

Moisture Absorption of Filled Silicone Rubber Under Electrolyte

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ABSTRACT: Moisture absorptions of filled silicone rubber (SiR) under strong electrolyte have been investigated in the temperature range of 25–60°C by weight-gain experiments. Tests were performed with the materials exposed to NaCl, HNO₃ solution, and deionized water. The diffusion results have been analyzed in terms of the Fickian diffusion law. The apparent maximum moisture content and the apparent diffusion of filled SiR in different solutions were deduced.

The influences of the solution concentration and temperature on the diffusion process of filled SiR were discussed, and the microphotos of the surface of the immersed specimens were taken and analyzed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2253–2257, 2006

Key words: absorption; electrolyte; diffusion; silicone rubber

INTRODUCTION

Silicone rubber (SiR) is widely used in industries and is often reinforced with fillers to obtain some excellent properties such as high strength and resistance to ultraviolet light. Although the filled SiR has an outstanding performance in preventing the ageing, it would fail after long-term exposure in rigorous condition. Humidity ageing is widely recognized as one of the main cause of long-term failure of organic composites exposed to the atmosphere or in contact with aqueous media. The humid ageing of the composite materials is ascribed to the moisture absorption, and it has been investigated by assuming that the moisture absorption process follows Fick's law.^{1–3}

Several authors have examined the diffusion of various solvents through natural and synthetic rubbers. Riggs et al. investigated the water uptake characteristics of silicone polymer containing additives, and calculated the diffusion coefficients of different SiRs.¹ Kee et al. presented the results of permeation experiments with different solvents into natural, nitrile, and bromobutyl rubber membranes at different temperatures and elongations. Test results showed that an increase in temperature lead to an increase in permeability, and a small extension does not cause a significant change in the diffusive properties.³ Hwang et al.

have studied the diffusion and absorption behavior of glycidyl methacrylate in styrene butadiene rubber (SBR), using the gravimetric absorption method. They observed that diffusion of glycidyl methacrylate in SBR follows the typical Fickian diffusion process.⁴ Unnikrishnan et al. investigated the absorption and diffusion of four aromatic hydrocarbons through filled natural rubber, and found that the mechanism of transport in filled natural rubber follows an anomalous trend as indicated by the deviations from the theoretical curves describing Fickian transport.⁵ In addition, some other researches showed that the water absorption process in composite materials obeys Fick's law.^{6,7} All the aforementioned studies are of water or common solvent absorption of rubber matrix composites and composite materials; however, the moisture absorption study of filled SiR under strong electrolyte attack is rather limited.

The objective of the present work is to determine the moisture absorption characteristics of filled SiR composites under strong electrolyte. The weight change of the material as a function of time and temperature was measured with samples of the material immersed in deionized water, HNO₃, and NaCl solution at different concentration.

FICKIAN THEORY

The diffusion has been extensively studied theoretically in the past, and the basic equation describing the diffusion process involves Fick's second law. For diffusion running in the directions of the x, y, and z axes, the law is represented by⁸

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$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + D \frac{\partial^2 c}{\partial y^2} + D \frac{\partial^2 c}{\partial z^2}, \quad (1)$$

where D is the coefficient of diffusion, c is the concentration of media, and t is the time.

Consider the diffusion as running only in the x axis direction, then eq. (1) will take the form

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

On introducing the initial conditions, i.e.,

$$c = c_0 \quad x \leq 0 \quad \text{and} \quad t = 0$$

$$c = 0 \quad x > 0 \quad \text{and} \quad t = 0$$

the eq. (2) can be solved

$$c = \frac{c_0}{2} \left[1 - \psi \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (3)$$

where

$$\psi_{(\xi)} = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\xi^2) d\xi \quad (4)$$

$$D = \frac{x_0^2}{\pi t} \quad (5)$$

Where x_0 is the depth of diffusion, and ψ is the Gauss error integral.^{8,9}

From eq. (5), it can be seen that the diffusion coefficient D represents the "velocity" of the liquid entering into the material (the larger it is, the faster the liquid enter into the material), which reflects the character of the material preventing the moisture. To evaluate the diffusion coefficient D , the test is retained when the mass gain is stabilized, i.e., the absorption equilibrium is established. If ΔM is the mass gain for a sample with initial mass M_0 , the relative mass gain $m = \Delta M/M_0$ and its equilibrium value is $m \rightarrow m_\infty$ when $t \rightarrow \infty$.

Assuming that the moisture absorption process followed Fick's law, the relative mass gain is plotted against the square root of time. If the initial part of the curve (typically until $m_\infty/2$) is linear, one determines its slope $dm\sqrt{t}$ and the equilibrium moisture concentration, then the coefficient of diffusion (D_x) for transport normal to the surface of the material can be obtained as

$$D_x = \frac{d}{16M_\infty^2} \left[\frac{M_2 - M_1}{t_2^{1/2} - t_1^{1/2}} \right]^2 \quad (6)$$

where d is material thickness, and M_1 and M_2 are moisture concentrations (in weight) after times t_1 and t_2 . M_∞ is the equilibrium or maximum moisture concentration at a particular relative humidity (RH) at $t = \infty$. The term in square brackets is the slope of the linear part of the moisture curve at constant temperature and RH. In practice, experiments cannot be carried out on infinite plates, and so data from coupon tests have to be corrected for edge effects. The approach of Shen and Springer^{10,11} can be used to account for diffusion through all six faces or edges of cubic element:

$$D = D_x \left[1 + \left(\frac{d}{b} \right) + \left(\frac{d}{l} \right) \right]^2 \quad (7)$$

where b and l are coupon breadth and length, respectively.

If the D and m_∞ are determined and incorporated into the following equation to generate theoretical sorption curves,^{5,12} then

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D(2n+1)^2\pi^2 t}{d^2}\right) \quad (8)$$

where M_t is the mass percent increase in absorption at time t .

EXPERIMENTAL

The filled SiR is used as a protector of composite insulators. The SiR samples were manufactured by high temperature vulcanization technique in laboratory, i.e., the mixture of silicone and fillers were vulcanized at 170°C for 10 min. The silicone in our test is polydimethylsiloxane, and the fillers were mainly Al(OH)₃ and carbon black. The content of Al(OH)₃ and carbon black is about 40 and 15% by weight, respectively. For diffusion experiments, SiR samples were cut into the dimension of 30 × 30 × 2 mm³. Before placing the specimens into the moist environment, the specimens were cleaned with alcohol and dried in a desiccator at the same temperatures as the absorption tests. Dry weights of the cut samples were taken before immersion into different liquids on an electronic analytical balance with the accuracy of 0.0001 g. The dry specimens were then placed in different kinds of solutions. The solution volume was 80 mL in each test body and was kept invariable. The samples were removed at periodic intervals, the wet surfaces dried between filter papers, and the samples weighed immediately. They were then placed back into test bottles. The process was continued until equilibrium swelling was achieved. The experiments were

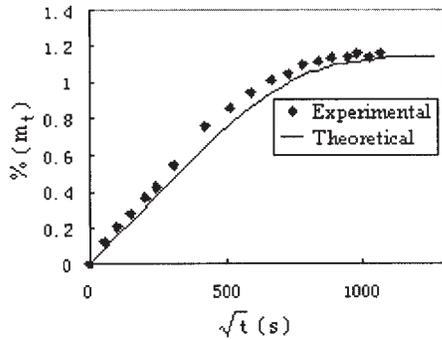


Figure 1 Experimental results for the absorption of deionized water in SiR. The line represents the theoretical prediction for Fickian diffusion.

conducted at 25, 40, and 60°C in an oven temperature controlled. After the immersion tests were finished, the samples were placed into a KYKY-2800 scanning electron microscope and SEM micrographs of the specimen surface were taken, with an accelerating voltage of 25 kV.

RESULTS AND DISCUSSION

Diffusion process of filled SiR in different solutions

The results of absorption experiments are expressed as percent weight change as a function of square root time. Some typical absorption results of SiR samples in different solutions are given in Figures 1–3. Figure 1 shows the absorption of the SiR specimen immersed in deionized water at 60°C, and the line represents the theoretical prediction for Fickian diffusion. It can be seen that the weight change of the specimen vary linearly with the square root of time in the initial part of the curve, then it reached the equilibrium, i.e., the absorption curve follows Fick's law, with the apparent maximum moisture content (M_m). The experimental

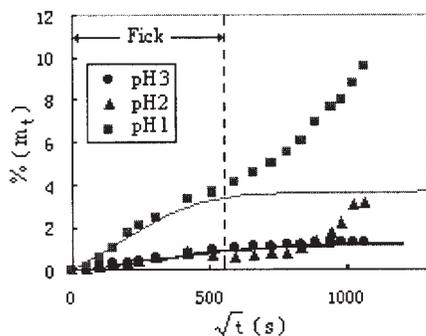


Figure 2 Experimental results for the absorption of HNO_3 solution in SiR at 60°C. The line represents the theoretical prediction for Fickian diffusion.

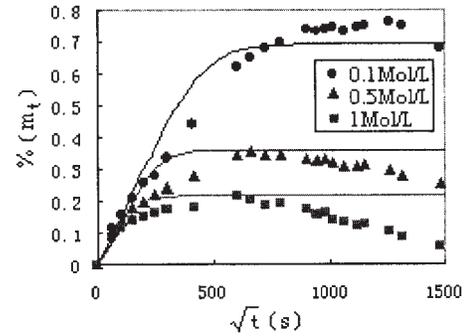


Figure 3 Experimental results for the absorption of NaCl solution in SiR at 40°C. The line represents the theoretical prediction for Fickian diffusion.

result agrees well with the theoretical prediction for Fickian diffusion.

Figure 2 shows the absorption result of SiR specimens immersed in HNO_3 solutions of different concentration at 60°C; the lines represent theoretical prediction for Fickian diffusion. From the figure, it can be seen that the diffusion process follows Fick's law in the initial process; however, the measured weight increased once the apparent maximum moisture content was reached. In this case, the apparent maximum moisture content was taken at which the weight changes seemingly leveled off. The absorption of some SiR specimens in NaCl solution at 40°C are shown in Figure 3, and the measured weight decreased after the apparent maximum moisture content was reached. Only in the initial stage of moisture exposure, the absorption process approximately followed the Fick's law. Because of the attack of strong electrolyte, there may exist some chemical reactions in the diffusion process. From the aforementioned test, it can be seen that the diffusion process is little influenced in the initial process.

Influence of solution concentration

The calculated results of M_m and D values are listed in Table I. It shows the influence of concentration on the apparent moisture content and the apparent diffusion. When the specimens were immersed in HNO_3 solution, both M_m and D values increase with the increase of solution concentration. However, for the specimens immersed in NaCl solutions, M_m decreases with the increase of solution concentration, and D has the same trend as that in HNO_3 solution.

At the same time, it shows that the M_m values for specimens immersed in NaCl solutions are less than that in deionized water, but the D values increased markedly. The NaCl solutions accelerate the diffusion process, but it reduces the quantity of the water entering into the material. In the HNO_3 solutions, even if the concentration is much lower than that of NaCl

TABLE I
Diffusion Testing Results of Filled SiR Immersed
in Different Solutions

Temperature (°C)	Concentration (mol/L)	M_m (%)	$D \times 10^7$ (mm ² /sec)	
HNO ₃	25	0.001	1.0	3.5
		0.01	1.2	6.9
		0.1	3.5	23.0
	40	0.001	1.1	7.6
		0.01	1.2	9.7
		0.1	3.9	29.0
	60	0.001	1.2	14.3
		0.01	1.25	14.7
		0.1	3.6	35.3
NaCl	25	0.1	0.72	17.7
		0.5	0.31	68.5
		1	0.2	186.6
	40	0.1	0.69	37.1
		0.5	0.36	104.5
		1	0.22	201.4
	60	0.1	0.65	70.3
		0.5	0.30	198.8
		1	0.21	366.8
Deionized water	25	—	1.0	3.2
	40	—	1.30	6.8
	60	—	1.15	13.9

solution, M_m has increased, and it increases more with the increase of the acid solution concentration. The diffusion of the acid solutions into the SiR involves the chemical reactions between the acid and the SiR running parallel with the purely physical processes of diffusion, it will be discussed subsequently.

Influence of temperature

The absorption process is also affected by the temperature of the solution. From Table I, it can be seen that the apparent diffusion D is strongly affected by the temperature, while M_m is relatively insensitive to temperature. D increases with the rise of the temperature, and it is possible that the higher temperature will increase the energy of the molecules entering into the filled SiR specimens. These results are consistent with those observed in other composite materials.¹¹ According to the Arrhenius law, diffusion is a kinetic process of constant increases with temperature, thus moisture equilibrium should be reached more rapidly at higher temperatures.

Appearance

Figure 4 gives some SEM observations for the specimen surface after immersed in different solutions,

each specimen was immersed about 20 days. Figure 4(a) shows the original surface before immersion (at 3000 \times), in which some filled particles can be observed. Figure 4(b) shows the surface immersed in 0.1 mol/L NaCl solution. It can be seen from the figure that the surface is smooth, and there are some holes in the surface, which maybe the filler particles falling off from the surface of the specimen due to the swelling and dissolution of the material after long term immersion. At the same time, the silicone chain in the SiR may suffer some changes due to the complex physical and chemical reaction in the NaCl solution after long-term immersion. So, the filled rubber is aged by the ionic solution and some filler are detaching from the rubber surface. Some weak places on the surface are destroyed, and it forms a small hole. It is the main cause of why the measured weight decreased after the maximum moisture content reached, the falling of the filler lighted the filled rubber weight. In Figure 4(c), the case is similar to that in Figure 4(b), the filler particles are detached from the surface. In addition, there exist several even smaller holes. This can be attributed to the result of corrosive reaction between the fillers such as Al(OH)₃ in SiR and the HNO₃ solution, and it is obvious from Figure 4(d), which has a higher immersion concentration than that in Figure 4(c). There are more small holes on the surface when the SiR subjected to immersion of higher concentration. After the HNO₃ solution enter into the SiR through the small holes, the HNO₃ solution reacts with the SiR.

In the case of specimens immersed in NaCl solution, after the specimen reach the maximum moisture content, the surface of the material was dissolved continually, and the weight of the lost material exceeded the weight of the absorbed moisture, and so the weight of the specimen decreased. In the specimens immersed in HNO₃ solutions, owing to the chemical reaction, small holes developed on the surface and inside the material, moisture rapidly entered into the material, causing the increase in weight, and the moisture gain was greater than the material lost, thus the weight of the specimen increased.

CONCLUSIONS

Moisture absorptions of NaCl and HNO₃ solution with different concentration and deionized water into filled SiR have been investigated in the temperature range of 25–60°C by weight-gain experiments. The apparent maximum moisture content M_m and the apparent diffusion coefficient D of filled SiR in different solutions were obtained. Both M_m and D values increase with the increase of solution concen-

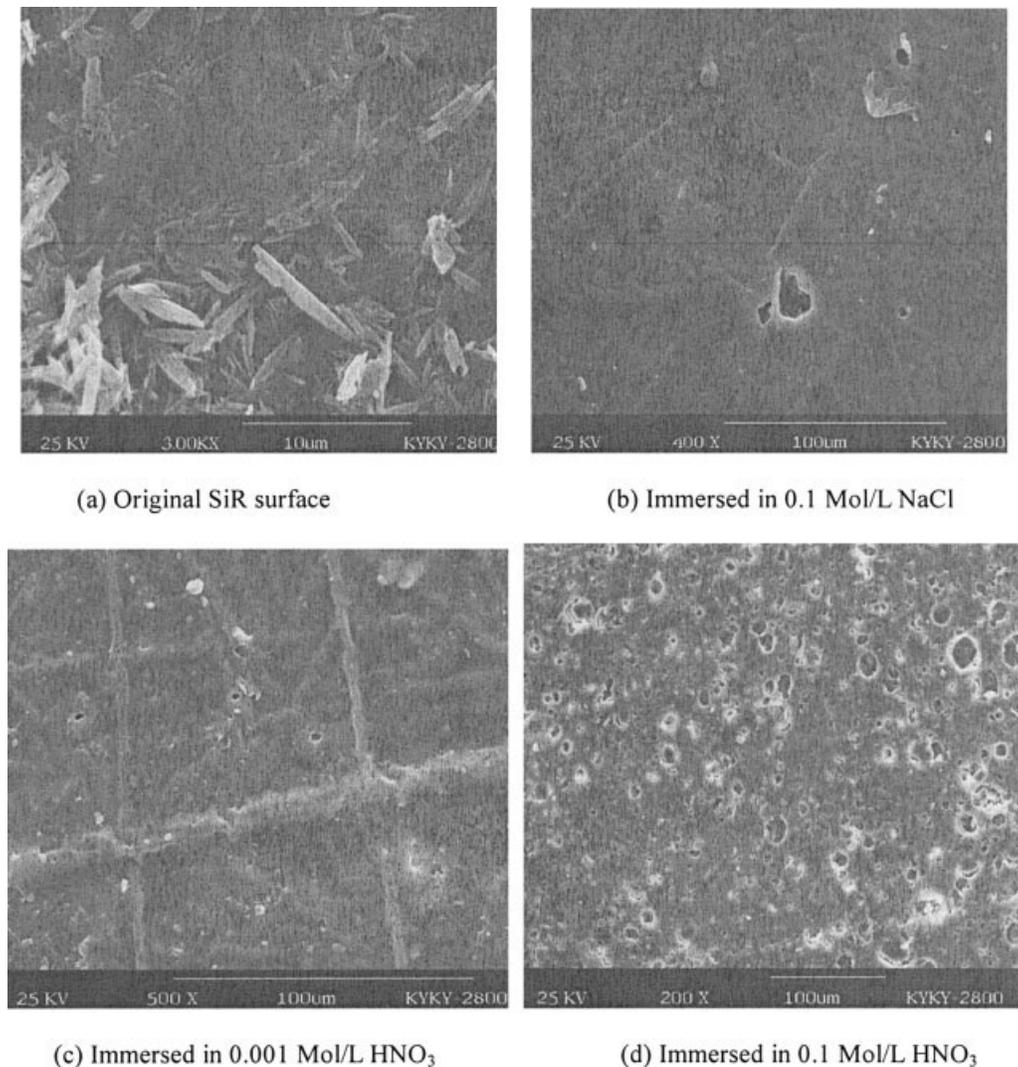


Figure 4 SEM micrographs of filled SiR specimens surfaces. (a) Original SiR surface, (b) immersed in 0.1 Mol/L NaCl, (c) immersed in 0.001 Mol/L HNO₃, and (d) Immersed in 0.1 Mol/L HNO₃.

tration when the specimens were immersed in HNO₃ solution. However, for the specimens immersed in NaCl solutions, M_m decreases with the increase of solution concentration. In all the cases, D increases as the rise of the environment temperature, while M_m is relatively insensitive to the temperature change. The microphotos of the surface of the immersed specimens show that there are some small holes on the surface of the specimens immersed in HNO₃ solution. There exist some chemical reactions between the fillers in the SiR and the ionic solution, and some fillers are detached from the rubber surface. Thus, the diffusion process is affected by chemical reactions between the SiR and the acid solution, and the measured weight increases after the maximum moisture content is reached.

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