by B.-H. Choi, M. Cassiday, and P. Jimenez

IMPROVEMENT OF THE TEST PROCEDURE OF AN ENVIRONMENTAL STRESS CRACKING RESISTANCE TEST OF HIGH-DENSITY POLYETHYLENE

The environmental stress cracking resistance (ESCR) testing is aligned to the polyolefin's business that uses this test. This test is necessary to understand the resistance of polyolefins against common environmental stress cracking (ESC) agents such as soapy water, silicon oil, and insect repellent. The main need of improving the ESCR test is to get improved data that are used to avoid unexpected long-term failures of polyolefin products. For semicrystalline polymers such as polyethylene (PE), it is known that ESCR is less severe than in amorphous polymers. However, exposing PE to stress crack agents results in unexpected brittle fracture.[1,2] Crazes are accompanied by this fracture, and this cannot be determined by conventional mechanical properties of the polymer but rather by the ESCR tests. But recently, the practical relationship between ESCR and some physical properties, such as the strain hardening modulus,[3] creep deceleration factor,[4] tie chain concentration, and permeability,[5] is proposed for the qualitative evaluation of ESCR properties of polymers. There are some known major environmental factors governing ESCR such as the exposure time of the stress cracking agent, exposure temperature, concentration of the stress cracking agent, and level of strain on or in the polymer.[6]

The ESCR test is very frequently requested in polyolefin research efforts; however, the reported data vary greatly with external elements such as location, process, equipment, operators, etc.[7] Currently, many chemical companies in North America widely accept the test defined as ASTM D1693[8] and ASTM F2136[9] as a standard ESCR test for high-density polyethylene (HDPE) and medium density polyethylene resins. However, this test method was developed for wire and cable applications, and so the environmental effects such as chemical agent and temperature were set for this very specific case. This test method was developed by Bell Laboratory and was originally designed for testing ESCR performance of PE cable insulation. Variations in stiffness (density) between polymers impose different stress levels at the notch region. It is not clear whether the differences in ESC failure times observed between samples are a true reflection of their different resistances to stress cracking or simply a reflection of the higher level of stiffness of the specimens.

Because ESC is not significant for the early stage of product use, detection of deficiencies by the product manufacturer is difficult. The main defects or weaknesses of ESCR testing are variability and inaccuracy of ESCR test results. Environmental stress cracking resistance test results have the additional variability that can be introduced by the individual tester, test environment, and uniformity of specimen even though all the test conditions are the same. Improving the ESCR test procedure by reducing variability while following ASTM standards is very important for quality control purposes.

Clearly, it is very important to understand the root cause of the big variation in ESCR values. In this article, the root causes of the variability of ESCR test data focused on ASTM D1693 are investigated using statistical or Six Sigma methodology. Based on investigated root causes, some critical steps of the ESCR test procedure are proposed to modify the test. Finally, a newly designed notcher is introduced to help eliminate the variability of notch fabrication.

CURRENT ESCR TEST PROCEDURE

In Fig. 1, a process map of the current ESCR test based on ASTM D1693 is shown. Some steps are defined by the standard, but some critical aspects of the test, such as specimen thickness measurement and observation methodology, are not clearly defined.

There are some defects in the current ESCR test that are responsible for large variations in the ESCR data. According to the appendix of ASTM D1693, two major variables that are classified as "very significant" are specimen thickness and notch depth. There are very strict guidelines as to the allowable size of specimen thickness and notch depth, as is shown in Table 1. Specifically, according to field observation of this test procedure, there are a couple of critical problems that should be studied: (1) notch depth variation and shape (nonuniform notch depth along a notch envelope) and (2) modification of ESC observation methodology. According to ASTM D1693, the concentration of Igepal of type A and type B specimen during the ESCR test is 10% and that of type C is 100%. It is known that the relationship between Igepal concentration and ESCR is not linear. According to the report on ESC propagation by Qian et al.,[7] the aggressiveness of ESC is not proportional to the concentration of Igepal. The severest ESC propagation is observed around 30–50% of Igepal instead of 100%. The reason for this nonlinear relationship between aggressiveness and concentration of Igepal may be explained by the permeability of solution into the polymer. Water may be a carrier of Igepal, so if water content is too small, the aggressiveness due to Igepal is decreased.

In Fig. 2, a run chart of ESCR data of two different HDPE materials recorded for a year is shown. By investigating these data, it can be noticed that there are very large variations of reported data (lack of reproducibility) and there is a trend of high peak (approximately from January to February) and a stabilized report period (approximately May to September). Large variations can be explained by defects as described, but the trend is not easy to explain.

B.-H. Choi (bhchoi@korea.ac.kr) is an assistant professor in the Department of Mechanical Engineering, Korea University, Seoul, Korea. M. Cassiday is the Olefin Elsatomers team leader and P. Jimenez is the senior research leader with The Dow Chemical Company, Freeport, TX.

doi: 10.1111/j.1747-1567.2008.00366.x

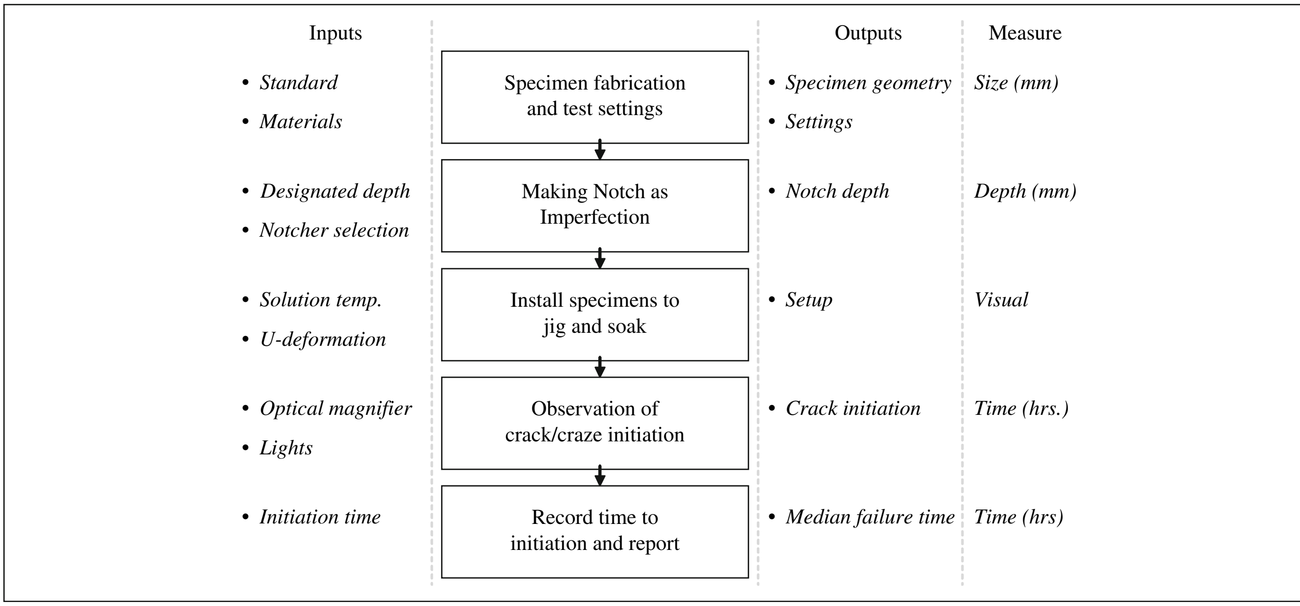

Fig. 1: Process map of current ESCR test

ROOT CAUSE ANALYSIS OF VARIABILITY OF ESCR TEST

Root causes of such a large variability of the ESCR test results were investigated by brainstorming sessions and related literature searches (including Ritchie,[10] Wright,[11] Lustiger,[12] and Schiers[13]). There are four possible root causes: (1) operators; (2) materials and specimen preparation; (3) inherent methodology; and (4) machine and equipment. Some major root causes from the fish-bone diagram (Fig. 3) can be validated as follows:

Improper Notching Device Design

Due to improper notching device design, the geometry of the notch that is cut into the specimen is not uniform. As ASTM D1693 depicts, the notch depth uniformity affects the qualitative ESCR validation. The current notcher as depicted in D1693 makes a notch shape that cannot be uniform unless the cutting point is exactly calibrated. This point will be described in detail later in this article.

Methodology of Definition of ESC Initiation

Unlike the notched constant ligament stress (NCLS) test (ASTM F2136[9]), according to ASTM D1693, ESCR test results should be reported based on the time of crack detection as observed by the naked eye. However, it is very difficult to define the time of crack initiation using this observation method, and the reported time may vary extensively. Unfortunately, there is no detailed description of the observation methodology in the current ASTM procedure. As a result, each operator uses his own way of observing crack initiation. The procedure to determine crack initiation needs to be clearly stated in the standard, yielding more uniform ESCR data.

Interval of Replacing Razor Blade

The razor blade blunts whenever operators nick the specimen to make a notch. A blunt blade itself can be a direct root cause of improper notch depth, but more importantly, blunt razor blades create variations in notch geometry and unexpected residual stresses around the notch. According to current ASTM D1693, the same razor blade can be used until 100

Table 1—Sample preparation and test temperature

CONDITION		SPECIMEN THICKNESS mm	SPECIMEN THICKNESS in	NOTCH DEPTH mm	NOTCH DEPTH in	BATH TEMPERATURE, °C
Type A	Minimum	3.00	0.120	0.50	0.020	50
	Maximum	3.30	0.130	0.65	0.025	
Type B	Minimum	1.84	0.0725	0.30	0.012	50
	Maximum	1.97	0.0775	0.40	0.015	
Type C	Minimum	1.84	0.0725	0.30	0.012	100
	Maximum	1.97	0.0775	0.40	0.015	

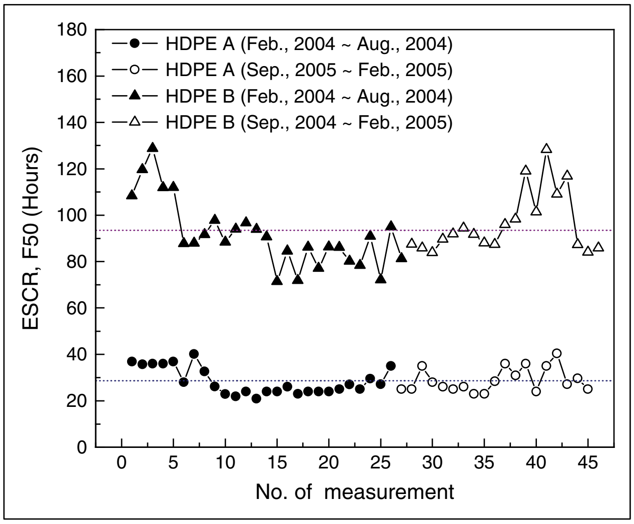

Fig. 2: Run chart of ESCR measurement variability

nicks have been made with proper examinations; however, it is not easy to examine the razor blade after installing the blade to the notching device.

Unclear Definition of Test Procedure

The test procedure should be clearly described to obtain reproducible results. However, ASTM D1693 omits describing some important steps that affect the ESCR data, such as specimen thickness measurement, notch depth validation, and observation interval. In this study, an improved process map will be introduced for giving more reproducible ESCR data. Some basic features such as making the Igepal solution, ergonomic issues during the ESCR test, and a new process due to the introduction of a new notching device will also be covered.

Specimen thickness is a critical factor when determining ESCR data due to the stress and strain formed at the surface. If there is no defect inside the specimen, a microcrack should initiate at the surface. The maximum surface strain (at the outer surface of the specimen from Fig. 4) without considering notch is calculated by[11]:

$$\varepsilon_{\max} = \frac{t}{r} \cong \left(\frac{t}{w-t}\right), \tag{1}$$

where r is the radius of the curved specimen, w is the width of the specimen holder, and t is the thickness of the specimen (Fig. 4).

If the specimen thickness increases, the maximum strain increases as an order of magnitude. Of course, stress is also increasing due to high strain, but there is stress relaxation during the ESCR test.

Control of the thickness of the specimen is important not only for quality control of the specimen but also for having reliable ESCR data; however, there is no step for measuring the thickness in the current test procedure. In addition, it is well known that thickness variations of compression molded plaques are high due to polymer flow during the molding process resulting in thermal expansion and shrinkage. So, after fabricating a compression molding plaque for ESCR specimens, the thickness of the samples should be measured for validating the variation of the sample thickness.

VARIATION OF NOTCH GEOMETRY WITH CURRENT NOTCHER

As mentioned earlier, due to inherent design defects of the current notching device, ESCR data can vary greatly. Some of the most common problems of the current notching device are as follows:

Notch Depth Not Uniform Due to Irregular Impact Force by Operator

Depending upon the operator, the impact force is not uniform, so the notch depth will vary. If impact load is too low, notch will be shallow. The notch depth will be deep if load is too high. Moreover, there is an ergonomic problem with the current notching device.

Difficulty of Calibration of Impact Point

Calibration of the impact point of the razor blade is not easy due to the geometry of the notching device. The current fodder-chopper-type notching device will generate a notch

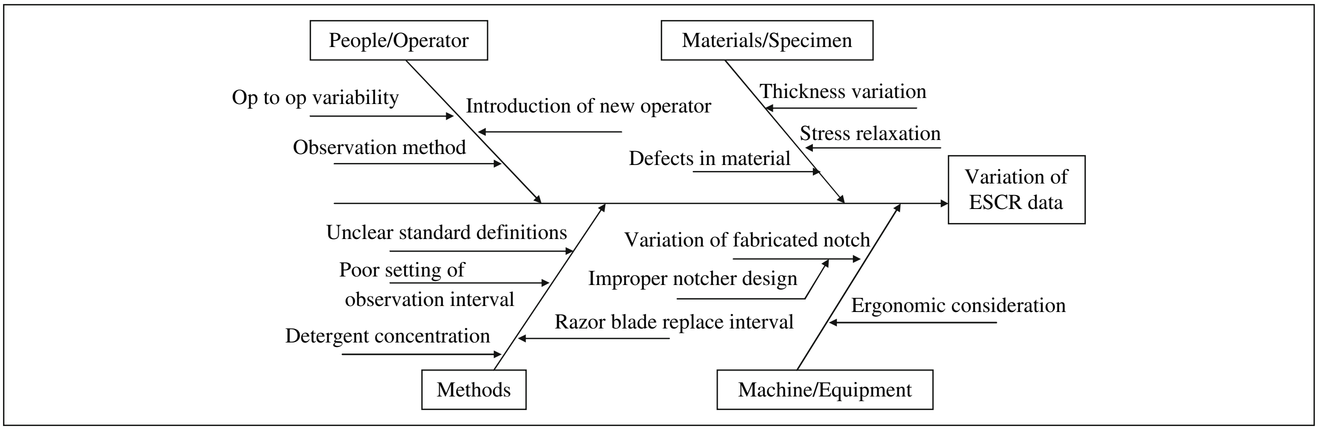

Fig. 3: Fish-bone diagram for the root cause analysis of ESCR test

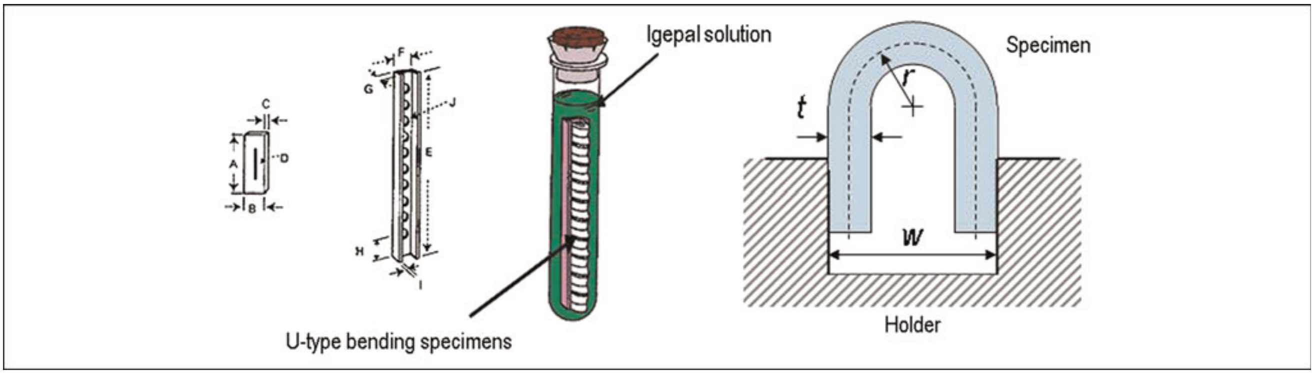

Fig. 4: Strip bent test based on ASTM D1693

with uniform depth along the notch when the impact point is exactly parallel to the hinge of the lever. If this calibration is not good, the notch will be inclined along the fabricated notch.

No Support of Specimen When Specimen Is Installed to Notching Device

Support of specimen is important to have a straight notch. However, there is no support of the specimen when the specimen is placed in the notching device, so the specimen is free to pivot on the razor blade. When the impactor hits the specimen surface, an angled notch is fabricated on the rotated specimen.

To examine notch uniformity fabricated by the current notching device, the notch geometry was checked by a scanning electron microscope (SEM). A new razor blade was installed, and specimens that were collected from the 1st, 10th, 20th, 40th, 70th, and 100th nick were measured for notch depth variation. One more sample (sampling after the 20th nick) was added to observe notch shape. Test specimens were cut at the center of the notch line, and the specimen cross-sections were cryo-polished using a diamond knife on a Leica UCT microtome (Leica, Wetzlar, Germany). A Hitachi H-4100 FEG SEM (Hitachi, Tokyo, Japan) was used under secondary electron imaging at 5 kV accelerating voltage.

In Fig. 5, an example of the observed notch mouth by cross-section of specimen is shown. In the case of Fig. 5a, the shape of the notch mouth is relatively clean cut. But the notch mouth in Fig. 5b is apparently plastically deformed due to a blunted razor blade.

In Fig. 6, the variation of the observed notch depth is shown. The hatched area is an allowable range of notch depth as defined by ASTM D1693, but most notches are out-of-spec, and the average of data is meaningless because of the large scatter of notch depth. By t-test of notch depth variation by JMP statistics, Z long-term sigma value is only 0.73.

Another major defect of the current notching machine is that the notch profile, that is, notch depth along a notch, is not uniform. The notch depth profile is obtained by SEM observation of notched specimens prepared by freeze fracture using liquid nitrogen. In Fig. 7, the measured and projected notch profile based on the observed notch depth is shown. As expected, the notch is severely inclined, the difference between the maximum and the minimum notch depth is

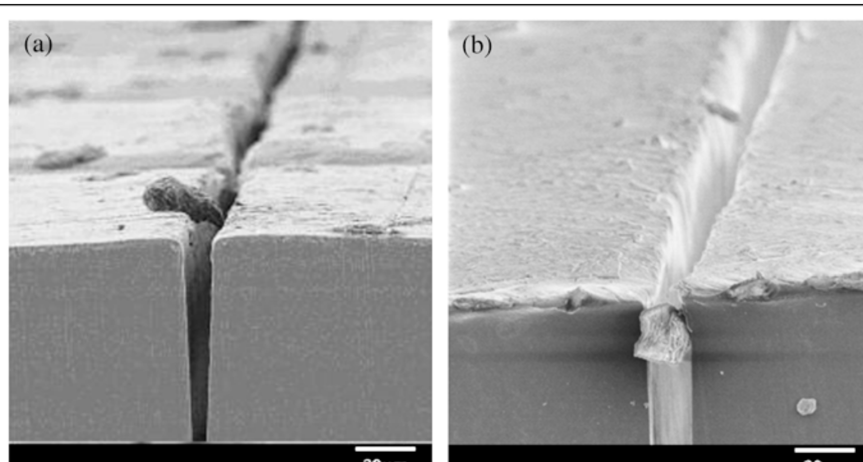

Photo of notch mouth (10th nicks)   Photo of notch mouth (100th nicks)

Fig. 5: SEM photos of notch mouth after the 10th and 100th nicks

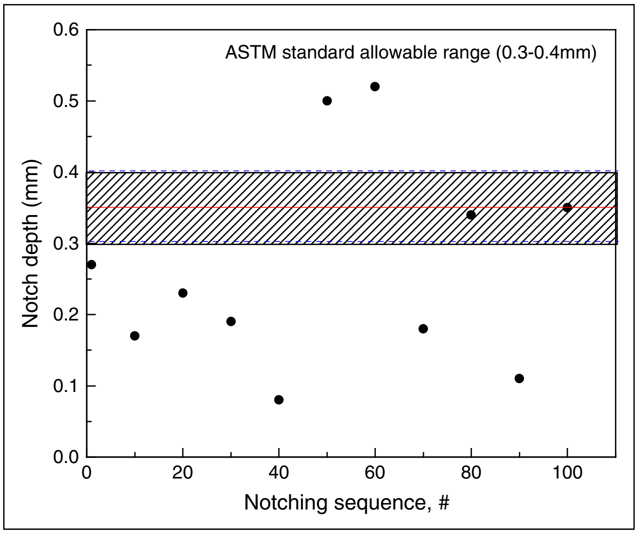

Fig. 6: Variation of notch depth at the center of the fabricated notch with current notcher

around 0.13 mm for full notch length. Notch misalignment is not a big factor that affects ESCR data, but a misaligned angle of notch is observed up to approximately 5.5°.

Statistically, it is very clear that the notch depth should be improved, but there is a limitation for improvement in using the current notching machine. So, a new ESCR notching machine is necessary to improve notch geometry and fabricate a reliable notch.

DESIGN OF NEW NOTCHING DEVICE

There are many things to consider when designing a new notching device. The key requirements should include the following:

Enhance Notch Reproducibility

Uniform notch depth along the notch is important to have reproducible maximum stress and strain formation at the surface. A uniform notch depth will generate ESCR data that are less variable.

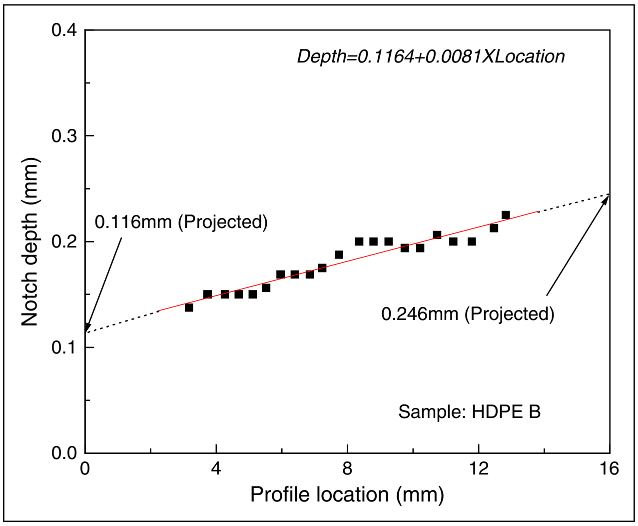

Fig. 7: Variation of notch profile with current notcher

Uniform Notching Force to Create a Reproducible Notch

Notching force is closely related with notch depth, so reducing variation of notching force will give less variability of the ESCR data.

Multiple Notching Slots

Multiple notching slots are needed to enhance the speed of specimen preparation. In addition, notching slots should be designed to improve the efficiency of the notching process.

Easy Control of Notch Depth by Changing Shims

There are two locations for conveniently inserting shims to control notch depth, and all test conditions (type A, type B, and type C) can be fabricated with one machine after very simple calibration.

Introducing Pneumatic Notching System

The current notcher, a fodder-chopper type, is operated manually and transmits a high level of impact back to the operators whenever they fabricate ESCR specimens. The new notching machine will be operated by a pneumatic system to relieve the tester's effort and resolve ergonomic issues.

Work Safely with Double Action Button System

Notching is executed with very sharp razor blade, and notching load is quite high. So, it is important to have a safer option to help avoid any accident during the notching process.

To satisfy all conditions described above, a new notching machine was designed as a guillotine-type notching machine with pneumatic operation. A guillotine-type notching machine can fabricate a notch with uniform depth along the notch, and pneumatic operation enhances notch reproducibility and relieves the ergonomic issues the operators were exposed to with the former notching method. In Fig. 8, the schematic diagram of the newly designed ESCR notcher is shown.

Calibration of the new ESCR notching machines is done primarily by control shims inserted in the reciprocating top part and the stationary specimen slots. If notch depth is too deep, shims should be inserted in the reciprocating top part. On the contrary, if notch depth is too shallow, shims should be located on the bottom of stationary specimen slots. Here are calibration procedures:

(1) Measure notch depth of specimen without any shims.
(2) Define the necessary thickness of shims by matching average shift of notch depth based on the middle point of the allowable depth as defined by ASTM standard: shims adjustments: shims at top part (for shallower notch) and specimen slots (for deeper notch).
(3) Confirm notch depth and check sigma level.
(4) All calibration should be applied to both stationary slots separately (if the surface of bottom part is not uniform).

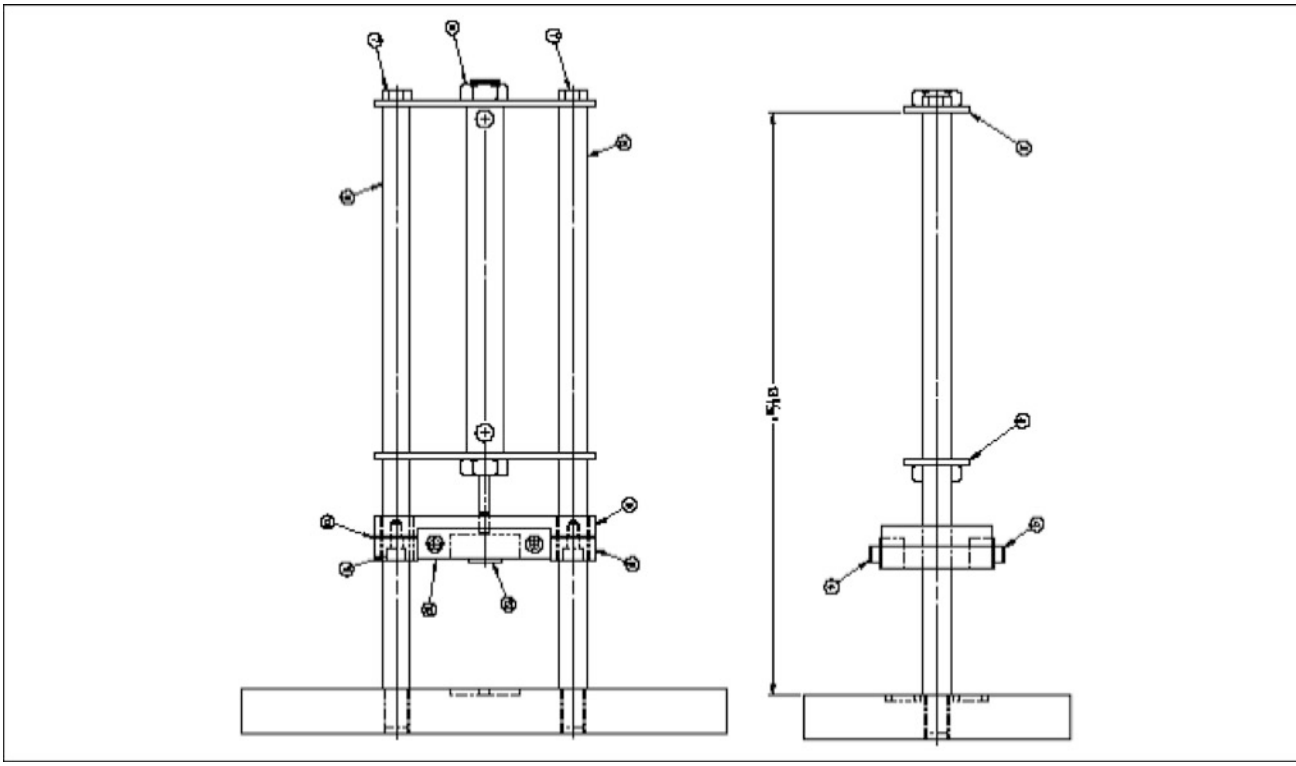

Fig. 8: Schematic diagram of the newly designed ESCR notcher

In Fig. 9, the installed new ESCR notching machine is shown. By several preliminary tests of notching and examination of notch by optical observation, pneumatic pressure, and pressing time are determined. A pneumatic pressure of 0.172 MPa was determined to be an optimum pressure, and the pressing time of 2 s is adequate for that pressure.

VALIDATION OF IMPROVED CAPABILITY OF NEW ESCR NOTCHER

For actual measurement of notch depth, out-of-spec specimens by specimen thickness were discarded after measuring the thickness of the specimens. Shims with proper thickness were selected based on the calibration process, and the notch depth was measured by SEM. Razor blades were changed after the 10th nicking for eliminating blunting issue. Five specimens were used for each slot, so 10 specimens with notches were fabricated for this confirmation.

In Fig. 10, notch depth variation at the center of the notch for the tested specimen is shown. Comparing Fig. 5, the reproducibility of the notch is much improved, and all specimens except one satisfy the allowable notch depth range defined by ASTM D1693. Clearly, the reproducibility with the new notcher is greatly improved. Based on a t-test of notch depth variation by the JMP statistical analysis tool from SAS Institute (Cary, NC, USA), Z long-term sigma value for notch depth fabricated by the new notching device improved from 0.73 to 2.78. Later, it was found that the one specimen that did not satisfy the range was fabricated with the wrong selection of shims.

Fig. 9: Installed new ESCR notching machine

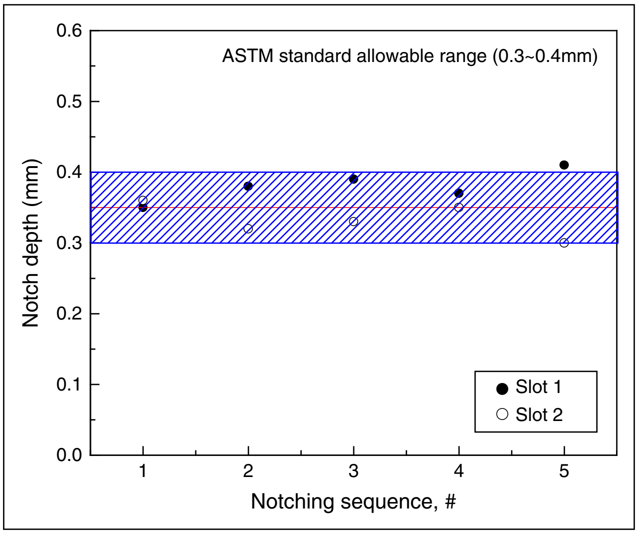

Fig. 10: Variation of notch depth at the center of the fabricated notch with new notcher

In Fig. 11, the notch profile measured along a notch is shown. The notch profile that was fabricated by the new notching device is constructed via SEM observation. Unlike Fig. 7, a very uniform notch profile along a notch length is observed. The difference between maximum and minimum notch depth observed in Fig. 11 improved from 0.13 to 0.034 mm for full notch length.

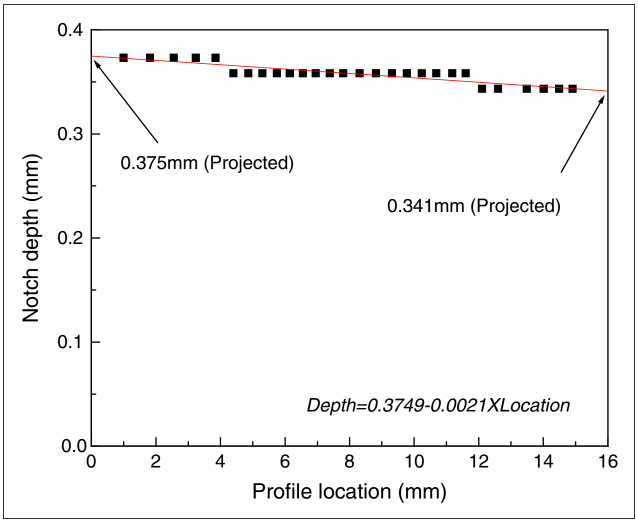

Fig. 11: Variation of notch profile with new notcher

OBSERVATION OF FRACTURE SURFACE OF ESC

For the determination of the time of ESC initiation, the investigation of the cracking mechanism of ESC is important. The study on the fracture surface reveals the origin of the crack initiation and the direction of the crack propagation if the crack growth is of a semi-brittle nature. Of course, the fracture mechanism changes such that brittle, semi-brittle, and ductile can also be identified by the investigation of the fracture surface.

In Fig. 12, the fracture surface of an HDPE sample by freeze fracture is shown. It is clear to identify the boundary of the environmental stress (ES) crack and the freeze-fracture surface.

As shown in Fig. 13a, it is interesting that the ES crack is initiated from the notch root and propagates in a radial direction. The loading condition of the ESCR test is bending, so the highest bending stress is at the surface. However, due to the surface notch that is fabricated parallel with the longitudinal direction of the specimen, the stress concentration is happening at the notch root (Lustiger et al.[14]). So, ES crack initiated from the notch root and propagated slowly in a radial direction around the notch until the crack reaches to the surface. Lustiger[12] and Lustiger et al.[14] also described very similar behavior of subsurface crack initiation under ESCR test, but they did not observe the actual fracture surface. The shape of ES crack is gradually changed into a half-elliptical shape due to the variation of crack driving forces, which are related to the applied bending stress and geometry. After the crack reaches to the surface, crack growth is accelerated with a large amount of fibrillation as shown in Fig. 13b. In field observations, there are often complaints with regard to the difficulty in identifying the appearance of the initial crack. These complaints are understandable based on the location of the crack initiation, that is, ES crack initiates not on the surface but from the notch root.

IMPROVEMENT OF ESCR TEST PROCEDURE

Some key improvements of the ESCR test procedure are proposed based on the observations above, but all modifications are restricted by ASTM D1693. Here are some key modifications of the ESCR test procedure:

Measurement of Thickness of Test Specimen

The thickness variation of the test specimen fabricated by compression molding should be addressed. It is well known that thickness of a compression molded plaque is not uniform, but there is no step for measuring thickness of the specimen to be notched for this test in the current test procedure. The

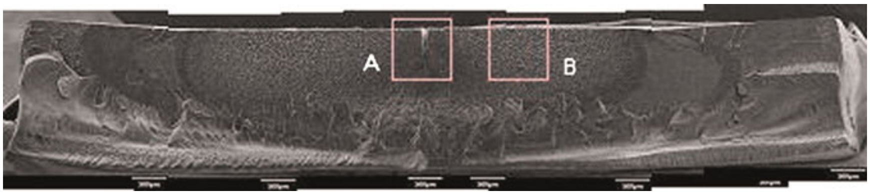

Fig. 12: Fracture surface of ESC

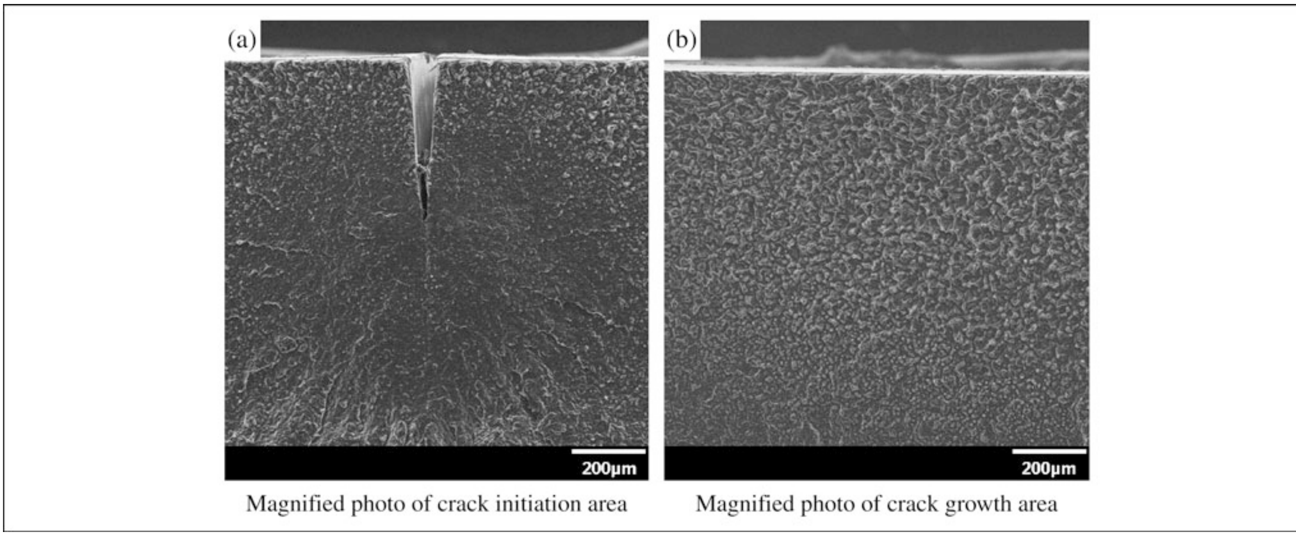

Fig. 13: Magnified photos of fracture initiation and propagation of ESC. (a) Magnified photo of crack initiation area and (b) magnified photo of crack growth area

specimen thickness should be measured, and out-of-spec specimens according to ASTM D1693 should be discarded.

Shim Selection Based on Specimen Thickness

Using the proper shim for the newly developed notcher is very important. Even though there is another plan to eliminate the sensitivity of specimen thickness for this new notching device, shim selection should be added to the test procedure until the modification is finished.

Razor Blade Replacement Timing

The razor blade is very critical to maintaining uniform notch depth and shape. So, Scheirs[13] suggested that the razor blade should be replaced every 10–20 times; otherwise, unreliable results will be obtained. However, considering the hardness of test materials, the proper timing of notching should be determined by inspection of the razor blade.

Observation of Crack Initiation

Observation of crack initiation is mainly an operator decision process, but the observation method should be standardized. All observations of crack initiation should be executed by using a proper magnifier with a light source to identify small variation of whitening due to the crack initiation from the notch tip inside of the specimen.

In Fig. 14, a new process map for the ESCR test based on the proposed modifications is shown.

CONCLUSION

The ESCR test is one of the most essential mechanical properties of a blow molding product, but it is not easy to have very consistent ESCR data due to many reasons such as location, process, equipment, operators, etc. In this report, the root cause of the variability of the ESCR test is investigated, and

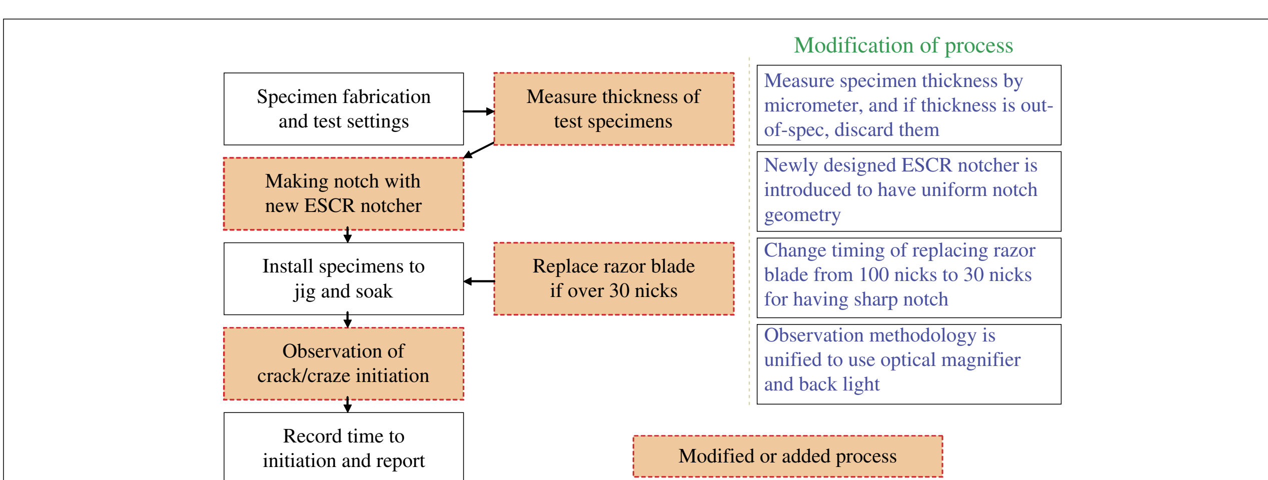

Fig. 14: Modified process map of ESCR test

the solution for improving the variability is proposed. Here are the key suggestions for improving ESCR variability:

(1) New guillotine-type ESCR notching device is introduced for reducing the variability of notch depth and notch geometry. This new device is designed to generate reproducible notches as well as reduce ergonomic issues for operators.

(2) Implementation of the new ESCR notcher. As a result of using the new notching device, the sigma value of the notch depth is improved dramatically from 0.73 to 2.78, and the notch geometry is also improved, producing a less inclined notch.

(3) The test procedure is improved and modified based on published literature; however, the new procedure still follows the existing ASTM standard. The major modifications recommended to ASTM D1693 are the following: (1) razor blade replacement time is reduced from 100 to 30 nicks; (2) observation methodology of ESC initiation is standardized; and (3) specimen thickness measurement process is added to the ASTM standard.

ACKNOWLEDGMENTS

The authors wish to thank Babli Kapur, Colin Li Pi Shan, and Willem deGroot for their valuable discussion on this work, and the authors also thank Hollis Hall, Ruben Sanchez, and Lisa Kohlenberg for help during the experimental and validation steps.

References

1. Ward, A.L., Lu, X., Huang, Y., and Brown, N., "The Mechanism of Slow Crack Growth in Polyethylene by an Environmental Stress Cracking Agent," *Polymer* **32**:2172–2178 (1991).

2. Fleissner, M., "Experience with a Full Creep Test in Determining the Stress Crack Performance of Polyethylenes," *Polymer Engineering and Science* **38**:330–340 (1998).

3. Kurelec, L., Teeuwen, M., Schoffeleers, H., and Deblieck, R., "Strain Hardening Modulus as a Measure of Environmental Stress Crack Resistance of High Density Polyethylene," *Polymer* **46**:6369–6379 (2005).

4. Rose, L.J., Channell, A.D., Frye, C.L., and Capaccio, G., "Slow Crack Growth in Polyethylene: a Novel Predictive Model Based on the Creep of Craze Fibrils," *Journal of Applied Polymer Science* **54**:2119–2124 (1994).

5. Choi, B.-H., Weinhold, J., Reuschle, D., and Kapur, M., "Investigation of Fracture Mechanism of HDPE Subjected to Environmental Stress Cracking," *Proceedings of ANTEC 2007*, Cincinnati, OH (2007).

6. Scholten, G.L., Pisters, J., and Venema, B., "A More Reliable Detergent for Constant Load Experiments on Polyethylene," *Polymer Testing* **8**:385–405 (1989).

7. Qian, R., Lu, X., and Brown, N., "The Effect of Concentration of an Environmental Stress Cracking Agent on Slow Crack Growth in Polyethylene," *Polymer* **34**:4727–4731 (1993).

8. ASTM D1693–01. *Standard for Test Method for Environmental Stress-cracking of Ethylene Plastics*, ASTM International, West Conshohocken, PA (2007).

9. ASTMF2136–01. *Standard Test Method for Notched, Constant Ligament-stress (NCLS) Test to Determine Slow-crack-growth Resistance of HDPE Resins or HDPE Corrugated Pipe*, ASTM International, West Conshohocken, PA (2001).

10. Ritchie, P.D., *Physics of Plastics*, D. Van Nostrand Company Ltd., Princeton, NJ (1965).

11. Wright, D., *Environmental Stress Cracking of Plastics*, Rapra Technology Ltd., Shawbury, UK (1996).

12. Lustiger, A., "Environmental Stress Cracking: the Phenomenon and Its Utility," Brostow, W., and Corneliussen, D., (eds), *Failure of Plastics*, Hanser, Munich, Germany, pp. 305–329 (1986).

13. Scheirs, J., *Compositional and Failure Analysis of Polymers*, John Wiley and Sons Ltd, Chichester, UK, pp. 546–586 (2000).

14. Lustiger, A., Markham, R.L., and Epstein, M.M., "Environmental Stress Crack Growth in Medium-Density Polyethylene Pipe," *Journal of Applied Polymer Science* **26**:1049–1056 (1981). ■