles were distributed in the rubber matrix and did not show the crystallinity as seen in inset image. In the micromolecular TEM image, we could not know exactly the function of zeolite in rubber but we speculate that zeolites act as strong adsorption sites for the rubber and ingredients such as plasticizers. In other words, the zeolite functions as a nucleus through the intermolecular interaction between the surface of nano-sized zeolite particles and the rubber.²⁰ Such interaction subsequently generates enhanced crosslinking of the rubber during vulcanization, and a greater adsorption of plasticizers and other ingredients. Finally, the supramolecule created from the zeolite and the rubber acts as an integrated unit to suppress the swelling of the rubber in liquid.

In order to fully understand the reason for the antiswelling and frost-resistant properties of a zeolite-containing rubber,

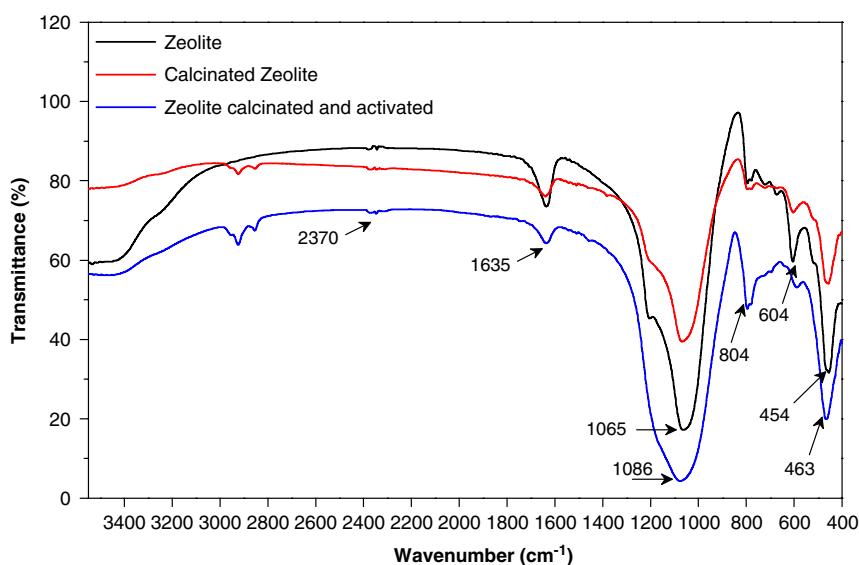


Figure 2. IR spectra of natural zeolite.

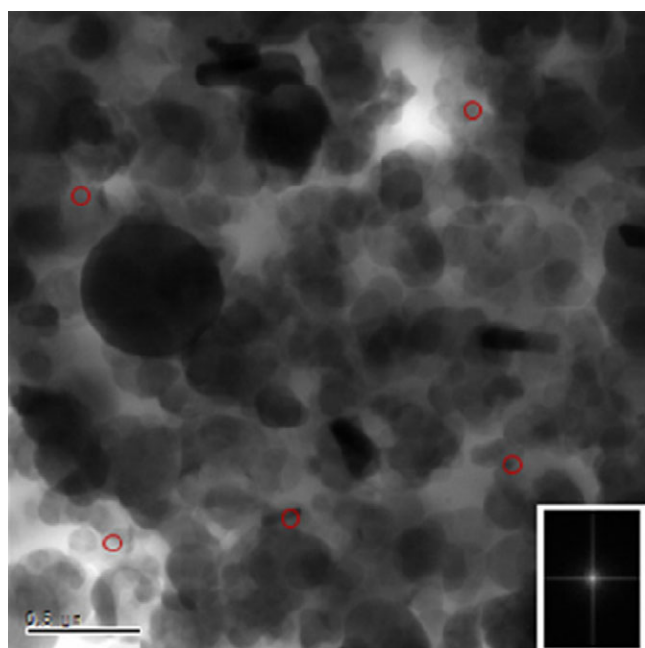


Figure 3. TEM images of rubber containing zeolite, which is marked with red dot. Inset is the diffraction pattern of zeolite.

the rubber composites were subjected to 2-year swelling tests by immersing them in oil and exposing them to the climatic environment of Yakutsk, the Republic of Sakha. The ambient temperature during testing varied from -42 and 18 °C; however apart from a slight variation in the strength of the rubber after an initial period of exposure, the strength of the rubber remained consistent. That is, no destruction of the polymer chains was observed, even after 2 years of immersion in oil. The same was observed in the case of the residual deformation of compression that characterizes the material's ability to recover elastically after unloading.

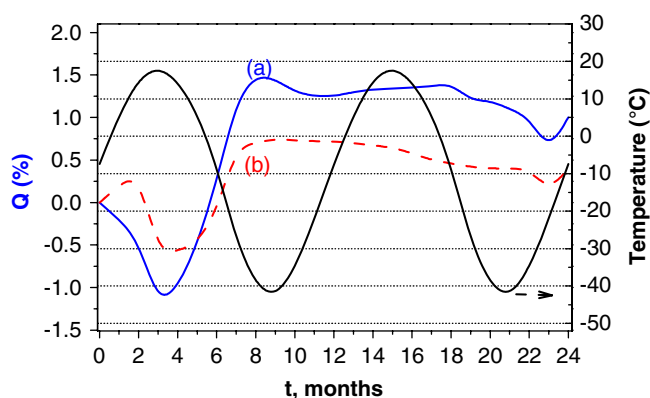


Figure 4. (Left) Degree (%) of swelling of BNR-18 in oil, and (Right) ambient temperature change for 2 years: (a) BNR-18 and (b) zeolite-containing BNR-18.

Figure 4 shows the degree of swelling of the rubber composite over time, which reveals that even after 2 years the degree of swelling in the zeolite-modified rubber is 2.5 times less than the original rubber. Furthermore, it is apparent from the IR spectroscopy results shown in Figure 5 that the addition of zeolite ensures a higher retention of DBP plasticizer when in contact with a hydrocarbon. As a result of this, the mechanical properties of the rubber were also improved. The frost-resistant coefficients of the rubbers at temperatures between -20 and -50 °C (Figure 6) demonstrate that adding calcinated and activated zeolites makes the rubber more frost-resistant.

Conclusions

The addition of nano-sized zeolite particles to a rubber has been demonstrated to suppress swelling and reduce the degree of plasticizer wash out, even after 2 years of oil immersion in a

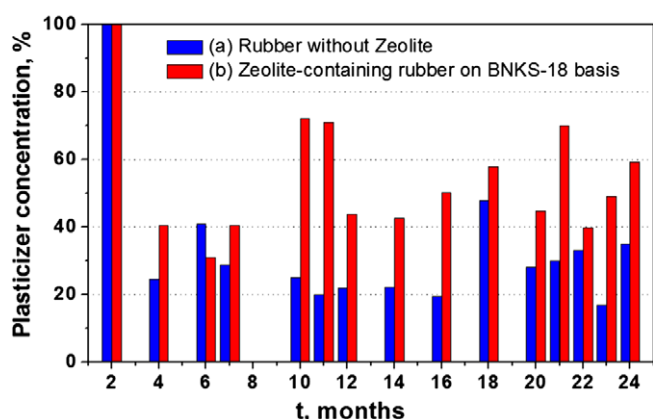


Figure 5. DBP concentration in rubbers immersed in oil under natural environment for 2 years: (a) BNR-18 and (b) zeolite-containing BNR-18.

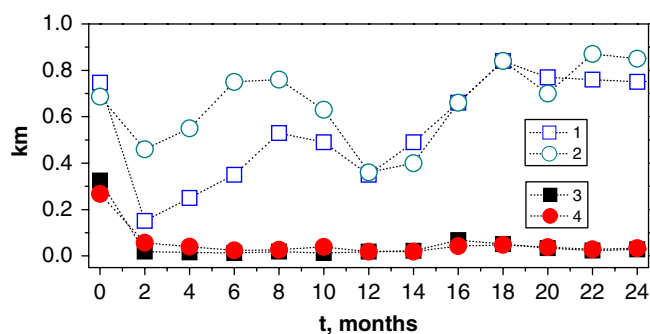


Figure 6. Frost-resistant coefficient (km) of BNR-18 exposed for 2 years under natural environment: 1, BNR-18 at -20°C ; 2, zeolite-containing BNR-18 at -20°C ; 3, BNR-18 at -50°C ; 4, zeolite-containing BNR-18 at -50°C .

low-temperature environment. The frost resistance was also found to be improved by the addition of zeolite, which is attributed to a previously identified increase in the crosslinking of the rubber during vulcanization and a greater adsorption of plasticizers and other ingredients around the nano-sized zeolite particles.

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