한국신·재생에너지학회 2007년도 추계학술대회논문집 pp.47~51

Rubber gaskets for fuel cells-
Life time prediction through acid ageing

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Key words : Fuel cell gaskets, acid ageing, life time prediction, Arrhenius relationship

Abstract : The present paper reports the life time prediction of Acrylonitrile-Butadiene rubber (NBR) fuel cell gasket materials as a function of operational variables like acid concentration, ageing time and temperature. 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.The acid ageing of the gasket compounds has been investigated at 120, 140 and 160℃, with aging times from 3 to 600 h and increasing acid (H_2SO_4) concentrations of 5, 6, 7 and 10 vol%. Material characteritics the gas compound such as cross-link density, tensile strength 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℃, but at 160℃ interestingly 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 increase in both the acid concentration & temperature. The life time of the compounds were evaluated using the Arrhenius equation.

1. 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.

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

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.

2. Experimental

2.1 Materials

The compound recipes are given in Table 1.

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The NBR 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℃ & 160℃ and aging time from 3 hours to 600 hours in increasing H_2SO_4 concentrations of 5, 6, 7, 10 vol %. The experimental procedure was similar to J.H.Jung.[12] The rubber strips(5mm×2mm×10mm) were placed in acid solution using pyrex glass tube.

Table 1 Compounding recipe.

Formulation	percent
NBR	50
Filler	25
Oil	13
Zinc oxide	2.6
Promotors	1.5
Vulcanizing ingredients	0.3
Sulfur	0.26

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 hours and then dried for 3 hours at 60℃ in oven. Secondly, the weights of the swollen samples were measured. Finally, the crosslink density was calculated using the well known Flory-Rehner equations.

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

Where x (0.5 at 25℃) 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.

3. Results and Discussion

3.1 Effect of Accelerated aging on mechanical properties: Tensile strength

Figure 2(a), 2(b) and 2(c) shows the tensile strength-aging time relationship of the NBR samples. The tensile strength decreases as the H_2SO_4 concentrations and temperature increase.

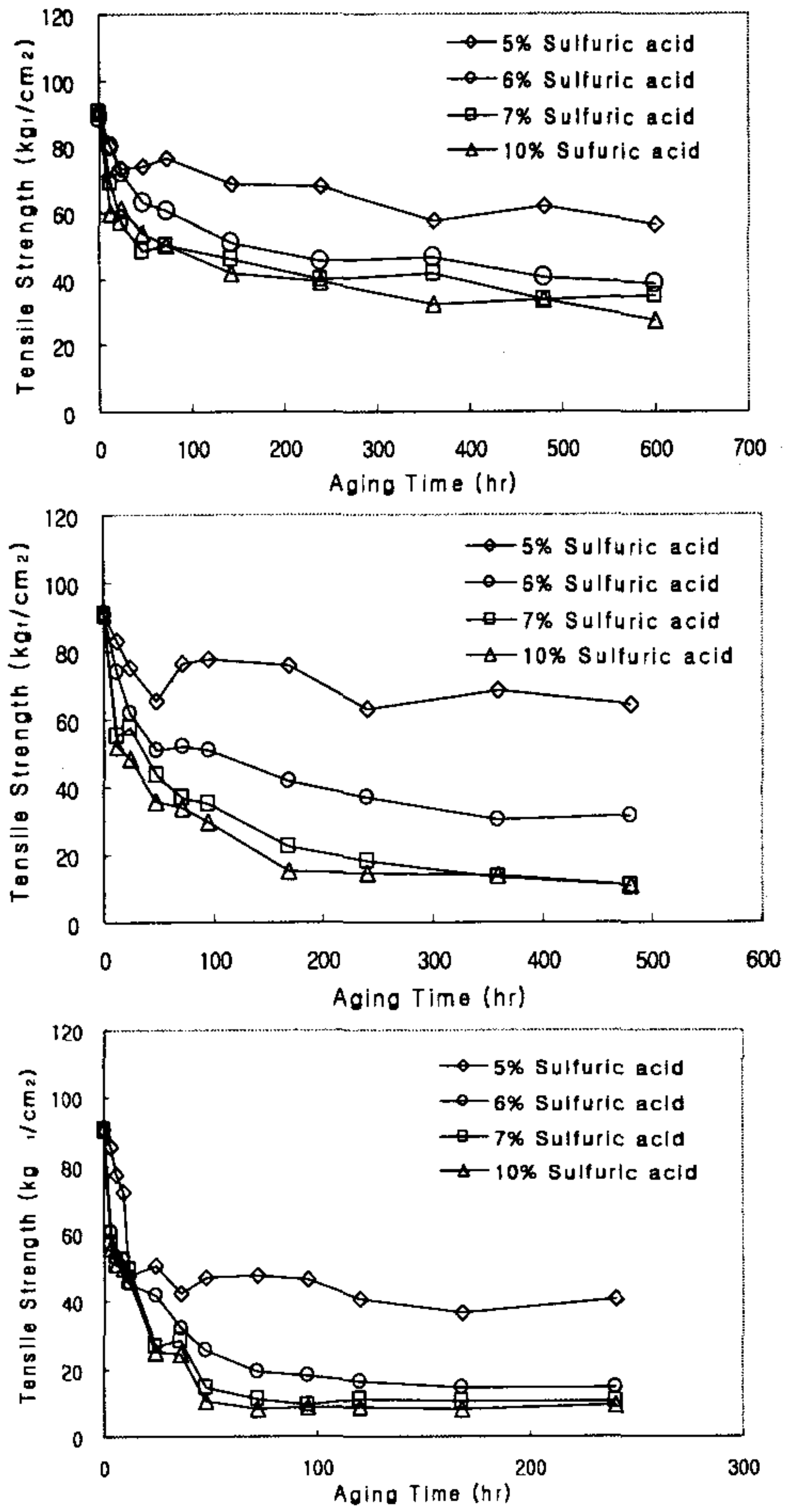


Figure 2. Effect of aging time on tensile strength (kg_f/cm^2) of NBR rubber sample under 5, 6, 7, 10 vol% H_2SO_4 solution (a) 120℃ (b) 140℃ (c) 160℃.

Exposure of NBR rubber to H_2SO_4 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 H_2SO_4 solution 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 extent of unsaturation in elastomer since acids primarily attacks the double bonds.

3.2 Effect of Accelerated aging on mechanical properties: Elongation at break

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. Figure 3(a), 3(b) and 3(c) shows the variation of elongation at break (EB) with aging time in NBR composites. At 120℃ (Figure 3(a)), the decrease in EB is almost constant as the aging time increases. However as the temperature increases, variation in elongation varies with acid concentration but remains unchanged at higher ageing times.

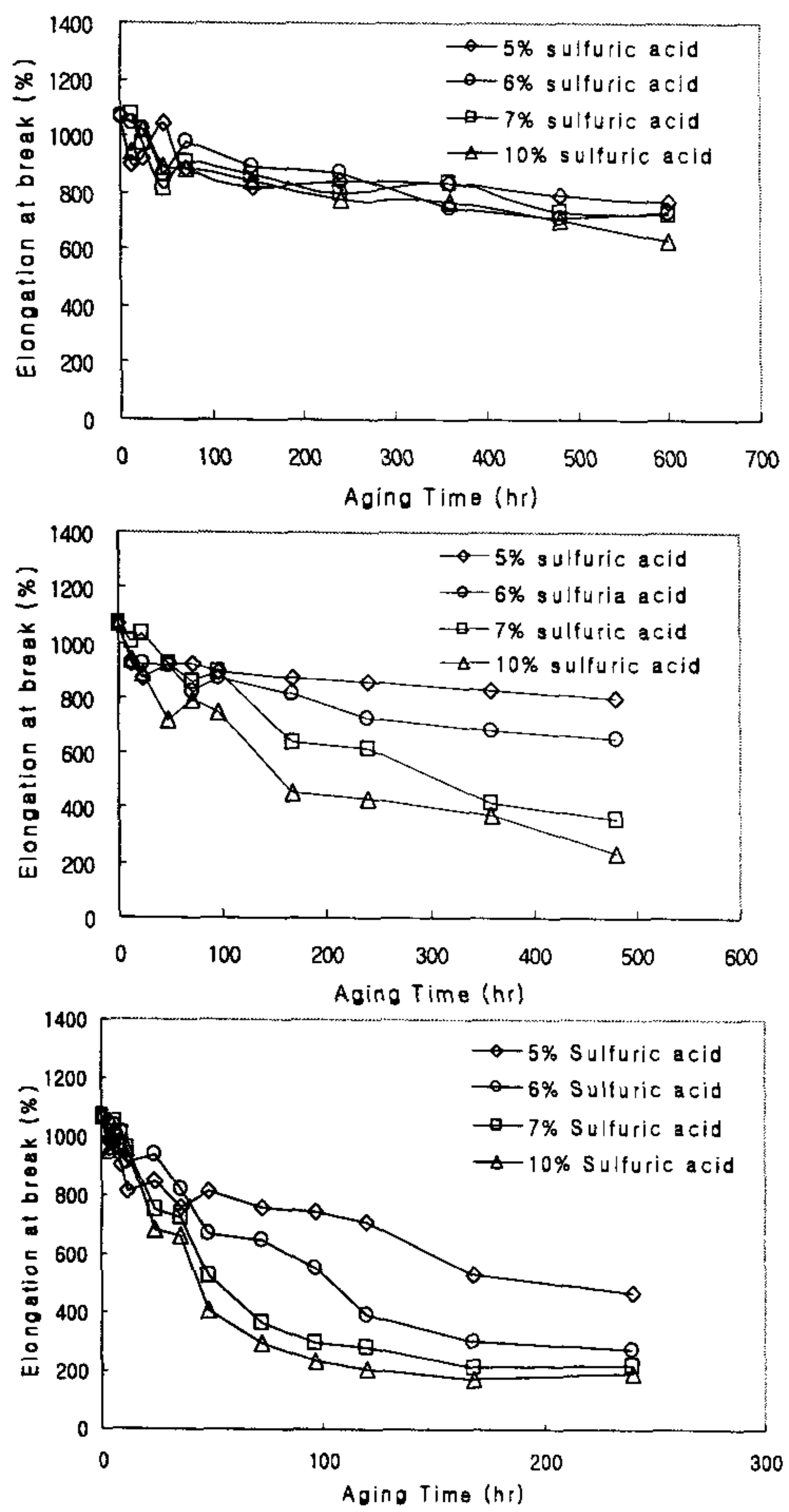
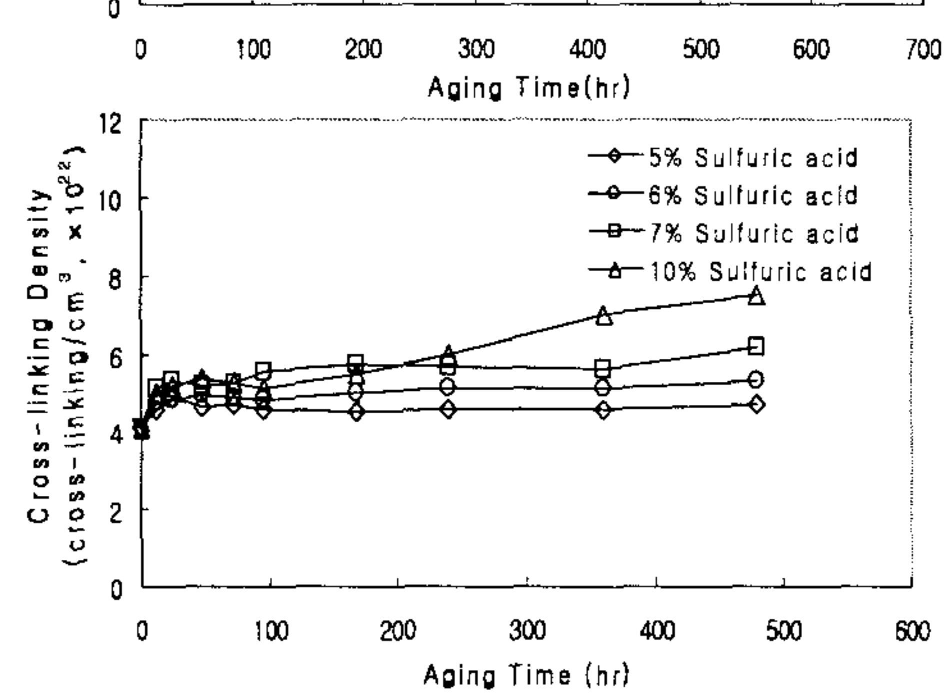


Figure 3. Effect of aging time on Elongation at break(%) of NBR rubber sample. under 5, 6, 7, 10.vol% H_2SO_4 solution (a) 120℃ (b) 140℃ (c) 160℃.

3.3 Effect of Accelerated aging on cross link density

A rubber network consists of chemical crosslinks, entanglements, and loose chain ends. The effective crosslink density(CLD) of a elastomer has contributions from chemical crosslinks, chain entanglements and loose chain ends. Though there are a number of ways to estimate CLD, most common and widely used methodology is by swelling measurements. 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℃. At 120℃ cross-linking density remains stable as the aging time increases. Although the cross-linking density also remains constant at 140℃ however, it becomes acid concentration dependent. The result shows that the concentration lowers, the higher the cross-linking density. On further increase in temperature to 160℃, there is relative change in behavior, showing that cross-link density increases with longer exposure time and greater acid concentration. In some instances, the crosslink density is much higher than the original sample.



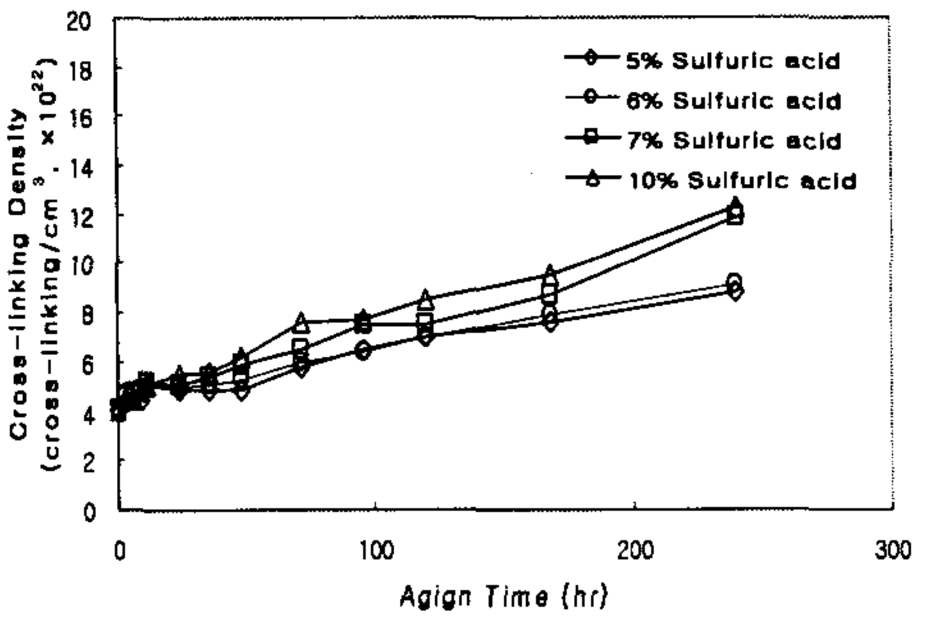


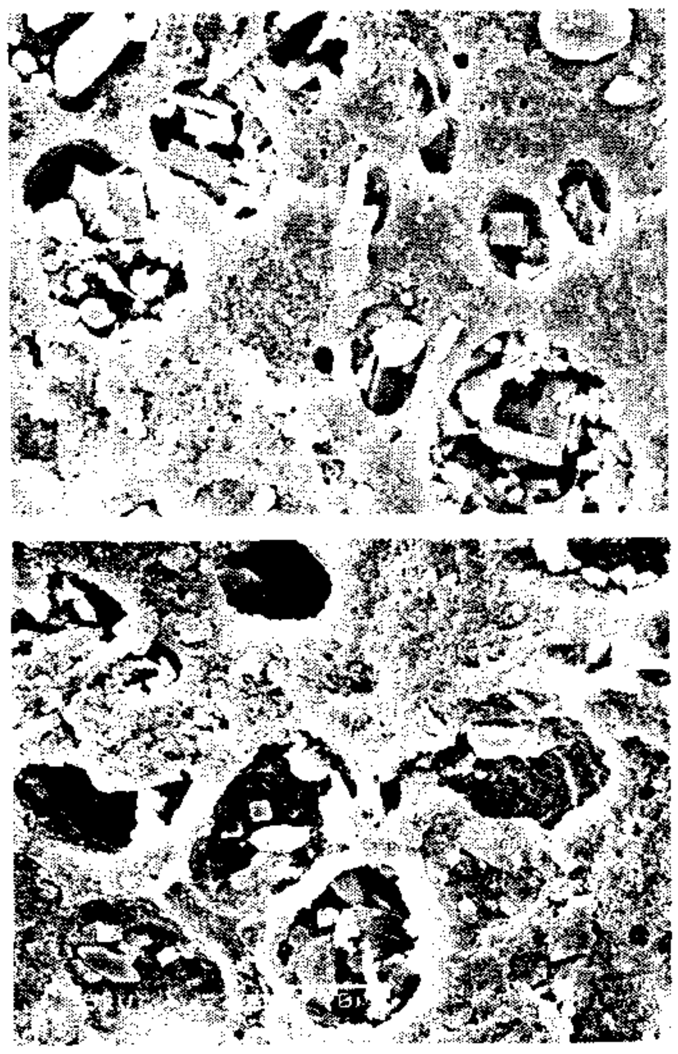
Figure 4. Effect of aging time on cross-linking density (cross-linking/cm^3, $\times 10^{22}$) of NBR rubber sample under 5, 6, 7, 10 vol% H_2SO_4 solution (a) 120℃ (b) 140℃ (c) 160℃.

The variation in crosslink density of NBR samples after the acid heat aging is due to the formations of additional crosslinks and dissociations of the existing crosslinks. Increase in cross link density can be observed when formations of new crosslinks occur more than the dissociations of the existing crosslinks in a cured rubber composite during aging. On the contrary, the crosslink density increases when the dissociations of the existing crosslinks surpass the formations of new crosslinks. Increase in cross links have been observed in our case.

3.4 Effect of Accelerated aging on Morphology

Inorganic acids, when concentrated, are very aggressive and can chemically attack conventional elastomers. In severe cases the elastomeric materials can be completely deteriorated. 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 representative SEM micrographs of the effect of increasing acid concentration but shorter exposure time (240hours) and higher temperature (160℃). With increasing acid concentration, formation of blow holes in the compounds can be observed which can be attributed to the oxidization of the filler particles.



(a) 7 vol%

(b) 10 vol%

Figure 5. Effect of increasing acid concentration at 160℃ for 240 hours.

3.5 Arrhenius Plot

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 value of 70% property retention as the limiting value has been chosen. By means of Arrhenius equation, the activation energy, Ea can be determined by slope of the plot of ln(Lt(Hr)) against 1/T (K) as shown in Figure 6. Choosing 80℃ as the standard environmental temperature and for fuel cell at service F= 0.13(hours/day) for 5% H_2SO_4 solution aging for 6.0 years, the reduction of tensile strength was 30%, which is based on data from aging. Table 2 gives the prediction results for the NBR samples. It is also observed that the actually aged samples are found to lie close to the data predicted by taking acid-aging.

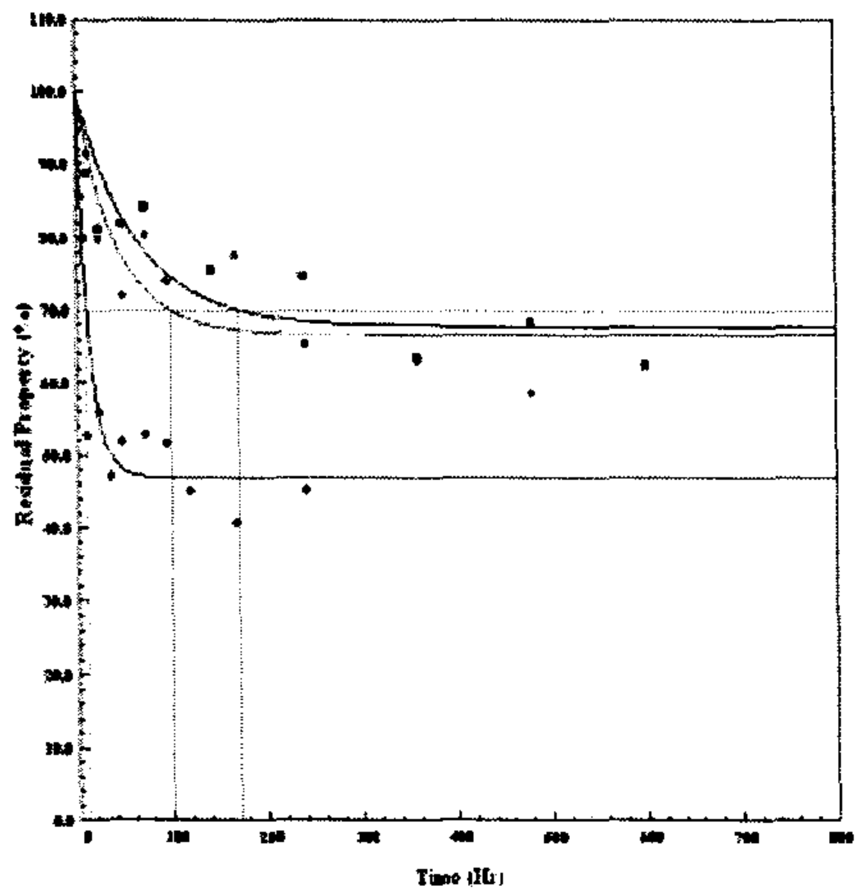


Figure 6 Representative Arrhenius plot based on tensile strength.

Table 2 Predicted life time based on 30% degradation in tensile strength and 80C.

Name	Service Time (year)	Service life (h/day)
5% sulphuric acid	6.0	0.13
6% sulphuric acid	0.9	0.13
7% sulphuric acid	0.1	0.13
10% acid	0.1	0.13

Conclusions

An Arrehenius type of equation for prediction of the long-term behavior of NBR based gasket sealing materials for fuel cell applications has been studied. Our 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.

References

M.S.Kim, J.H.Kim and J.K.Kim, Macromolecular Research, 15(4), 315-323, 2007.