

Life Time Prediction of Rubber Gasket for Fuel Cell through Its Acid-Aging Characteristics

Mi Suk Kim, Jin Hak Kim, and Jin Kuk Kim*

Department of Polymer Science and Engineering, College of Engineering, Gyeongsang National University, Jinju, Gyeongnam 660-701, Korea

Seok Jin Kim

R&D Center, Dong-A Hwa Sung Co. Ltd., Gimhae, Gyeongnam 621-834, Korea

Received December 4, 2006; Revised February 16, 2007

Abstract: The present manuscript deals with the prediction of the lifetime of NBR compound based rubber gaskets for use as fuel cells. The material was investigated at 120, 140 and 160 °C, with aging times from 3 to 600 h and increasing H₂SO₄ concentrations of 5, 6, 7 and 10 vol%. Both material and accelerated acid-heat aging tests were carried out to predict the useful life of the NBR rubber gasket for use as a fuel cell stack. To investigate the effects of acid-heat aging on the performance characteristics of the gaskets, the properties of the NBR rubber, such as cross-link density and elongation at break, were studied. The hardness of the NBR rubber was found to decrease with decreasing acid concentration at both 120 and 140 °C, but at 160 °C, the hardness of the NBR rubber increased abruptly in a very short time at different acid concentrations. The tensile strength and elongation at break were found to decrease with increases in both the H₂SO₄ concentration & temperature. The observed experimental results were evaluated using the Arrhenius equation.

Keywords: life time prediction, fuel cell gasket, NBR, arrhenius equation.

Introduction

A fuel cell is an electrochemical device that combines hydrogen fuel and oxygen from the air to produce electricity, heat and water. Fuel cells operate without combustion, so they are virtually pollution free. Since the fuel is converted directly to electricity, a fuel cell can operate at much higher efficiencies than internal combustion engines, extracting more electricity from the same amount of fuel. The fuel cell itself has no moving parts-making it a quiet and reliable source of power.¹

As hydrogen flows into the fuel cell anode, platinum catalyst on the anode helps to separate the gas into protons (hydrogen ions) and electrons. The electrolyte in the center allows only the protons to pass through the electrolyte to the cathode side of the fuel cell. The electrons cannot pass through this electrolyte and flow through an external circuit in the form of electric current. As oxygen flows into the fuel cell cathode, another platinum catalyst helps the oxygen, protons, and electrons combine to produce pure water and heat. Individual fuel cells can be combined into a fuel cell "stack". The number of fuel cells in the stack determines the

total voltage and the surface area of each cell determines the total current. Multiplying the voltage by the current yields the total electrical power generated. However, the problem of gas supply and preventing leak indicates the design is somewhat more complex because the electrodes must be porous to allow the gas in and thus they allow the gas to leak out of their edges. The result is that the edges of the electrodes must be sealed. Sometimes this is done by making the electrolyte somewhat larger than one or both of the electrodes and fitting a sealing gasket around each electrode. The polymer membrane must be hydrated with liquid water to maintain adequate conductivity. The operating temperature of the polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC)^{2,3} is limited to 80 °C or lower and fuel cell stack condition is pH = 1-2. The commonly used membrane for fuel cell is Nafion[®] because of its excellent thermal and mechanical stability. Nafion[®]'s unique ionic properties are due to sulfonic group, which can hydrolyzed or it can be transferred the type of ion of H₃O⁺, H₅O₂⁺ and combination of hydro molecules. Since the system must be sealed with rubber gasket and due to acid environment, the rubber gasket can be broken with time. Because of this, the rubber gaskets for fuel cell must be designed in such a way that it can withstand the acid and

*Corresponding Author. E-mail: rubber@gnu.ac.kr

thermal environment in long period of time. In addition, the mechanical properties must be maintained in these surroundings during its long-term service.

A lot of research data on the lifetime predictions of polymers especially elastomers in air (oxygen containing) environments from accelerated aging experiments and extrapolation models were published by Gillen *et al.*^{4,9} In general, the life time prediction is done by carrying out accelerated aging experiments at several elevated temperatures and extrapolate the results to the operating temperature by means of the time-temperature superposition principle. Usually, the shift factor is determined by the so-called Williams-Landel-Ferry (WLF) equation or by the Arrhenius approach. LeHuy and Evrard¹⁰ have discussed the methodologies for life time prediction of elastomers using the WLF model illustrated by the creep behaviour of styrene butadiene rubber/natural rubber (SBR/NR) and the Arrhenius model illustrated by thermal ageing of nitrile butadiene rubber/poly(vinyl chloride) (NBR/PVC) blends and the ageing of hydrogenated nitrile rubber (HNBR) in gaseous fluids. Recently, Denardin *et al.*¹¹ studied the time-temperature dependence of the thermo-oxidative aging of polychloroprene rubber using the time-temperature transformation superposition method from thermo- gravimetric (TG) data. Nakauchi¹² studied the decay and service life of rubber products by micro and fine analyses and concluded that large differences in properties were found between the surface and the bulk of model aged samples and natural aged products. These differences are attributed to diffusion and reaction of oxygen with rubber. Streit and Achenbach¹³ proposed a lifetime prediction technique based on the principle of chemical deterioration rates and the strain energy density concept using finite element method (FEM) technique for the useful life of an elastomeric sealing element exposed to any severe service environment.

In this study, NBR compound was used as material for sealing gasket in application to fuel cell. The accelerated acid-heat aging test of the rubber compound was carried out to predict the useful life of NBR rubber gasket for fuel cell stack. The effects of acid-heat aging on the material properties like, crosslink density, hardness, elongation at break, stress-strain curves were determined.

Arrhenius Model for Lifetime Predictions. The Arrhenius equation, which is well known in chemical kinetics, can ascertain thermo-oxidative ageing or the chemical degradation of polymers in the absence of mechanical stress. It can also represent physico-chemical change under stress, which combines viscoelasticity and aging as such. The method generally used by practitioners to determine lifetimes is based on the Arrhenius model of time-temperature equivalence. This method refers more particularly to Standards NFC 26-301/1990 (Test method for insulating materials determining thermal endurance properties of electric insulating materials) and ISO 11346/1997 (Rubber, vulcanized or thermo-

plastic estimation of lifetime and maximum temperature of use from an Arrhenius plot). The aging acceleration method consists of increasing the reaction speeds of the material without modifying the degradation mechanisms that are liable to occur with the long-term use of the material. This usually amounts to increasing the exposure temperatures over an interval relatively close to the service conditions.

By way of a series of conceptual leaps and bounds, the practitioners proceed from the Arrhenius law to the Arrhenius model of lifetime predictions, by transposing:

- an elementary chemical act to an overall complex process,
- a speed constant to a lifetime,
- a concentration of chemical species to one or more physical properties.

Most commonly, aging is a complex mechanism resulting from a combination of several elementary processes that may have different activation energies. The lifetimes are evaluated more often than the speed constants. These lifetimes are determined using a conventional end-of-life criterion, on the basis of physical measurements (mechanical properties, loss of mass, etc.), which have relations with the chemical changes that are by no means always clearly established. However there are methods of studying the aging of polymers, based on an approach that is both chemical and mechanical, often win which heterogeneous character of the aging reactions in the material thickness is taken into account. For all these reasons, a restricted approach that consists in monitoring aging through a single experimentation with a single exposure time is insufficient. It is necessary to know the trend curves for the material's properties with test times for several experimental conditions in order to extrapolate a useful lifetime. The lifetime is defined conventionally as being the time (t_i) taken for a physical or chemical property to attain a threshold consistent with the function (y_i), called end-of-life criterion. The relation between the lifetime and the absolute temperature is shown on an Arrhenius plot called thermal endurance profile.

Experimental

The compound recipes are given in Table I. The NBR

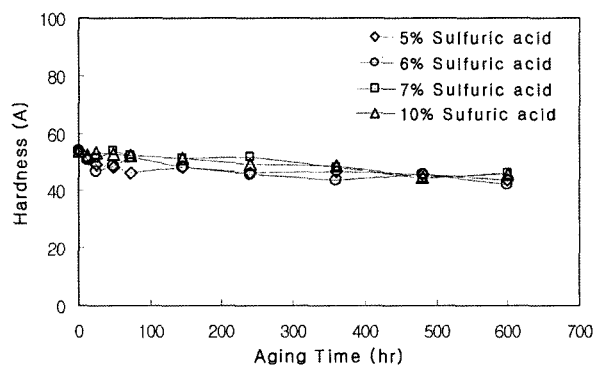
Table I. The Compound Recipes

Formulation	Percent
NBR (KNB35L, KUMHO petrochemical Co., Korea)	50
FEF(N-550), SRF(N-774), CaCO ₃	25
Oil (BISOFLEX 111, Laporte Co., England)	13
Zinc oxide	2.6
Promoters	1.5
Vulcanizing ingredients	0.3
Sulfur	0.26

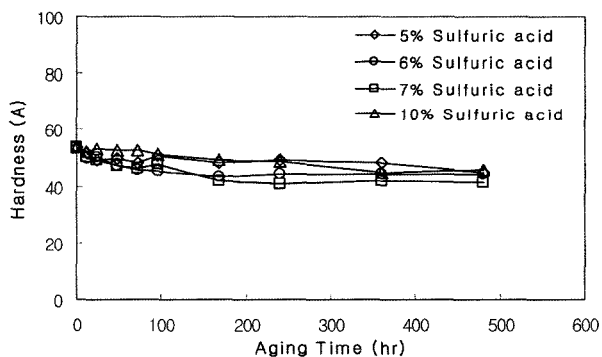
compound was procured from the Dong-A Hwa Sung Co., Ltd. by sulfur-cure system. The accelerated material aging was investigated at different temperatures at 120, 140 and 160°C and aging time from 3 to 600 h in increasing H₂SO₄ concentrations of 5, 6, 7, 10 vol%. The experimental procedure was similar to J. H. Jung.¹⁴ The rubber strips (5 mm × 2mm × 10 mm) were placed in acid solution using pyrex glass tube.¹⁵

To monitor the aging characteristics, the mechanical properties were measured at given temperature, time and acid

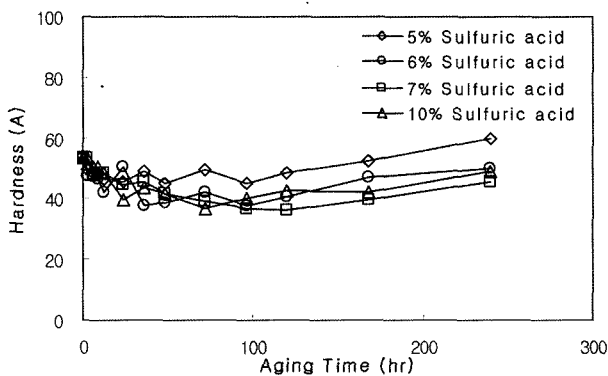
concentration using a Tensometer universal testing machine (Tensometer 2000; South Korea). Crosslink densities of the samples before and after the acid-aging were measured by swelling method using toluene as the solvent. Firstly, organic additives in the samples were removed by extracting with acetone for 6 h and then dried for 3 h at 60°C in oven. Secondly, the weights of the swollen samples were measured. Finally, the crosslink density was calculated using Flory-Rehner equations.^{16,17} The crosslink density is frequently calculated from equilibrium swelling data by means of the Flory-Rehner equation, which relates crosslink



(a) 120°C

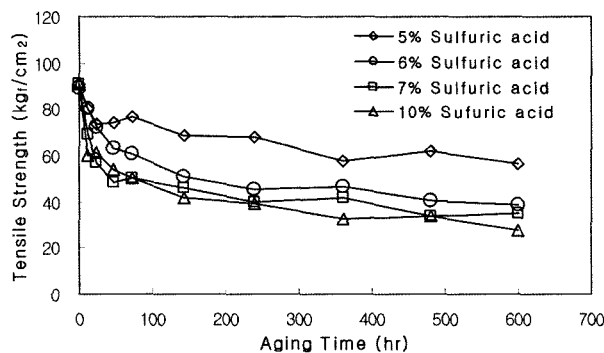


(b) 140°C

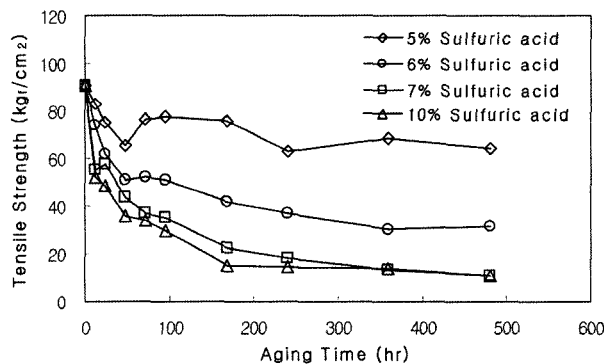


(c) 160°C

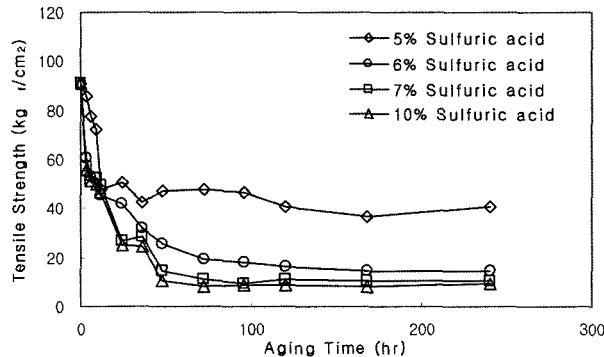
Figure 1. Effect of aging time on hardness (A) of NBR rubber sample under 5, 6, 7, 10 vol% H₂SO₄ solution. (a) 120°C, (b) 140°C, and (c) 160°C.



(a) 120°C



(b) 140°C



(c) 160°C

Figure 2. Effect of aging time on tensile strength (kg/cm²) of NBR rubber sample under 5, 6, 7, 10 vol% H₂SO₄ solution. (a) 120°C, (b) 140°C, and (c) 160°C.

density to v_r (Kraus equation), the measured volume fraction of polymer in a sample which has reached its equilibrium swollen state.

$$-\ln(1 - v_r) - v_r \chi v_r^2 = 2V_0 n_{swell} \left(v_r^{1/3} - \frac{v_r}{2} \right) \quad (1)$$

where χ (0.5 at 25°C) is the polymer-solvent interaction parameter, V_0 is the molar volume of solvent, and n_{swell} is the crosslink density.

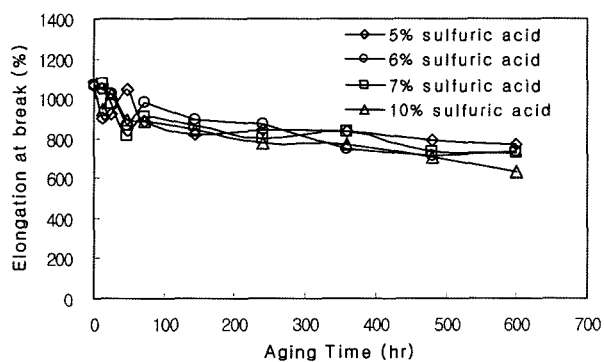
Morphology of the aged specimens was analyzed using a

scanning electron microscope (SEM; Jeol JFC-6400; Tokyo, Japan) after sputtering the samples with a fine coat of gold.

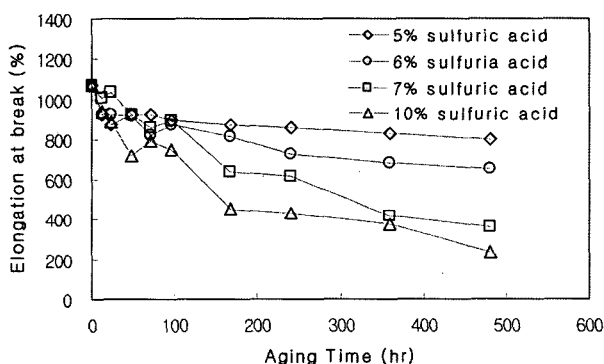
Results and Discussion

Effect of Accelerated Aging on Mechanical Properties.

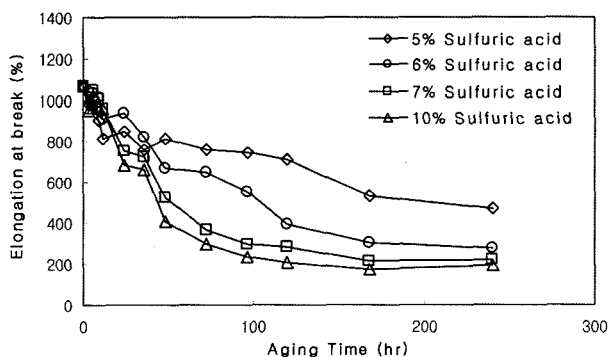
Figures 1(a), 1(b), and 1(c) show the effect of aging time on the hardness of NBR samples after subjecting at different acid concentrations. The hardness decreases as the H_2SO_4 solution and temperature increases, which is well pronounced for 120 and 140°C. Because the elastomeric com-



(a) 120°C

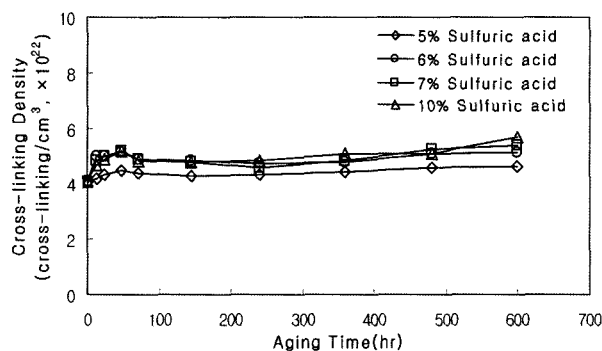


(b) 140°C

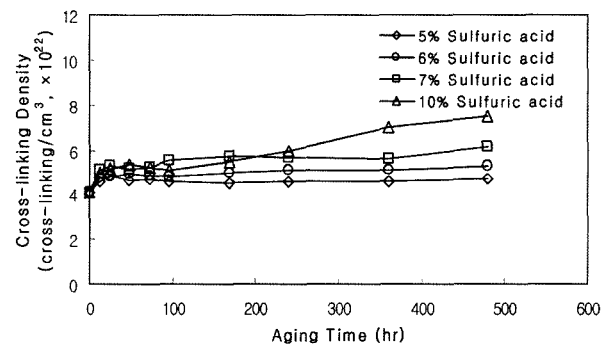


(c) 160°C

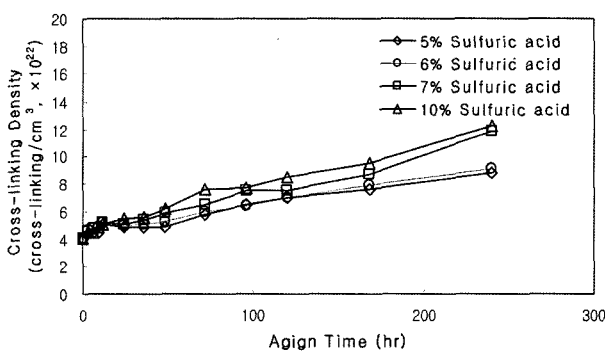
Figure 3. Effect of aging time on elongation at break (%) of NBR rubber sample under 5, 6, 7, 10 vol% H_2SO_4 solution. (a) 120°C, (b) 140°C, and (c) 160°C.



(a) 120°C



(b) 140°C



(c) 160°C

Figure 4. Effect of aging time on cross-linking density (cross-linking/ cm^3 , $\times 10^{22}$) of NBR rubber sample under 5, 6, 7, 10 vol% H_2SO_4 solution. (a) 120°C, (b) 140°C, and (c) 160°C.

ponents exposed to acid solution for extended periods and at high temperatures may absorb very large amounts of water and swell enormously thereby the material softens. In the case of 160 °C, hardness of the NBR rubber decreases abruptly at very short time at different acid concentrations. However, at longer aging time, the hardness starts to increase. This may be explained that NBR becomes hard and brittle after acid heat aging due to the formation of new crosslinks. Figures 2(a), 2(b) and 2(c) show the tensile strength-aging time relationship of the NBR samples. The tensile strength decreases as the H₂SO₄ concentrations and temperature increase. Exposure of NBR rubber to H₂SO₄ solution and temperature result in extensive changes in their molecular structure. These changes are very similar to those caused by heat aging. The polymer chains may be cross-linked to form a three-dimensional network or may be cleaved into smaller molecules. Inorganic acids such as H₂SO₄ solution can chemically attack the conventional elastomers. It can severely attack the surface of nonresistant elastomers, causing clearly visible crazing (alligatoring) perpendicular to the direction of stretch. In severe cases the elastomeric materials can be completely deteriorated. It is primarily controlled by the backbone of unsaturation level of elastomer since acid attacks the double bonds.

The ability of rubber to stretch to several times its original length is one of its chief characteristics. Hence, the elongation at break is one important factor in the rubber study,

which can be related also to the aging time of rubber samples. Figures 3(a), 3(b) and 3(c) show the variation of elongation at break (EB) with aging time in NBR composites. At 120 °C (Figure 3(a)), the decrease in EB is almost constant as the aging time increases. However as the temperature increases, EB becomes acid concentration dependent but remains constant for all concentrations as the aging time increases. The elongation at break decreases as the H₂SO₄ concentrations & temperature increases.

Crosslink Density. A rubber network consists of chemical crosslinks, entanglements, and loose chain ends. The physically effective crosslink density contains a contribution due to the chemical crosslinks and another due to the chain entanglements and loose chain ends acting as crosslinks in rubber. This is usually estimated by swelling measurements, from modulus values in the rubbery region or from stress-strain data. The physically effective crosslink density is in general higher than estimates of pure chemical crosslinks without contributions of chain ends and entanglement.¹⁸⁻²⁰

Figures 4(a), 4(b) and 4(c) show the variation of the crosslink density of NBR rubber immersed in different acid concentration and different temperature as a function of time. Initially at a short time, cross-linking density slightly increases at 120 and 140 °C. At 120 °C cross-linking density remains stable as the aging time increases. Although the cross-linking density also remains constant at 140 °C however, it becomes acid concentration dependent. The result

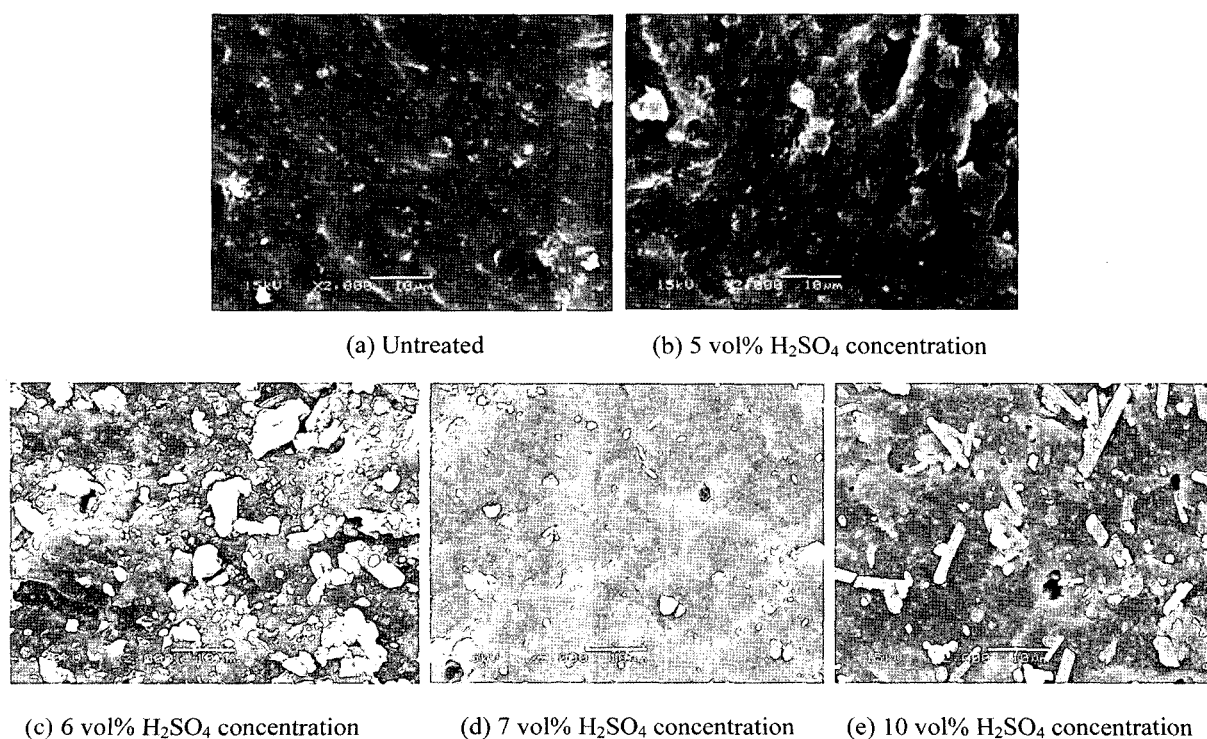


Figure 5. Effect of increasing acid concentration at 120 °C for 600 h.

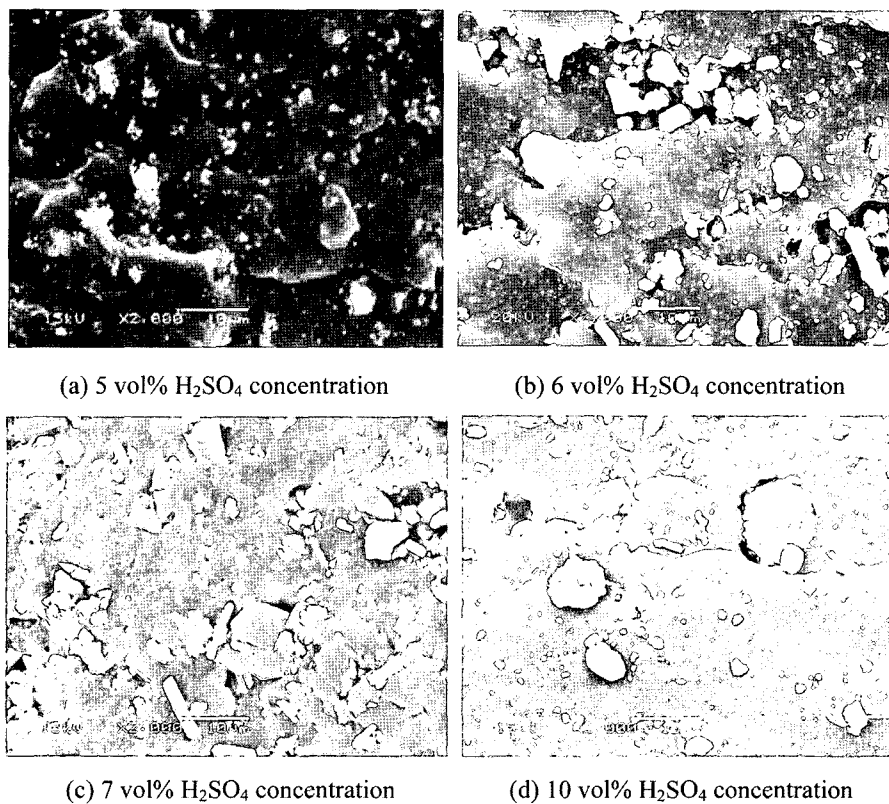


Figure 6. Effect of increasing acid concentration at 140°C for 480 h.

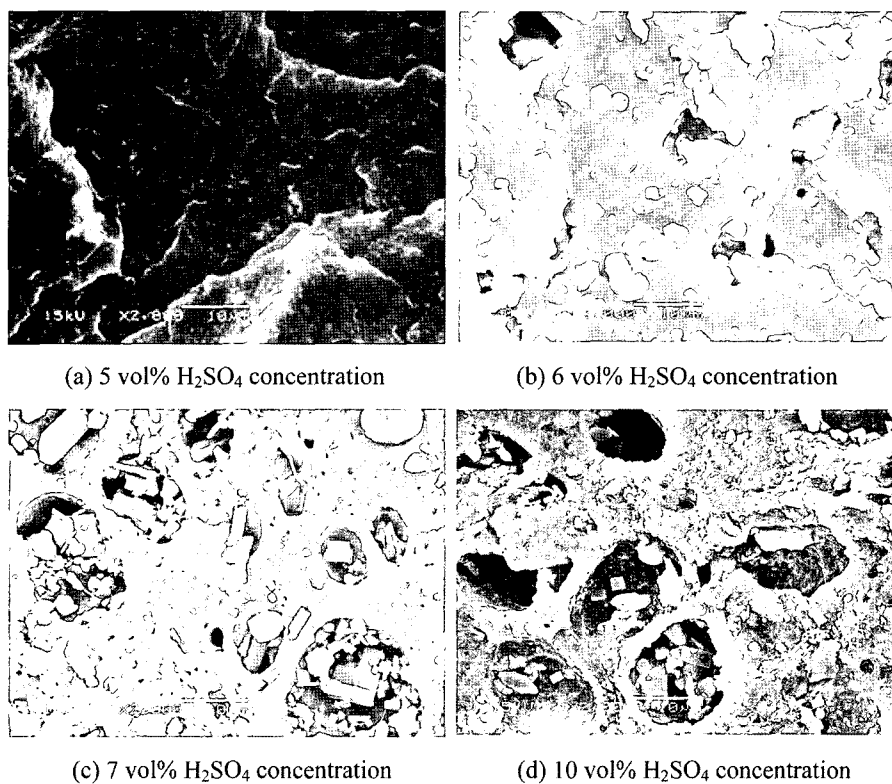


Figure 7. Effect of increasing acid concentration at 160°C for 240 h.

shows that the concentration lowers, the higher the crosslinking density. On further increase in temperature to 160 °C, there is relative change in behavior, showing that crosslink density increases with longer exposure time and greater acid concentration. In some instances, the crosslink density is much higher than the original sample. Changes of the crosslink densities of the NBR samples after the acid heat aging are due to the formations of new crosslinks and the dissociations of the existing crosslinks. When the formations of new crosslinks occur more than the dissociations of the existing crosslinks in a cured rubber composite during aging, the crosslink density increases.²¹ On the contrary, the crosslink density increases when the dissociations of the existing crosslinks surpass the formations of new crosslinks.

Morphology. Inorganic acids, when concentrated, are very aggressive and can chemically attack conventional elastomers. In severe cases the elastomeric materials can be completely deteriorated.²² All the changes observed in

mechanical properties caused by the chemical crystallization due to acid-aging could be supported with SEM micrographs.

Figure 5 shows the morphology of NBR compounds to various acid concentrations at 120 °C and 600 h, a comparative SEM micrograph of fresh NBR vulcanizate is shown in Figure 5(a) for comparative purposes. From the Figures 5(b) to 5(d) it can be observed that increasing acid concentration has detrimental effect on the morphology of the NBR compounds with the highest acid concentration (Figure 5(e)) showing characteristics of 'chalking'. Increasing concentration of the acid leads to oxidation of the compounds which will form a protective oxidated layer on the compounds. On drying this layer contracts to produce crazing cracks which can be observed in the SEM pictures. A similar line of explanation can be extended to the SEM micrographs of NBR compounds exposed to increasing acid concentration at 140 °C 480 h that has been shown in Figure

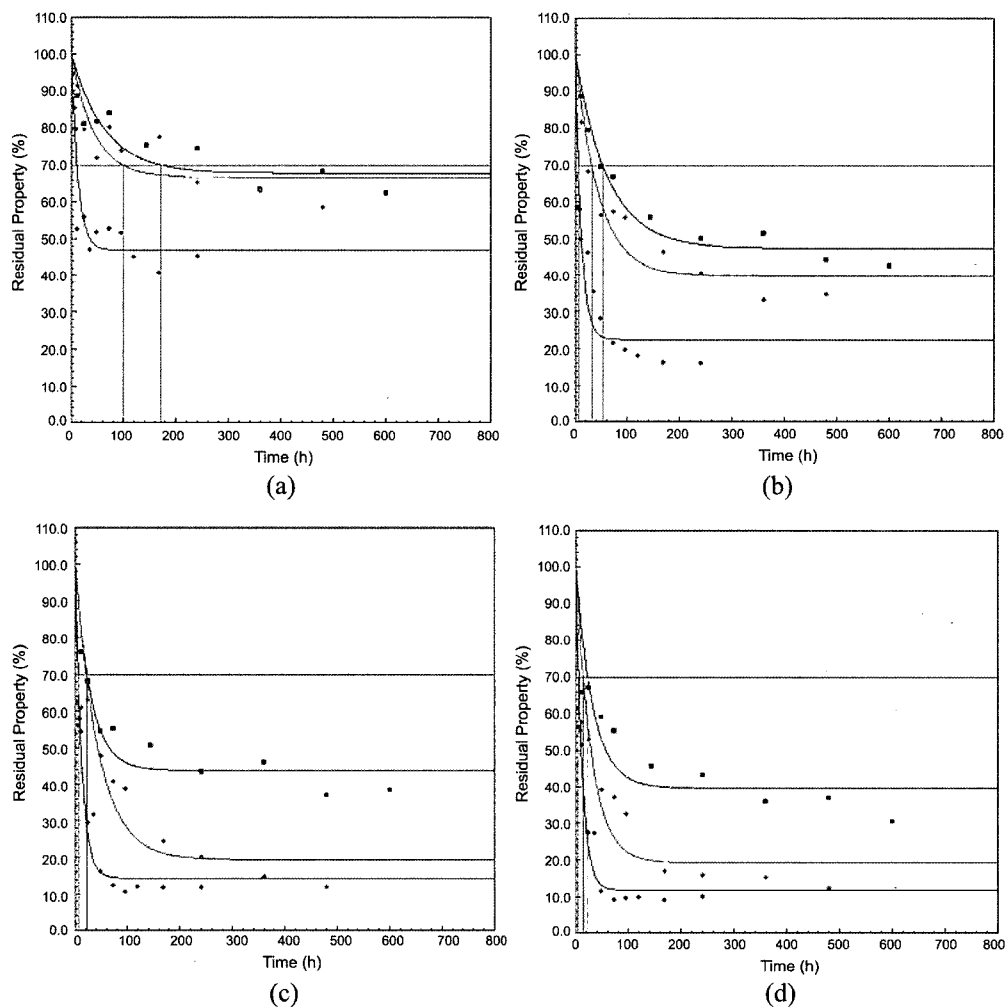


Figure 8. Tensile strength (kg/cm^2) of NBR samples : Change in property versus time (h) at four different H_2SO_4 concentrations and three different temperatures. (a) aging of 5% H_2SO_4 solution, (b) aging of 6% H_2SO_4 solution, (c) aging of H_2SO_4 solution, and (d) aging of 10% H_2SO_4 solution.

6. In these pictures too an increase in surface roughness with increasing acid concentration can be observed. Figure 7 shows the effect of increasing acid concentration but shorter exposure time (240 h) and higher temperature (160 °C). With increasing acid concentration, formation of small blow holes in the compounds can be observed which can be attributed to the oxidization of the filler particles.

Arrhenius Plot of Tensile Strength. The tensile strength results from the acid-heat acceleration test is show in Figure 8. Here, we compare the tensile strength residual property with applied H_2SO_4 concentrations on the lifetime. The data at different 120, 140 and 160 °C and aging time 3 to 600 h in increasing H_2SO_4 concentrations of 5, 6, 7, 10 vol%. The loss of properties increased with increasing acid concentrations and temperature as expected. The study covers the lifetime prediction for fuel cell gaskets to prevent leaks at an average temperature of use of 80 to 100 °C. These fuel cell gaskets are representative of fuel cell gaskets aged naturally

for 5 years.

Assuming the residual property 70% tensile strength, we can draw the aging temperature curve against the lifetime. The choice of 70% retention of tensile strength as a criterion of aging performance was not arbitrarily chosen but instead it is the maximum allowable service limit in fuel cell gasket quality specifications. Also, this has been used because there is not a simple relationship between degradation and time that is applicable to all rubber compounds. Over a long period, slight discrepancies in the maintenance of aging temperature can cause variability in aging performance in addition to the errors that are normally expected during testing, so the use of a high level of retention as 70% to the limit the time scale is preferable. By means of the Arrhenius approach, E_a (activation energy) is determined by slope of the plot of $\ln(Lt(Hr))$ against $1/T$ (K) as shown in Figure 9. Choosing 80 °C as the standard environmental temperature and for fuel cell at service $F = 0.13$ (The apparatus was used

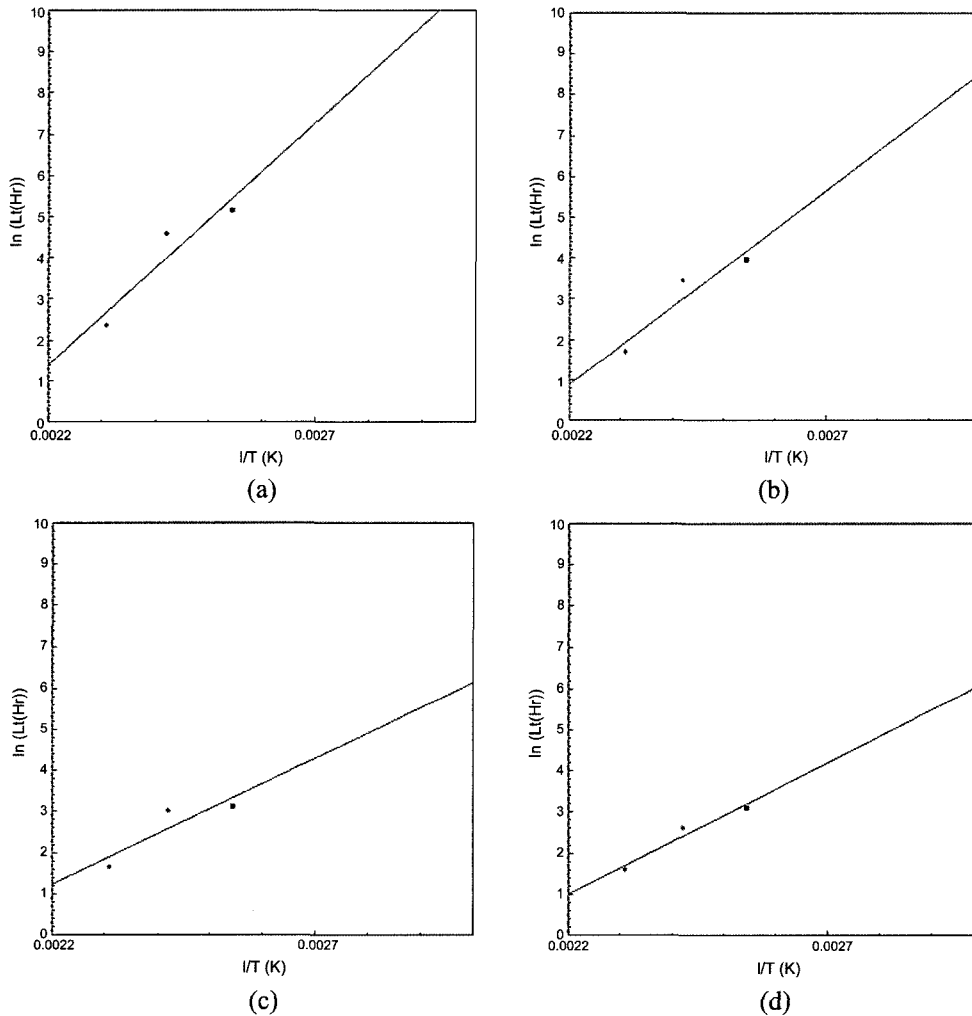


Figure 9. Arrhenius plot with acid concentrations for 70% residual tensile strength. (a) aging of 5% H_2SO_4 solution, (b) aging of 6% H_2SO_4 solution, (c) aging of 7% H_2SO_4 solution, and (d) aging of 10% H_2SO_4 solution.

Table II. Prediction Results for Fuel Cell Gaskets

Name	Condition		Prediction	
	Residual Tensile Strength (%)	Service Temperature (°C)	Service Time (year)	F (h/day)
5% Sulphuric acid	-30	80	6.0	0.13
6% Sulphuric acid	-30	80	0.9	0.13
7% Sulphuric acid	-30	80	0.1	0.13
10% Sulphuric acid	-30	80	0.1	0.13

for 3 h every day)²³ for 5% H₂SO₄ solution aging for 6.0 years, the reduction of tensile strength was 30%, which is based on data from aging. Table II gives the prediction results for the NBR samples. Thus, one can predict the lifetime as shown in Figure 9. It is also observed that the actually aged samples are found to lie close to the data predicted by taking acid-aging.

Thus, we can conclusively say that both environment temperature as well as acid concentration can be used for predicting the lifetime of fuel cell NBR gaskets very accurately.

Conclusions

An Arrhenius type of equation for prediction of the long-term behavior of NBR based gasket sealing materials for fuel cell applications has been studied. The choice of the prediction model will be based on a detailed analysis of the chemical and physical mechanisms of aging. This analytical approach is essential for establishing boundaries between the ranges in which the environments considered and the temperature and acid concentration levels under study.

This paper gives an insight into the complexity as well as the possibility of predicting the lifetime of fuel cell rubber gaskets from results of accelerated testing involving Arrhenius method, with special emphasis on the effect of environment temperature and acid concentration. The experimental results show that the testing procedure, although relatively simple, gives good service life time prediction, which has been proved to be accurate when compared to the actual aged specimens, it is not always easy to set up testing program that will deliver sufficient information to make a reliable estimate of the lifetime. Nevertheless, this additional information gathered is more than sufficient for the engineers and constructors for designing high quality rubber gaskets for longer service life for future quality demanding fuel cell rubber gaskets.

Acknowledgments. This work was supported by Ministry of Commerce, Industry and Energy (MOCIE, project of components & materials technical development, ITEP10014437), Korea, Mi Suk Kim is grateful to the second stage of BK21 program for supporting a fellowship.

References

- (1) J. Larminie and A. Dicks, *Fuel Cell Systems Explained*, 2nd ed., Wiley, UK, 2003.
- (2) H. D. Cho, J. Won, H. Y. Ha, and Y. S. Kang, *Macromol. Res.*, **14**, 214 (2006).
- (3) J. Li, C. H. Lee, H. B. Park, and Y. M. Lee, *Macromol. Res.*, **14**, 438 (2006).
- (4) K. T. Gillen, R. Bernstein, and M. H. Wilson, *Polym. Degrad. Stabil.*, **87**, 335 (2005).
- (5) K. T. Gillen, R. Bernstein, and M. Celina, *Polym. Degrad. Stabil.*, **87**, 257 (2005).
- (6) K. T. Gillen, R. Bernstein, and D. K. Derzon, *Polym. Degrad. Stabil.*, **87**, 57 (2005).
- (7) K. T. Gillen, M. Celina, and R. Bernstein, *Polym. Degrad. Stabil.*, **82**, 25 (2003).
- (8) M. Celina and K. T. Gillen, *Polym. Preprints*, **42**(1), 367-368 (2001).
- (9) J. Wise, K. T. Gillen, and R. L. Clough, *Polym. Degrad. Stabil.*, **49**, 403 (1995).
- (10) M. LeHuy and G. Evrard, *Die Angewandte Makromol. Chem.*, **261/262**, 135 (1998).
- (11) E. L. G. Denardin, P. R. Janissek, and D. Samios, *Thermochimica Acta*, **395**, 159 (2003).
- (12) H. Nakauchi, *Kautsch. Gummi Kunstst.*, **49**, 843 (1996).
- (13) G. P. Streit and M. Achenbach, *Tribology 2000-Plus: 12th International Colloquium*, Ostfildern, Germany, January, pp. 1419-1431 (2000).
- (14) J. H. Jung, *A study on Life Time Prediction and Aging property of Rubber Products for Automobile*, Gyeongsang national Univ., M.S. thesis (2005).
- (15) S. J. Kim, *Kinetics of Dilute Acid Pretreatment of Woody Hemicellulose*, Gyeongsang National Univ., M.S. thesis (1997).
- (16) P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 521 (1943).
- (17) P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
- (18) D. S. Campbell and A. V. Chapman, *J. Nat. Rubber Res.*, **5**, 246 (1990).
- (19) C. G. Moore and W. F. Watson, *J. Polym. Sci.*, **19**, 237 (1956).
- (20) L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).
- (21) S. G. Kim and S. H. Lee, *Polymer (Korea)*, **18**, 176 (1994).
- (22) Khairi Nagdi, *Rubber as an Engineering Material: Guideline for Users*, Hanser Gardner Publications, Munich, 1993.
- (23) J. H. Jung, *A study on Life Time Prediction and Aging property of Rubber Products for Automobile*, Gyeongsang national Univ., M.S. thesis (2005).