

Non-destructive test for geomembranes by visible near-infrared spectroscopy

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ABSTRACT: Geomembrane liner sheets can be inspected for degradation by performing destructive tests where small samples are cut from the sheets and examined using strength testing. However cutting out samples compromises the most important function of liner sheets which is to prevent water leakage and ideally should not be performed. The aim of this study is to develop an on-site non-destructive testing method to detect the degradation of geomembrane liner sheets at a landfill site using visible near-infrared (VNIR) spectroscopy. The author shows that the reflectance spectrum of a geomembrane changes at particular wavelengths after the geomembrane has been soaked in chemicals, and there is a correlation between the change of reflectance spectrum and the change of strength, stretch and weight of the geomembrane. The author also explains the mechanism of degradation of the geomembrane by using a microscope and FTIR analysis. The degradation of polyvinyl chloride (PVC) occurs when the plasticizer and filling material dissolves from the main body of PVC, causing a change in the VNIR spectrum.

1 INTRODUCTION

Geomembrane liner sheets in landfills fulfill the important role of avoiding groundwater and soil pollution by preventing seepage of leachate. To maintain the performance for a long time, the liner sheets are required to withstand degradation due to physical and chemical factors such as weather, sun light, or acid and alkalis contained in the leachate. If part of the sheet deteriorates, it is difficult for it to remain waterproof and durable and so it is necessary to find where the deteriorated and damaged parts are as early as possible so they can be restored immediately.

At landfill sites there is usually a daily visual inspection to detect surface faults of liner sheets before the sheets are buried under landfill wastes but sometimes deteriorated parts can be missed. Occasionally a small part of the sheet is cut out as a sample and tensile tests are carried out on it to assess the sheet condition. Unfortunately once a piece is cut out, the sheet can no longer satisfy its required function of "water interception". That is, it is no longer completely waterproof.

In this study, the authors aim to develop a new non-destructive testing method for inspecting liner sheets for degradation quickly and conveniently on landfill sites. The method studied uses Visible Near-

infrared (VNIR) spectroscopy as a non-destructive analysis to examine reflectance spectra.

2 ACCELERATED DEGRADATION TEST

In the test, 3 kinds of geomembrane materials, which are high density polyethylene (HDPE), flexible polymer alloy (FPA) and polyvinyl chloride (PVC), were used and each was subjected to accelerated deterioration by soaking one surface of each liner sheet in concentrated sulfuric acid (H_2SO_4), 40% sodium hydroxide aqueous solution (40%NaOH) and distilled water (H_2O). Soaking periods were set to 1 day, then 1, 2, 3, 5, 7, and 10 week intervals. The basic physical characteristics of each kind of geomembrane is shown at Table 1.

Table 1. Basic characteristics of liner sheets.

Kind	Surface color	Tensile strength (N/cm ²)	Elongation rate (%)
HDPE	White (Black is Black)	3500	800
FPA	Black	2000	800
PVC	Black	1600	300

2.1 Change of durability

To examine the change in physical property of the liner sheets caused by the soaking, tensile tests that followed JISK6251 "tensile test method of the vulcanized rubber" were carried out. Retention of tensile strength (= amount of change/initial $\times 100$), retention of elongation at break (= amount of change/initial $\times 100$) and retention of weight were obtained. In the tensile test, tension rate was set to 50 mm/min.

The result of the tensile test is shown at Table 2. The initial physical characteristics of HDPE and FPA sheets remained after soaking in the chemicals. This is not surprising as HDPE and FPA are firm crystalline polymers with right molecular sequences which mean they have a strong tolerance to chemicals.

Figure 1 shows the physical characteristics of PVC sheets changed after soaking in H_2SO_4 . The PVC sheets lost flexibility, became hardened and decreased in weight. Most of the deterioration of PVC occurred in one day and there was almost no change during the remaining period. The hardening and decrease in weight was due to the breakdown of both the plasticizer and filling material. The plasticizer is added to give flexibility to the sheets and the filling material adds weight. There was also slight discoloration and the sheets changed from black, which aids weather resistance, to brown. This may be due to the carbon

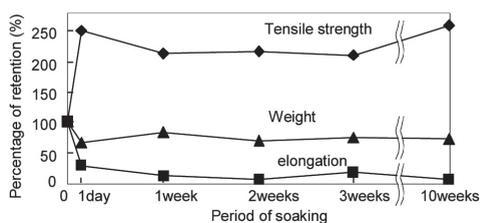


Figure 1. Retention of tensile strength, elongation, and weight of PVC after soaking in H_2SO_4 .

black leaching from the sheets with the eluviation of the plasticizer and the filling material. Carbon black is added to improve weather resistance.

2.2 Change of hydraulic conductivity

Hydraulic conductivities were measured for the PVC sheets which had significantly changed its physical characteristics after soaking in H_2SO_4 especially by 1 day after. The soaking periods in H_2SO_4 were changed to 3, 6, 12, and 24 hours.

To obtain the hydraulic conductivities the water vapor permeability test followed the calcium chloride method of JISL1099 "water vapor permeability test method of textile product". A test-piece was made as follows: 10 g calcium chloride was put into aluminum

Table 2. Result of tensile test.

Soak	Kind	Measuring item	Retention (%)						
			1 day	1 week	2 weeks	3 weeks	5 weeks	7 weeks	10 weeks
H_2O	HDPE	Tensile strength	103	106	105	104	103	102	104
		Elongation	102	104	104	103	103	102	103
		Weight	100	100	100	100	100	100	100
	FPA	Tensile strength	102	105	104	96	95	94	96
		Elongation	101	110	103	98	96	95	96
		Weight	100	100	100	100	100	100	100
	PVC	Tensile strength	99	98	103	109	101	99	102
		Elongation	98	97	88	99	93	96	89
		Weight	100	100	100	100	100	100	100
H_2SO_4	HDPE	Tensile strength	105	105	105	102	107	103	101
		Elongation	100	99	99	103	107	102	97
		Weight	100	100	100	100	100	100	101
	FPA	Tensile strength	102	103	113	100	99	98	99
		Elongation	103	101	105	95	98	92	97
		Weight	100	100	100	100	100	100	100
	PVC	Tensile strength	251	213	215	209	207	259	260
		Elongation	29	11	6	18	17	6	5
		Weight	67	83	70	74	71	69	72
40% NaOH	HDPE	Tensile strength	99	97	108	97	96	98	96
		Elongation	98	103	101	99	101	101	97
		Weight	100	100	100	100	100	100	100
	FPA	Tensile strength	102	106	105	89	87	90	92
		Elongation	99	100	103	93	94	92	94
		Weight	100	100	100	100	100	100	101
	PVC	Tensile strength	106	109	103	112	104	101	106
		Elongation	97	93	92	93	103	97	98
		Weight	100	100	100	100	100	100	100

cup of 70 mm inner diameter, and the PVC sheet which had been soaked was put over the cup to act as a lid. The gap between the sheet and the brim of the cup was then sealed with wax. The water vapor transmissivity was estimated on the basis that any change in the weight was due to the amount of water vapor that permeates the sheet. Equation (1) calculates the hydraulic conductivity from the water-vapor transmissivity.

$$k = t \times P_A/S \times (R_2 - R_1) \quad (1)$$

Where, k [cm/sec] is hydraulic conductivity of the sheet, t [cm] is thickness of the sheet, P_A [gf/cm²/h] is water vapor transmissivity, S [gf/cm²] is saturated vapor quantity at the temperature in the test, R_1 [%] is humidity in the cup, and R_2 [%] is humidity of outside of the cup.

The calculated hydraulic conductivities are shown in Figure 2. The hydraulic conductivity of the PVC sheet which was soaked in H₂SO₄ was about 1×10^{-11} cm/sec, and this was a little higher than the initial value. However, this degradation was not considered to be a large problem for water interception performance because the hydraulic conductivities after soaking satisfied 3×10^{-9} cm/sec, the standard value necessary for liner sheets.

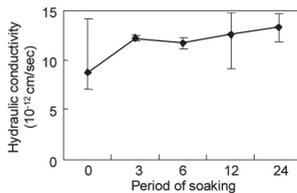


Figure 2. Hydraulic conductivity of PVC soaked in H₂SO₄.

2.3 Degradation mechanism

The mechanism of the accelerated degradation process for the PVC sheet can be clarified here.

Initially surface and cross section samples of PVC sheets were soaked in H₂SO₄ for 3, 6, 12 or 24 hours then viewed under an optical microscope. Photographs of the surface and the cross section pieces are shown in Figure 3 and Figure 4, respectively. In the photographs of the surface we can see that the minute ruggedness at the surface gradually disappears and becomes smooth during the soaking period. The photographs of the cross section show that the whitening occurs from the surface (upper side in Figure

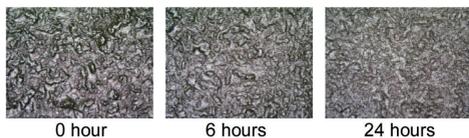


Figure 3. Surface of PVC soaked in H₂SO₄ observed with an optical microscope.

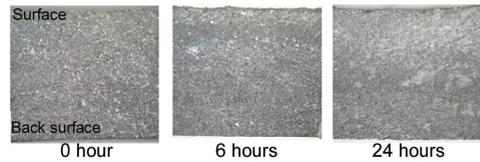


Figure 4. Cross section of PVC soaked in H₂SO₄ observed with an optical microscope.

4) to the back surface (lower side in Figure 4). This could be caused by the desorption of the carbon black colorant or because the amount of white substances seen scattered in the cross section of the initial sheet decreased during the soaking period. The result of SEM-EDX analysis showed the main component of the white substance was calcium carbonate which is added as a filling material. From the above results, we confirmed that soaking a PVC sheet in H₂SO₄ causes the gradual whitening of the surface of the sheet due to the eluviation of calcium carbonate.

The composition change of the liner sheet was examined using FT-IR. After they had been soaking for 3, 6, 12, or 24 hours, the PVC sheets were thinly cut at 150 μm thickness from the surface using a microtome. FT-IR spectra with a range of wavelengths 4000 to 650 cm⁻¹ were used and the surfaces of the sliced samples measured using the micro ATR method. Figure 5 shows the FT-IR spectrum of the PVC sheet and absorption peaks at certain wavelengths. These peaks correspond to the main components of the PVC sheet such as the plasticizer, filler and PVC itself. Secondary differential coefficient spectra from FT-IR spectra were used to unify the base lines of the spectra. Figure 6 shows the changes of the secondary differential coefficients of the absorption peaks. The absorption peak at 2930 cm⁻¹, which resulted from the functional group of CH₂ in PVC main body, shows the secondary differential coefficient kept almost the same value throughout the soaking period, and there was almost no change in average depth from the surface. The absorption peaks at 2960 cm⁻¹ and 1720 cm⁻¹ resulted from CH₃ and C=O functional groups respectively. These components are found in the plasticizer and their values decreased during the soaking period at the surface of the sheet. The absorption peak at 875 cm⁻¹, results from CaCO₃

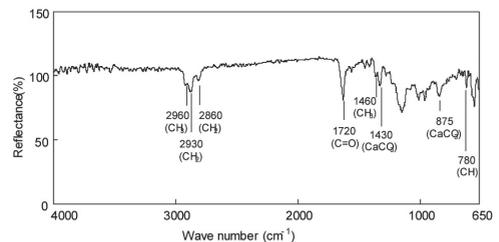


Figure 5. FT-IR spectrum of PVC before soaking.

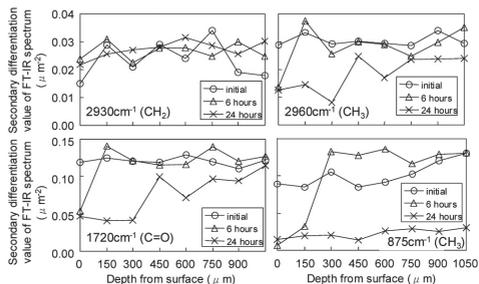


Figure 6. Change of second differential coefficient at absorption peaks resulting from PVC, plasticizer and filling material.

added as a filling material and shows a similar change to CH_3 and $\text{C}=\text{O}$. The above results confirm that soaking a PVC sheet in H_2SO_4 causes the eluviation of the plasticizer and the filling material gradually from the sheet surface.

3 APPLICABILITY OF VNIR SPECTROSCOPY

In order to develop a technique that enables a degradation inspection of geomembranes without cutting out samples we examined the applicability of VNIR spectroscopy. For this study the Field Spec Pro JR from Analytical Spectral Devices Inc was used. This device is a VNIR spectroradiometer designed for field measurements and measures VNIR reflectance spectra in the wavelength range of 350 to 2500 nm.

The reflectance spectra of HDPE and FPA sheets were measured. Absorption peaks resulting from functional group CH_2 in HDPE were observed at wavelengths 1725 and 2315 nm. Since HDPE and FPA sheets did not deteriorate in the accelerated degradation test the spectra of HDPE and FPA did not change over the soaking period.

Figure 7 shows the spectra of the PVC sheets after soaking for 3, 6, 12, and 24 hours, while Figure 8 shows the mean values of reflectance at all wavelengths of the reflectance spectrum in the each soaking period. The spectral reflectance increased at all wavelengths as the soaking period increased. A possible reason

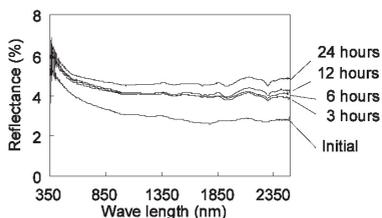


Figure 7. VNIR reflectance spectra of PVC soaked in H_2SO_4 .

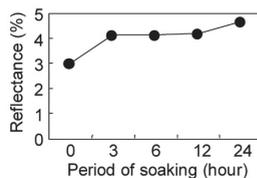


Figure 8. Change of average reflectance of all wavelength of VNIR reflectance spectrum of PVC over the soaking period.

for this is that the carbon black dissolved from the sheet surface during the time it was soaked in H_2SO_4 and the diffusion of the reflected light decreased as the rugged surface became smooth. In Figure 7, the part where the shape is concave (absorption peak) becomes gradually clear at some wavelengths. To emphasize these absorption peaks secondary differential coefficient spectrum of reflectance spectrum was calculated. The second differential coefficient spectrum of the PVC sheet that was soaked in H_2SO_4 for 24 hours is shown in Figure 9. In the second differential coefficient spectrum the concave parts of the reflectance spectrum became convex.

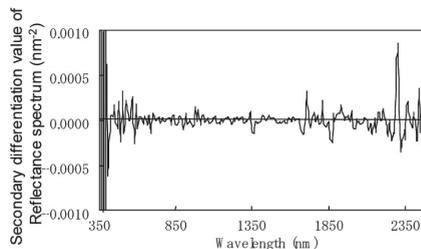


Figure 9. Second differential coefficient spectrum of PVC after soaking for 24 hours in H_2SO_4 .

Figure 10 shows changes in the second differential coefficients of the absorption peaks resulting from CH_2 , which is contained in PVC main body, and CH_3 , which is contained only in plasticizer. The absorption peaks of CH_2 at wavelengths 938, 1053, 1415, 1725, 1765, and 2315 nm, become sharper with longer soaking periods in H_2SO_4 . This appears to be because the absorption peak of the CH_2 functional group that originally existed in PVC main body has been shown more clearly by increase of the reflectivity

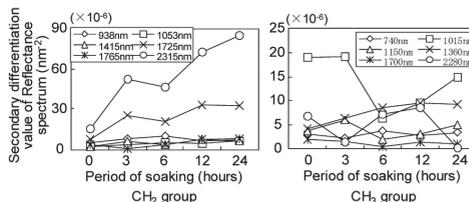


Figure 10. Change of second differential coefficient at absorption peak resulting from CH_2 and CH_3 groups.

of PVC sheet surface rather than because the quantity of the CH_2 functional group has changed. The absorption peaks of the CH_3 functional group occur at wavelengths of 740, 1015, 1150, 1360, 1700 and 2280 nm and FT-IR analysis shows the second differential coefficients at each absorption peak decreased at the sheet surface during the soaking period. The VNIR reflectance spectra are almost fixed regardless of the soaking period and this is probably caused by any increase in reflectivity of the PVC sheet surface being offset by a decrease as the plasticizer leached from the sheet surface.

Based on the above results we suggest that VNIR spectroscopy can be used to detect degradation of PVC sheets. Firstly to estimate the degree of the whitening of a PVC sheet based on the increase of reflectivity of the sheet and secondly to estimate the degree of the eluviation of plasticizer added to PVC sheets based on the change of sharpness of the absorption peaks resulting from CH_2 and CH_3 functional groups. Most importantly we consider that the degree of the eluviation of plasticizer can be an important index for indicating the degradation of PVC sheets because the amount of plasticizer is strongly related to the physical characteristics of PVC sheets.

4 CONCLUSIONS

In this study geomembrane liner sheets of HDPE, FPA and PVC underwent accelerated deterioration using chemicals then the changes in the durability and water interception (waterproofing) ability of the sheets were examined. The degradation mechanism was also explained and the applicability of VNIR spectroscopy as a non-destructive testing method for assessing the degradation state of the liner sheets was investigated. Because plasticizers are strongly linked to the physical characteristics of PVC, the measurement of any change of sharpness of absorption peaks related to the CH_2 and CH_3 functional groups can be used as an important indicator of the degradation state of PVC liners. Because the absorption peaks related to HDPE are observed in the VNIR spectra of HDPE liner sheets, if a deterioration of HDPE occurred, it would be possible to observe the change of the absorption peaks.

