ANALYSIS OF ENVIRONMENTAL STRESS CRACK RESISTANCE OF HDPE GEOMEMBRANES BY PREDICTION TOOL APPLICATION

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ABSTRACT

In this study, key properties of polyethylene resin and HDPE GM were tested for comparing their stress crack behaviors. Stress cracking time was differed from each type of resins and products. The failure times of ESCR test were too long compared to SP-NCTL's. The SP-NCTL results of RWOA was failed earlier than RWA's, GM1's and GM2's. But there was no difference between each sample of the results of ESCR test within short term testing duration. The ESCR test was influenced by stress relaxation during the test. The SP-NCTL test is reasonable for verifying stress cracking behavior and construction quality control. According to this study, ESCR test is not appropriate for determining the stress crack behavior, but SP-NCTL test is better test method for predicting the stress crack behaviors of HDPE GM.

Keywords: Single point notched constant tensile load (SP-NCTL), environment stress crack resistance (ESCR), resin chip without additives (RWOA), stress cracking behavior

INTRODUCTION

To prevent the stress cracking of HDPE geomembranes for landfill construction, various additives are mixed with the polyethylene resins, and the stress cracking resistance of the material is improved by the additives. Typical tests to check the stress cracking resistance are ESCR method and SP-NCTL method, which sometimes show rather different results and take much different time till they derive the results. In the previous study, it was suggested that ESCR method is not appropriate for the evaluation of stress cracking resistance because it showed the difference from the actual cracking in the field (Hsuan 1998, Hsuan 1995). In USA, its performance evaluation method and criteria were changed after the experimental verification Lord et al. 1995). The purpose of this study is to propose the level-up of product criteria in consideration of the safety rate applied to the field construction by

evaluating the performance level of the products manufactured in Korea and used in the field. Before studying the products used in the field, it is necessary to examine the appropriateness of ESCR method, which is actually being used to check the stress cracking of the product in the field, by collecting the resins used as raw material for Korean products and measuring their characteristic values related with stress cracking to compare and analyze them.

FACTURES INFLUENCING STRESS CRACKING RESISTANCE

Polyethylene Resin Parameters

a) Density: Of all the resin parameters, polyethylene resin density has the single biggest influence on stress-cracking resistance. The result of SP-NCTL test is quite sensitive to relatively small changes in resin density. For example, a 0.939g/cm3 resin has yield stress of 19.2 MPa requiring ~760g load in the NCTL test (60 mil sheet, 30% of the yield stress). A 0.935 g/cm3 resin has a yield stress of 17.1 MPa requiring ~670g load in the NCTL test. The higher density resin is subjected to 13% more load than the lower density resin. SP-NCTL is an index test that is based on resin properties. If the SP-NCTL is used as a performance test, then the resins are subjected to different test conditions.

b) Molecular Weight: Higher HLMI values (meaning lower molecular weight) give reduced stress crack resistance.

c) Oxidation Level: Oxidation is a form of degradation of HDPE. Oxidation can be measured

by the formation and growth of carbonyl bands in infrared spectra. If a sample was oxidized it will display significantly worse SP-NCTL values.

d) Additive Level: The addition of an antioxidant system to the samples improves the retention of stress crack resistance.

Extrusion Process Parameters

a) Thickness: Thinner samples give higher SP-NCTL values. It can be speculated that thinner samples cool more rapidly resulting in less crystallinity.

b) Orientation from the extrusion process: In comparing compression-molded samples (with no orientation) to sheet samples prepared on lab lines that are highly oriented, the lab-line sample give lower SP-NCTL values.

c) Carbon Black: The presence of carbon black tends to decrease SP-NCTL results.

Active Environmental Condition

The role of the active environmental in the ESC phenomenon is observed to be the acceleration of sample failure. This is believed to occur by absorption of the active environment by the polymer and subsequent 'lubrication' of polymer chains, resulting in earlier failure under Slow Crack Growth conditions. This effect is supported by the reduction of the activation energy seen in various papers. Molecules of detergent must diffuse inside the polymer and reduce the cohesion between fibrils formed at yield regions. The detergent seems to stabilize the crazing process, avoiding, in a sense, regular packing of the fibrils into a dense structure. When crack growth is attempted in the presence of the ESC agent, Igepal CO-630, the material within the crazes is less coherent with voids and large broken fiber ends visible. This is in contrast to the same experiments conducted in air where neither voids nor large broken fibrils were seen. Consequently, diffusion of detergent molecules into the polymer due to stress might result in increased chain mobility and therefore in a reduction of the activation energy (plasticizing effect) of the deformation process. The lubricating effect of the Igepal does not increase greatly as the concentration goes from 0.1 to ~20% as compared to the large effect between 0% and 0.1% concentration. In general, a lubricating film acts in this way. A film of lubricant of critical thickness can make a tremendous change in the coefficient of friction compared to a dry surface, whereas an additional increase in thickness of the lubricating film has a relatively smaller effect. After the asperities on a surface are covered by a lubricant, additional lubricant has a smaller effect on the coefficient of friction. The specifications propose a 100% concentration as the most severe condition for producing cracks. However, research shows that a 50% solution is more effective. The increase in time to failure from 50 to 100% concentration is probably related to the observation that the higher concentration produces a greater blunting of the notch. Instead of forming a craze as is the case at lower concentrations, a shear zone forms at the root of the notch (Fig. 1).

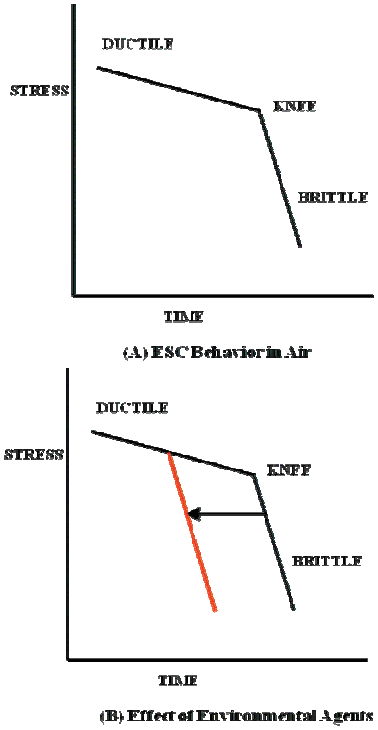


Fig. 1 Effect of environmental agents

EXPERIMENTAL

Preparation of Specimens

To compare ESCR method and SP-NCTL method that have been proposed as the evaluation method for stress cracking behavior and performance of HDPE water-blocking material which is used for the construction of waste landfill in Korea, two kinds of chip were manufactured: one that the additives were mixed with the raw material resin(RWA) used for Korean products and one without additives(RWOA). The chips were compressed with the compression moulder for 30 min at the pressure of 500psi and the temperature of 170℃ to have the form of sheet and then cooled at the rate of (15 ± 2) ℃/min.

The specimen without the additives (RWOA) did not contain the carbon black and the antioxidant

but the specimen with the additives (RWA) contained both of them. Additionally, GM1 and GM2 regional HDPE GM products were prepared for comparing with resin samples.

Table 1 Characteristics of raw material resin

Test Samples	Thickness	Density
	ASTM D 5199	ASTM D 1505
Resin without additives (RWOA)	1.85 mm	0.931 g/cm^3
Resin with additives (RWA)	2.51 mm	0.945 g/cm^3
Geomembrane 1 (GM 1)	2.01 mm	0.946 g/cm^3
Geomembrane 2 (GM 2)	2.05 mm	0.946 g/cm^3

Test Items and Equipments

The stress cracking characteristics of two specimens were evaluated to analyze the mechanism necessary for the selection of appropriate evaluation method and the set up of criteria. For this, the content of carbon black, the melt flow index and the oxidative induction time were checked along with ESCR test and NCTL test. To find out the contents of carbon black, the polyethylene was carbonized and the weight of residual ashes was measured with the thermo gravimetric analysis (TGA) using the principle in ASTM D 1603. For the melt flow index, the load of 2.16kg was applied for 10 min, as regulated in ASTM D 1238, and the weight of extruded polyethylene resin was measured. The oxidative induction time was obtained by measuring the oxidation time of each specimen under the standard compressive pressure in ASTM D 3895.

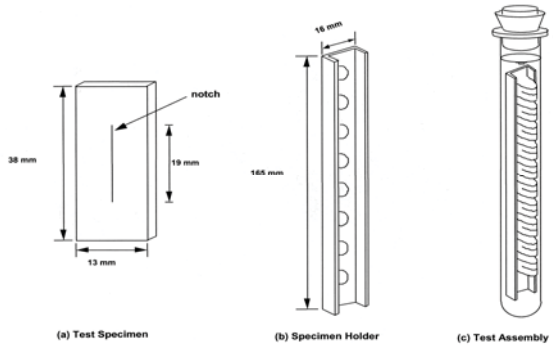


Fig. 2 ESCR Test specimen and equipment

For ESCR test, it is necessary that the specimen folded and fixed with a jig is immersed in the Igepal CO-630 solution in a test tube and sealed to be treated for a long time at 50℃, as shown in Fig. 2. So, the thermostat chamber which is regulated in ASTM D 1693 was used. In SP-NCTL test, the specimen is immersed in the test solution of 50℃ for a long time while receiving a certain amount of load and its cracking time is measured. For this, the NCTL-dedicated equipment regulated in ASTM D 5397 was used, as shown in Fig. 3. For ESCR test, the test condition in the standard of the waste landfill installment was applied; for SP-NCTL test, 30% of the yield stress strength was applied.

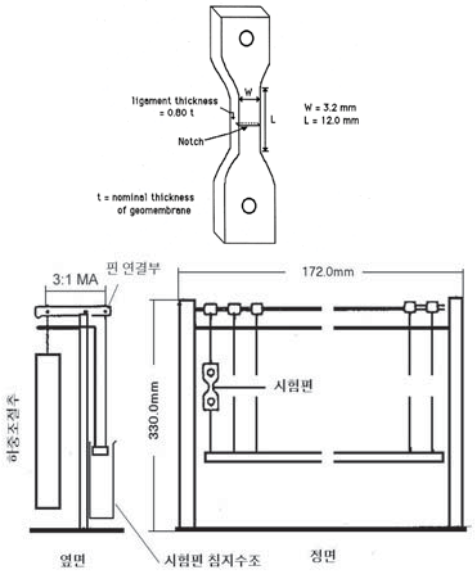


Fig. 3 NCTL test specimen and equipment

RESULTS and DISCUSSION

Carbon Black (CB) Contents Test

The carbon black is used in the resin to prevent the embrittlement of the material by the ultraviolet rays while being exposed outside for a long time when the HDPE GE product is covered on the field. In the product containing a certain amount of carbon black, the embrittlement of the material by UV rays can be prevented. And the result value of SP-NCTL gets less due to the carbon black. RWOA specimen did not contain the carbon black at all, but the carbon black contents of RWA, GM1 and GM2 specimen was 1.8%, 2.1% and 1.7%, respectively. According to some reports, if the carbon black mixed to increase the resistance against UV goes over a certain amount, the stress cracking of the material decreases. So, it is important to adjust its mixing amount for the management of product quality. In case of specimens used for this test, it seems very probable for the specimen with carbon black to have the stress cracking.

Melt Flow Index (MI) Test

MI value which is determined to some degree at the production stage of the resin has a relation with the molecular weight. As the MI value gets higher, the stress cracking tends to increase. RWOA specimen had MI value of 0.063 g/10min but the MI value of RWA, GM1 and GM2 specimen were 0.241 g/10min, 0.224 g/10min and 0.191 g/10min, respectively. RWA, GM1 and GM2 specimens showed a relatively higher value in comparison with RWOA specimen. The increase seems to be caused by the addition of carbon black, and so the possibility of the stress cracking can be said to get relatively higher.

Oxidative Induction Time (OIT) Test

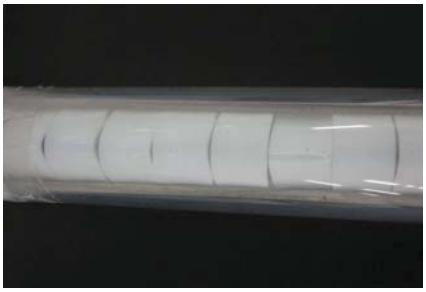
It is known that the material with UV stabilizer and antioxidant suffers less embrittlement by the oxidation than the materials without them when exposed to the external environment for a long time. But, once the antioxidant is totally dissipated, the oxidation occurs rapidly to degrade the physical properties. Oxidative induction time of RWA, GM1 and GM2 specimen were measured as 120min, 150min and 193min, respectively but in case of RWOA, it was about 5min. When comparing with RWOA and RWA specimens, we can see that the antioxidant prevents the embrittlement of the material for a considerable time and thus the stress cracking, too.

Environmental Stress Crack Resistance (ESCR) Test

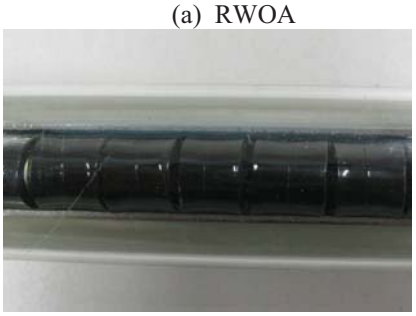
After giving a notch on its center, the specimen was folded by 180° and fastened with a holder. Then, it was immersed in 10% Igepal CO-630 solution. The container with the specimen was put into the thermostat of 50℃ for 1,500 hours and then the cracking of the specimen was observed.
Both of RWOA, RWA, GM1 and GM2 specimens did not show the stress cracking due to the long aging. As mentioned in the previous study, it seems that the stress relaxation of specimen has happened in the process of ESCR test. RWOA specimens were failed after 1,800 hours, see Fig. 4 (a).

Notched Constant Tensile Load (NCTL) Test

To find out the load equivalent to 30% of the yield tensile stress, a tensile test was carried out according to ASTM D 638. In accordance with the SP-NCTL test method in the appendix of ASTM D 5397, small-sized test specimens were collected for the tensile test and were immersed in the 10% Igepal CO-630 surfactant solution of the test equipment while the calculated stress is applied to each specimen according to the measured yield tensile strength. For RWOA specimen, the stress cracking was generated after around 150 hours; for RWA, GM1 and GM2 specimens, cracking was



(a) RWOA



(b) RWA

Fig. 4 ESCR Specimens after 1,800 hours

generated after around 150 hours; for RWA, GM1 and GM2 specimens, did not happen even after 200 hours. With this, it could be said that the additive gave an influence on the stress cracking.

Table 3 Test results in characteristic items of each specimen

Test Properties	Units	Test Method	Test Samples			
			RWOA	RWA	GM1	GM2
Carbon Black Contents	%	ASTM D 1603	0	1.8	2.1	1.7
Melt Flow Index	g/10min	ASTM D 1238	0.063	0.241	0.224	0.191
Oxidative Induction Time	min	ASTM D 3895	5	120	150	193
ESCR	hrs	ASTM D 1693	over 1,500	over 1,500	over 1,500	over 1,500
SP-NCTL	hrs	ASTM D 5397	151	over 200	over 200	over 200

CONCLUSIONS

Related Factors and Comparative Analysis of Test Results

In the basic condition of the specimen, RWOA has the relatively lower density and melting index than RWA, GM1 and GM2, therefore the stress cracking is hard to happen. But, in NCTL test, the stress cracking happened faster in RWOA than in RWA, GM1 and GM2. It is because, even though the high density and melting index of RWA, GM1 and GM2 specimen may increase the occurrence possibility of stress cracking, the antioxidant added with the carbon black increased the oxidation resistance and thus the stress cracking resistance.
As a factor in the extruding process, RWOA specimen was compressed and moulded about 0.5mm thinner than RWA specimen. Thus, RWOA specimen showed higher result in NCTL and ESCR tests than expected. It seems because RWOA specimen which was thinner than RWA specimen got cooled faster in the process and its crystallinity degree became lower.

Comparison of ESCR and SP-NCTL Test Results

As mentioned in the previous study, the appropriate test method is required to predict the stress cracking phenomenon. In ESCR test for RWOA, RWA, GM1 and GM2 specimens, the stress cracking which was confirmed in NCTL test process showed no difference within the standard 1,500 hours in the reinforcement regulation of Waste Management Act. With this, we could confirm the problem that, in ESCR test, the stress of the specimen became relaxed, making the test period longer, and the stress cracking phenomenon that can generate in the real field could not be quantified because the cracking time of the specimen was not known correctly. On the other hand, in SP-NCTL test, the time necessary for quantifying the results and confirming the quality for the characteristics of specimens was relatively short. Therefore, it seemed more appropriate method to evaluate the quality of the products which are used in the actual field.

Study on Revision of SP-NCTL Standard

This study has some limit in understanding the stress cracking because it compared and analyzed just two resin specimens that are used as the raw material of HDPE GM. According to the results of this study, we can propose the revision of specification and test method of stress cracking resistance to SP-NCTL method instead of ESCR method in KPS M 6000 standard for the stable quality management of waste landfill.

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