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Effects of cure system and filler on chemical aging behavior of fluoroelastomer in simulated proton exchange membrane fuel cell environment

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ABSTRACT

The chemical aging behavior of gaskets especially the chemical stability is crucial to the overall performance of PEMFC stack. The chemical stability of gaskets not only depends on the polymer but also heavily depends on the other ingredients. In this paper, we have studied the properties of fluoroelastomer with different amount of the cure agent, acid-acceptor and filler in the simulated PEMFC environment. The weight and volume change of samples was monitored. The surface conditions of the virgin and aged samples were observed using optical microscopy. Leachants in the soaking solution were detected using atomic emission spectrometry. ATR-FTIR was employed to determine the chemical change of samples. These results show that FKM cured with bisphenol system has the best comprehensive properties when the amount of bisphenol AF is set as 2.5 phr and the amount of $Ca(OH)_2$ is 6 phr. The inert filler $BaSO_4$ is not suitable for FKM because it has inferior effect on the compression resistance and chemical stability of FKM in this system.

Introduction

Proton exchange membrane fuel cell (PEMFC) is a device that directly converts the chemical energy from fuel to electricity. PEMFC stack usually contains many cells to meet the requirement of application [1–3]. PEMFC stack requires elastomeric gaskets in each cell to prevent gas from leaking or mixing. If any gasket fails, it not only affects the overall performance of PEMFC stack but also causes safety concerns. Gaskets in the cells stack are exposed to an acidic solution and humid gas as well as subjected to mechanical stress for assembly stacks [4–7]. So it is crucial to study the chemical aging behavior of gaskets in simulated PEMFC solution.

The chemical aging behavior and mechanism of elastomeric gaskets in various applications were studied in previous works. For instance, Mitra S et al. [8,9] investigated the time-dependent chemical degradation of pure fluoroelastomer and cross-linked fluoroelastomer in an alkaline environment. Cui et al. [10] reported the stress relaxation behavior of liquid silicone rubber under constant stress. Wang et al. [11] focused on the aging behavior of reactive blend fluoroelastomer with poly-phenol hydroxyl EPDM. There are also some literature concerning the chemical aging and its mechanisms

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of elastomeric gaskets in simulated PEMFC environment. Tan et al. [12–17] studied the chemical and mechanical degradation of fluoroelastomer, silicon rubber and EPDM exposed to simulated solution, which is close to the actual PEMFC environment and accelerated durability test (ADT) solution. Lin et al. [18,19] studied the chemical stability and change of dynamic mechanical properties of five elastomers (FKM, EPDM, LSR, FSR, CR) and found that FKM appears to be most stable among the five materials studied in the accelerated solution, while CR and LSR are not as stable as the other three materials.

The aging behavior of elastomeric gaskets not only depends on the polymer itself but also heavily depends on the other ingredients. A wide range of properties can be achieved by varying polymer structure as well as compounding technology. There are substantial literature about aging behaviors of different elastomeric gaskets, but few results were reported concerning the aging behavior of elastomeric gaskets with different ingredients. Good thermal resistance of elastomers can be achieved by choosing cure system and fillers [20]. Choi, S.S. et al. [21–24] studied thermal aging behaviors of natural rubber vulcanized with different cure systems and filler. They found that cure system not only influenced the curing efficiencies but also had effects on thermal aging resistance. Based on previous studies about thermal resistance of elastomers with different ingredients, it can be deduced that the chemical aging behavior of elastomers can be modified by adjusting the ingredients during compounding. However, to our best knowledge there is no open literature concerning the chemical resistance of elastomers with different ingredients in PEMFC environment.

FKM was widely used as gaskets in PEMFC, but the degradation of FKM also occurred in PEMFC environment [11,19]. FKM gaskets for practical application comprise many ingredients such as cure system, filler and so on. The mechanical properties and chemical aging behavior of FKM can be modified by choosing different ingredients. For example, the bisphenol cure system can result in FKM with low compression set and high heat resistance, but it doesn't react with the FKM without any accelerator, which is an onium (phosphonium, ammonium, etc.) salt in combination with a metal compound as an activator [25]. Therefore it is useful to study the effect of different amount of cure agent, acid-acceptor and filler on the chemical aging behavior of FKM. In this paper, FKM based gaskets with different ingredients were investigated in a simulated fuel cell environment. The properties of fluoroelastomer with different amount of cure agent, acid-acceptor and filler were studied. The surface morphology, chemical degradation on the surface of gaskets and the chemical leached from gaskets in the soaking solution were investigated by using optical microscopy, ATR-FTIR and ICP-AES, respectively.

Experimental

Materials

The material selected for this study is the product FE 2604 of Shanghai 3F company. It's vinylidene fluoride-hexafluoropropylene copolymer (VDF/HFP) $C_2H_2F_2{-}C_3F_6$ with the fluorine content of 65%. Carbon black (CB) N990 is supplied by Cancarb Corporation. Other components such as bisphenol AF, $Ca(OH)_2$, $BaSO_4$, wax and BPP in the recipe are provided by Shanghai Shifan Industry Co., Ltd.

Preparation of the vulcanizate

The basic recipe is composed of FE 2604, BPP, bisphenol AF, $Ca(OH)_2$, $BaSO_4$, carbon black and wax. All the components were mixed by two-roll open mill (Labtech, USA) at 60 °C. After mixing, the mass was sheeted out and then compression molded at 170 °C and a pressure of 16 MPa between polyester sheets in a press vulcanizing machine. The vulcanization time was set according to the cure curve. Then the vulcanizates were post-cured in a thermostatic oven at 250 °C for 10 h to develop optimum properties.

Characterization methods

The cure characteristics of the vulcanizate were determined using curemeter (Beijing Youshen Electronic Apparatus Factory) at 170 C. Maximum torque (MH), minimum torque (ML) and optimum cure time (T_{90}) were recorded.

The solution used to age gaskets in this study is similar to that in real PEMFC. It consists of 48% HF and 98% H_2SO_4 dissolved in deionized water. The final composition is 12 ppm H_2SO_4 and 1.8 ppm HF [17,19]. The aging test temperature was set as 80 °C, which is close to the real operation temperature of PEMFC. Round-shaped specimens were prepared and exposed to the simulated solution. Leachants in the soaking solution were detected using atomic emission spectrometry ICP-AES (Germany ARCOS) on a regular basis.

The surface conditions of the virgin and aged samples were observed using optical microscopy. The weight and volume change of the tested samples were measured by Matsu Haku High Precision Density Tester GH-120M with the formulation below. It has a resolution of 1 mg.

$$\text{weight change }(\%) = \frac{w_2 - w_1}{w_1} \times 100;$$

$$\text{volume change }(\%) = \frac{v_2 - v_1}{v_1} \times 100$$

Where w_1 (w_2) is the weight of the sample before (after) aging, v_1 (v_2) is the volume of the sample before (after) aging.

The mechanical properties such as tensile strength, elongation at break, hardness and compression set were characterized to determine the chemical stability of vulcanizate. Tensile strength, elongation at break of the samples before and after soaking were tested using a SANS CMT4104 Electronic Universal Testing Machine (Shenzhen, China) at a crosshead speed of 500 mm/min in accordance with ASTM D412 at 25 °C. At least five specimens for each sample were tested and the average value was calculated. Round shaped samples were used to measure the indentation hardness of the samples using a Shore A hardness tester (LX-A, Qianzhou Measuring Instruments Co., Ltd) according to ASTM D2240.

The compression set (CS) is tested according to the ASTM-D395, Method B, strain 25%. Cylindrical disc samples were compressed by to a constant deflection of 25% and kept them