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The Influence of Weathering Conditions on the Outer Membrane of Biogas with Plasticized PVC : A Study using Non-destructive Tests

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Abstract

The biogas holder is composed of an outer membrane and an inner membrane which are subject to outdoor exposure and gas exposure respectively. The influence of weathering conditions on the photo-degradation of a biogas holder was investigated. Tests were performed under three different methods - outdoor exposure tests (Seosan, Arizona), accelerated tests (Xenon-are lamp) with the outer-membrane of biogas. Moreover, the changes in the aging process were monitored using color difference, gloss, the contact angle and an optical microscope. Changes in physical properties, such as decrease reduction in gloss, decrease in the contact angle, increase in color difference were observed in the aging process. The comparison between membrane 3B, 4B and membrane 5B under xenon-arc were discussed. Membrane 5B was very sensitive to ultraviolet (UV) ray. There were many difficulties in the outdoor exposure test due to acid rain, dust, and stain resistance.

Keywords: Biogas, Poly vinyl chloride, Weathering, Non-destructive test

1. Introduction

Renewable energy is a future energy requiring reliable supply for the sustainable development of the national economy. It is desperately needed to develop alternative energy sources which can domestically be procured to prepare for the instability of energy supply and demand in the countries with high dependence on foreign energy supplies. For this, the Korean government has performed its best to develop alternative energy for several decades, investing enormous financial resources. In particular, the economic feasibility of biogas has stood out due to its features that it does not increase greenhouse gases and can domestically be supplied. The biogas storage tanks previously installed were mainly concrete tanks or the piston deck types of steel tanks, but need large investment costs and very high maintenance expenses. Accordingly, there is a growing trend that the double membrane holder with low investment costs and easy maintenance are largely used. The double membrane holder is composed of the inner and the outer membrane. There are performance standards such as air tightness, corrosiveness and mechanical properties for the inner membrane of biogas. However, there are no performance standards and test methods for the outer membrane of biogas even though it is exposed to the natural environment such as UV light, water and temperature, which causes the discoloration of fabrics and shortens life[1,2]. In this context, this study aims to evaluate the outer membrane of biogas through non-destructive measurement methods such as color difference, gloss and the contact angle, which can immediately and easily be measured and checked in the field in order to prepare test methods and performance standards.

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2. Experimental

2.1 Materials

The materials used in this study are 3B and 4B purchased from Hanwha Polydreamer producing the fabrics of the biogas storage tank and 5B purchased from M in Germany. As to material composition, polyester fibers and PVC resin were respectively used for the fabric and the degree of polymerization. In addition, primary plasticizer (C9) and cold resistant plasticizer were added. An acrylic treatment was made on the surface to maximize its durability.

2.2 Outdoor and accelerated weathering tests

The outdoor exposure test and the accelerated test were conducted at domestic and foreign exposure test sites to evaluate the long-term durability of the membrane of a biogas storage tank.

The outdoor exposure test had been conducted with a direct exposure testing method at the outdoor exposure test site with industrial climate features (installation angle of 37 degrees and southward), located at Seosan, Korea and a test site with desert climate features (installation angle of 34 degrees and southward), in Phoenix, Arizona, USA between October, 2011 and October, 2013 (50 MJ, 100 MJ, 150 MJ, 200 MJ, 300 MJ, 600 MJ/m^2 of UV irradiation).

The indoor accelerated test was conducted in a state of the radiance of 0.55 w/m^2, a black panel temperature of 70 degrees, a chamber temperature of 47 degrees and 50% humidity when the short-wavelength was 340 nm with ATLAS Weather Ometer Ci 5000 and the temperature of 38 degrees and the humidity of 95% when it was a dark cycle. As for xenon lamp filters, a right filter and a light filter were used as the inner and the outer filter. An evaluation cycle was set up as 500 kJ, 1000 kJ, 1500 kJ, 2000 kJ, 2500 kJ, 3000 kJ, 3500 kJ, 4000 kJ, 4500 kJ and 5000 kJ.

Table 1. Natural weathering testing sites

	Avg. Temp (°C)	Avg. Relative Humidity (%)	Total Rainfall (%)	Total radiation (UV) MJ/m^2
Seosan (Korea)	12.9	71	1175	5846 (274)
Arizona (USA)	20	37	255	8004 (333)

The weather and environmental conditions around outdoor exposure test sites are shown in Table 1.

2.3 Photo-degradation of plasticized polyvinyl chloride

The principle of the UV degradation mechanism in PVC involves the zip-elimination of HCL and the simultaneous formation of conjugated double-bond-containing sequences(polyenes) in the polymer chain, as shown in Eq. (1). The polyenes are highly reactive in absorbing light in the UV and visible regions, resulting in discoloration. In addition, polyenes react on oxygen yielding carbonyl products, leading to chain scission and cross-linking in the polymer.

$$\text{-CH2-CHCl-CH2-CHCL-} + hv \rightarrow \text{-CH=CH-CH=CH-} + \text{HCL} \quad (1)$$

Where -CH2-CHCl-CH2-CHCl- is the PVC polymer chain, hv the proton energy, with h and v representing Planck's constant and wavelength, respectively, -CH=CH-CH=CH- the polyene with conjugated double bond, and HCL the hydrogen chloride.

In plasticized polyvinyl chloride (PVC-P) materials, approximately 30~35% plasticized is blended with PVC resins to lower the glass transition temperature and increase the flexibility of the polymer. The plasticizer can also be degraded under UV light[3-6].

2.4 Measurement of color-difference

The surface color of unweathered and weathered samples depends on the procedure outlined in ASTM D2274. A Gretag Macbeth model color-Eye 7000A (USA) reflectometer from data color was used to measure colors in $L^*a^*b^*$ coordinates by sample at three locations. As defined by the Commission International d'Eclairage (CIE 1976 color space), L^* axis represents lightness, whereas a^* and b^* are the chromaticity coordinates. L^*, a^* and b^* color coordinates of each sample, before and after exposure to QUV testing, were calculated based on a D65 light source

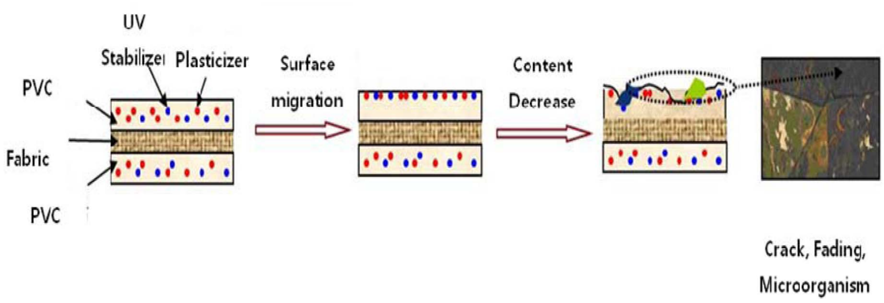


Fig. 1. Failure mechanism caused by additive surface migration.

as established by the CIE 1976[7].

The values of lightness and chromaticity coordinates before and after weathering tests were used to calculate the discoloration (ΔE^*) of the weathered sample using the following equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (2)$$

As pointed out in ASTM D2234, the magnitude, ΔE^*, gives no indication of the character of the color difference since it does not indicate the relative quantity and direction of hue, saturation, and lightness differences. The direction of the color difference is described by the magnitude and algebraic signs of the components ΔL^*, Δa^*, and Δb^*:

$$\Delta L^* = L_1^* - L_0^* \quad (3)$$

$$\Delta a^* = a_1^* - a_0^* \quad (4)$$

$$\Delta b^* = b_1^* - b_0^* \quad (5)$$

Where ΔL^*, Δa^*, and Δb^* are the differences between initial (0) and final (1) values of L^*, a^* and b^*, in the CIELAB coordinates, $+\Delta a^*$ is for red, $-\Delta a^*$ for green, $+\Delta b$ for yellow, $-\Delta b$ for blue, and $+\Delta L^*$ for light and $-\Delta L^*$ for dark.

2.5 Measurement of gloss

The gloss of unweathered and weathered samples was measured with the BYK (Gardner) Gmbh 82538 Model (Germany). The samples were measured 60 degrees An average of gloss for 3 times on each sample's surface was obtained at room temperature.

2.6 Measurement of contact angle

The contact angles of unweathered and weathered samples were measured with a camera, DropMaster DM300 Model equipped with a goniometer eyepiece. Distilled water was used as the wetting liquid. The goniometer-micro-scope eye tube was set horizontally. The specimen was rested on a bracket attached to the stage, and a small droplet of about 0.008 m*l* liquid distilled water was placed in the specimen with a micro-pipette. The mean contact angle of both left and right sides between each droplet and the sample surface was automatically stored in a computer at 2-second intervals. An average of contact angles for 5 droplets on surface of each sample was obtained at room temperature.

3. Results and Discussion

As a result of conducting the accelerated test with

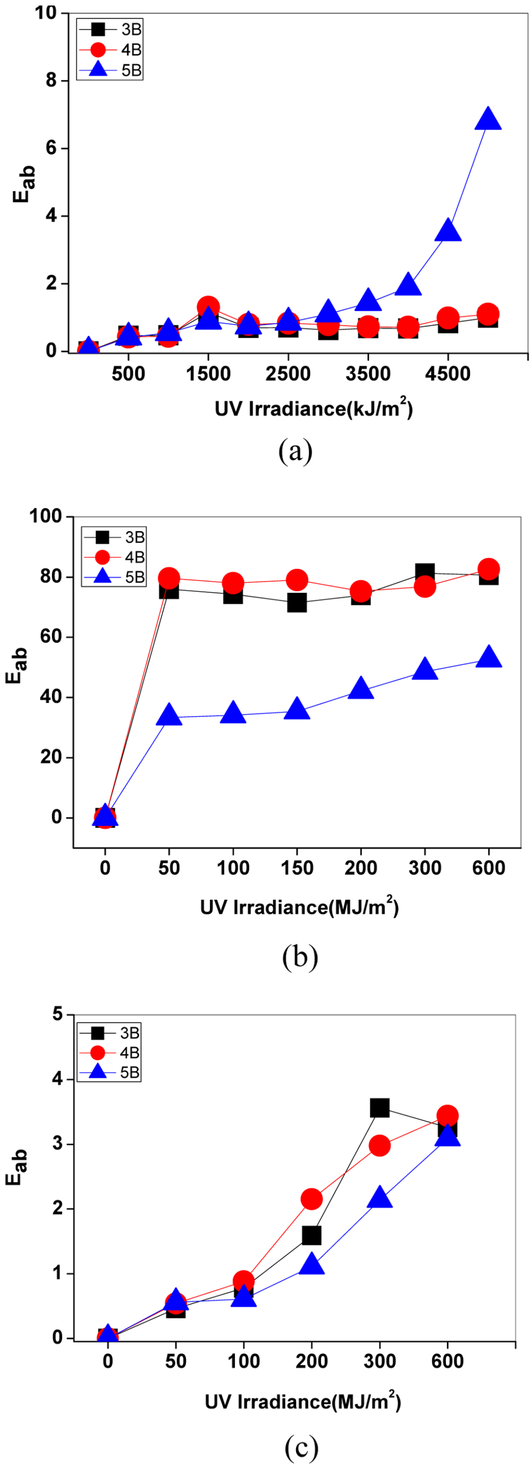


Fig. 2. Relationship between color difference and exposure test methods of (a) accelerated weathering test (b) outdoor weathering test (Seosan) (c) outdoor weathering test (Arizona).

Xenon, ΔE^* appears as 2 or less and there is no significant change in the domestic sample (3A and 4A). On the other hand, there is a fading phenomenon and the value of color difference sharply increases after 4500 kJ in the foreign sample (5B). ΔE^* appears

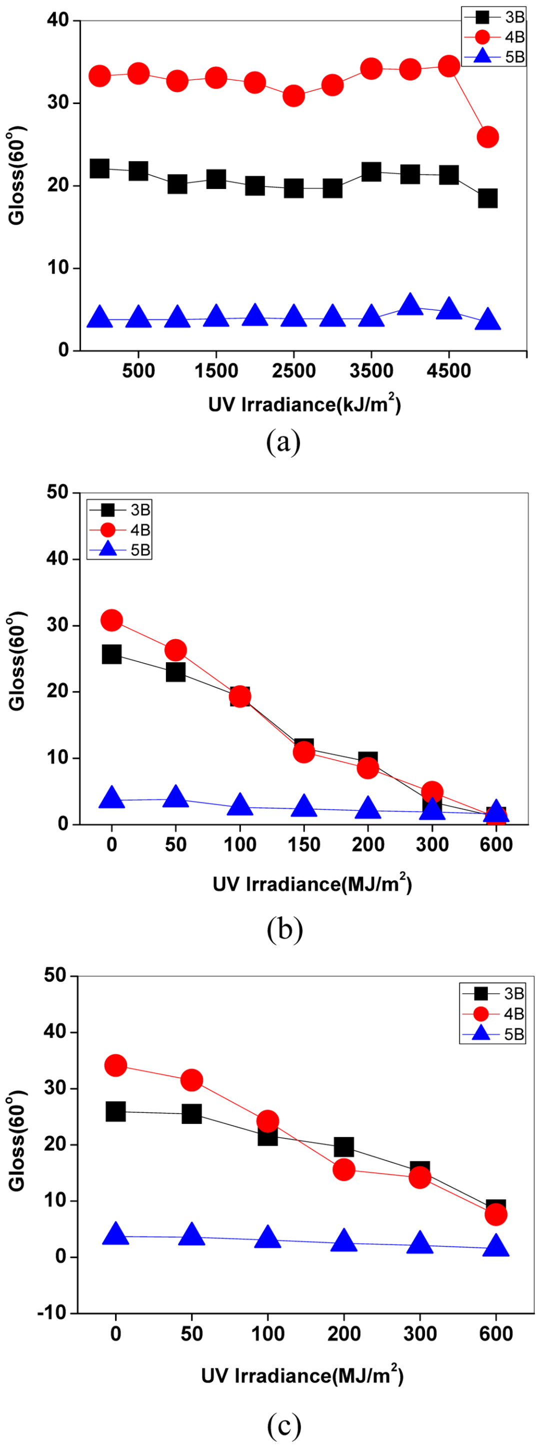


Fig. 3. Relationship between gloss and exposure test methods of (a) accelerated weathering test (b) outdoor weathering test (Seosan) (c) outdoor weathering test (Arizona).

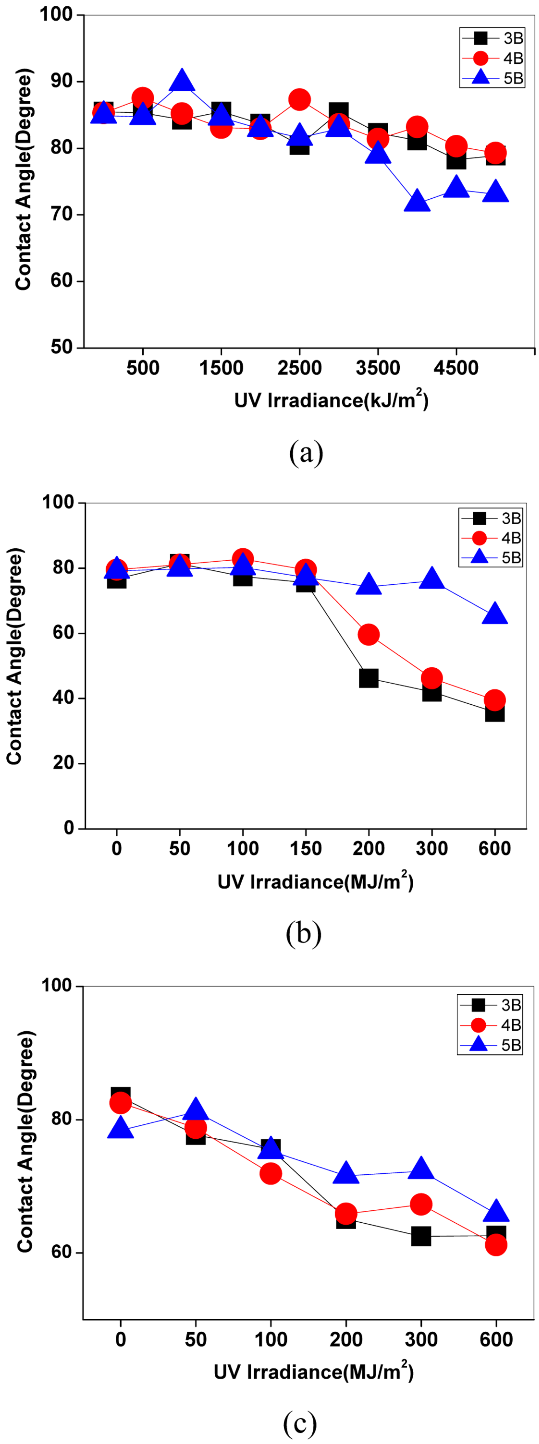


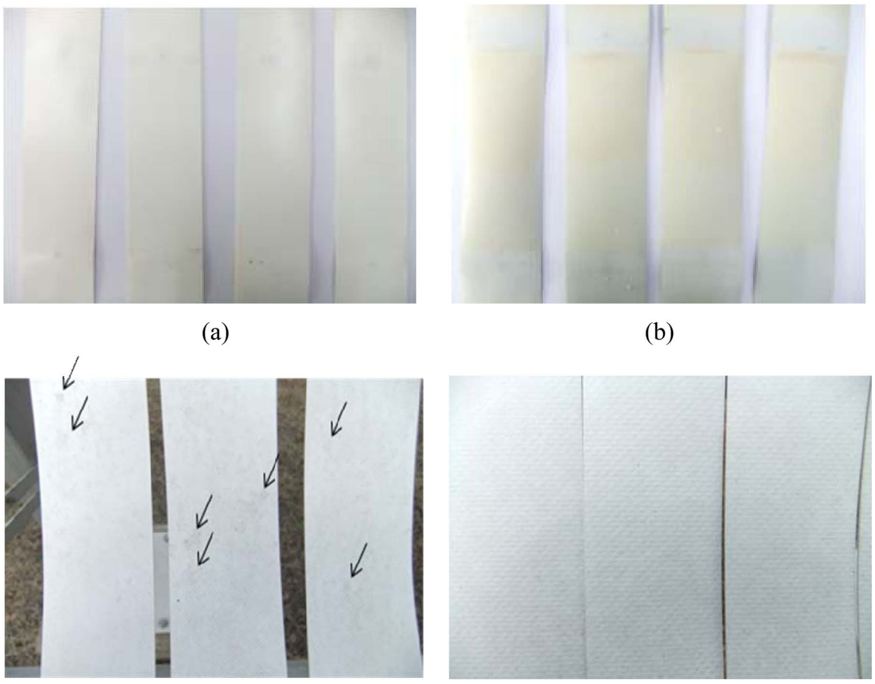
Fig. 4. Relationship between contact angle and exposure test methods of (a) accelerated weathering test (b) outdoor weathering test (Seosan) (c) outdoor weathering test (Arizona).

very high as about 80 in the outdoor exposure test conducted in Seosan, whereas ΔE^* is 4 or less in the outdoor exposure test conducted in Arizona. It is judged that there is not good stain resistance in the Seosan area, a maritime industrial area, because of humidity, rainfall, fine dust and others compared to the Arizona area. On the other hand, there is a low degree of surface contamination in the Arizona area because the Arizona area has better environmental conditions than the Seosan area as a clean area with desert climate.

The domestic sample has twice the initial gloss rate of the foreign one. This result is judged to be caused by surface coating treatments. As a result of the accelerated test, there is no significant difference in gloss compared to the initial stage. In case of the sample exposed to the Seosan area, most gloss retention rates were 0 in the domestic one, while there are few changes in gloss in the foreign one. Similarly, the domestic sample exposed to the Arizona area shows the gloss retention rate of about 10, whereas there is few changes in the gloss of the foreign one.

In case of the accelerated test with Xenon, the domestic sample is reduced by about 20%, while the foreign one is reduced by about 10% more than the domestic one. On the other hand, in case of the sample exposed to the Seosan area, the foreign sample shows better results (about 30%) than the domestic one. There is the same result in the sample exposed to the Arizona area. In other words, the foreign fabric shows better results than the domestic one.

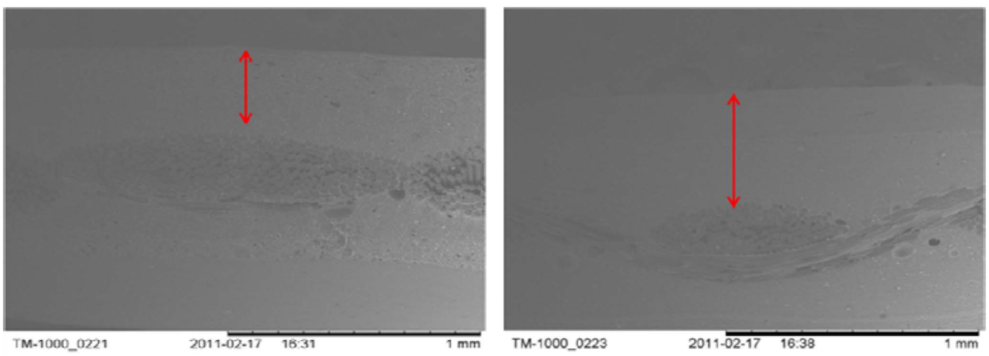
As a result of conducting the indoor accelerated test, the foreign sample shows more fading than the domestic one as shown in Fig. 5. It is identified that the foreign sample is rated as Grade 2 in the gray scale, whereas the domestic one is rated as Grade 3



(a) (b)

(c) (d)

Fig. 5. Pictures from the accelerated test of (a) Sample of H company (after 5000 kJ), (b) Sample of M company (after 5000 kJ) and the outdoor exposure test (Seosan) of (c) Sample of H company (after 600 MJ), (d) Sample of M company company (after 600 MJ).



(a) (b)

Fig. 6. The Cross-section Pictures of (a) Cross-section of the Sample of H company in Korea, (b) Cross-section of the Sample of M company in a foreign country.

or 4, very favorably. However, the degree of surface contamination is shown to be much more serious in the domestic sample than in the foreign one in case of the sample exposed to the Seosan area.

The cross-sections of the domestic and the foreign sample were photographed as shown in Fig. 6. It is shown that the foreign product has the less amount and the smaller size of fiber contained inside than the domestic one. It is identified that the foreign sample has the thicker coating layer than the domestic one.

5. Conclusions

A high degree of long-term durability is required because the outer membrane of biogas is exposed to UV rays, water and others in the outdoor environment for a long time. However, discoloration, cracking and others are caused by the causes of external failures. Therefore, non-destructive tests were conducted to identify these causes easily.

In case of the Korean and foreign sample used in this study, it was identified that the foreign fabric was sensitive to UV rays among the factors causing the failure and the Korean fabric was sensitive to other failure causes such as water, microorganisms and dust. This is judged as the cause resulting from acrylic coating on the surface. It will be necessary to improve the waterproof of the outer membrane of biogas through an analysis on failure causes by UV rays, water, humidity and other environmental factors. Moreover, this will be a guideline in determining the performance standards for the outer membrane of biogas.

Acknowledgments

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