3. Test Methods for Evaluation of ESCR of Plastics

A common laboratory request for ESC-prone polymers is to check ESCR performance for quality control, competitive product evaluations, and research and development work. There is a variety of test methods available for assessing the ESCR of thermoplastics and they can be divided into two groups: tests at constant strain and tests at constant load (stress). It should be remembered, that any test that involves the application of a constant strain is less severe than the apparently equivalent test involving the application of a constant load because the strain is not maintained constant during the test.[2] The stress in the sample induced by constant strain will decay with time due to stress relaxation, which makes the ESC conditions less severe.

3.1. Tests at Constant Strain

Constant strain methods are most commonly used because they are cheap to perform and the investment in equipment is small. The main limitation of using constant strain tests with plastics is that the stress will decay with time due to stress relaxation. It is important for the accuracy of the ESC tests to select the most appropriate strain applied on the sample, because high strain will result in cracking too quick to observe, and lower strain will cause long-term experiments. Wang et. al.[45] carried out investigations to determine the appropriate values of strain to be exerted in the ESC test of different kinds of plastics. They found that for the brittle plastics the strain should be selected in the elastic region of the stress-strain curve, while for toughened plastics the plastic region is the best selection.

3.1.1 Three-Point Bending Test

This normally involves the application of a mid-point deflection δ which generates a maximum surface strain. There are two major variants of the test which are shown in Figure 3.1.[2, 46] Samples are placed in the test device and the desired strain is attained by adjusting the screw. Deformed samples (strips) are immersed in the stress cracking agent. After a predetermined test period the samples are removed, rinsed with distilled water and allowed to dry at room temperature for 24 hours. Following this, the samples are inspected for crazing and their tensile properties are investigated.

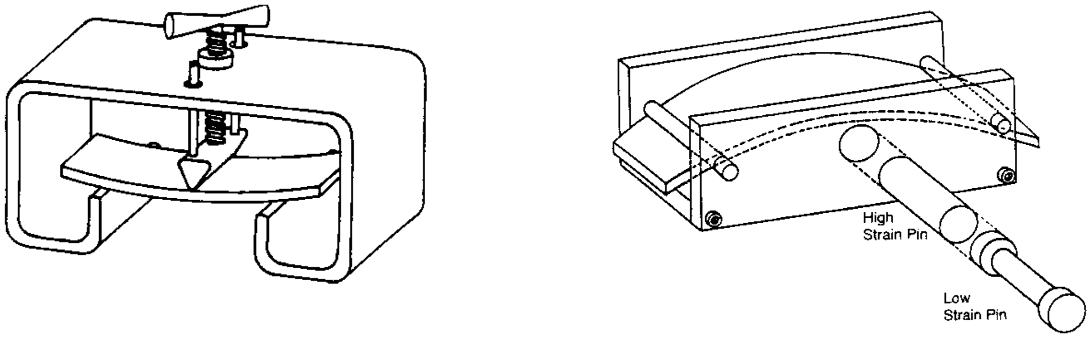

Figure 3.1 Three-point bending apparatus for testing the ESCR under constant strain.

3.1.2 Bell Telephone Test (BTT)

This test was developed by Bell Laboratories in the USA for testing the ESCR performance of polyethylene cable insulation.[1, 2, 47] The test specimens (38 x 13 x 3 mm) are notched and bent (at about 180°C) with the notch pointing upwards in a metal U-shaped specimen holder (Figure 3.2).

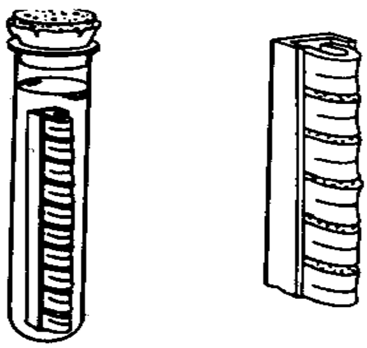

Figure 3.2 Bent-strip test for flexible materials (Bell telephone test).

The maximum surface strain is calculated by using the following equation:

$$\varepsilon_{max} = \frac{t}{w-t} \times 100 \text{, [\%]} \quad (3.1)$$

where t is the thickness of the sample and w is the width of the holder.

The holder is placed in a glass tube containing a 10 vol.-% Igepal CO-630 water solution. The tubes are sealed and placed in a water bath at 50°C. The number of samples that exhibit cracking is recorded as a function of time. Failure is determined as the appearance of any crack visible by the naked eye. Duration of the test should be at least 48 h. All samples have to pass the test. If one test specimen has failed, the test is to be considered as not passed.

BTT method has been widely adopted as the standard method. This method, however, cannot be easily automated. The occurrence of cracks or fracture in the test pieces is detected solely by visual evaluation conducted at fixed intervals. Thus, the method may give rise to an error. Saeda and Suzaka[48] proposed a method to measure the ESC at constant strain which is almost completely free from the influence of human error. This method is denoted as ORL method because the method was developed in Oita Research Laboratory, Showa Denko, Japan. The longitudinally sectioned view of the device is shown in Figure 3.3.

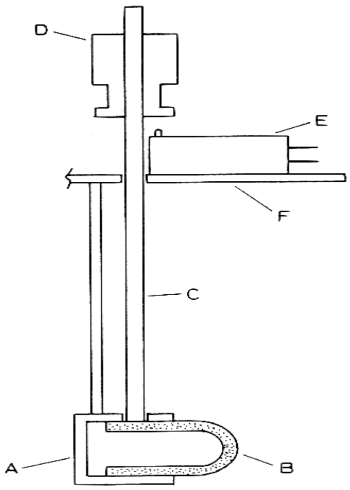

Figure 3.3 Oita Research Laboratory (ORL) ESCR test device.[48]
A – sample holder, B – bent strips, C – shaft, D – load, E – electric switch, F – supporting plate.

The sample holder is made the same size as the sample holder of ASTM-D1693 (Bell telephone test) which can hold ten bent strips in position for testing. While the BTT measures the time when a small crack appears in the specimen by visual means, the ORL method can detect the time to failure correctly by automated means (by using an electric device) without a human error.

3.2 Tests at Constant Load (Stress)

3.2.1 Constant Tensile Load Test

The test was developed by Lu and Brown[49, 50] for measuring the slow crack growth behavior of polyethylenes. The method involves a constant load test on a single edge notched specimen under plain strain conditions in air or stress cracking agent at various temperatures. Figure 3.4

shows a scheme of the device used for the test at constant load. A simple timer is used to record the failure time. The timer switches off when the specimen cracks. The rate of slow crack growth can be monitored with a microscope by measuring the crack opening displacement versus time.

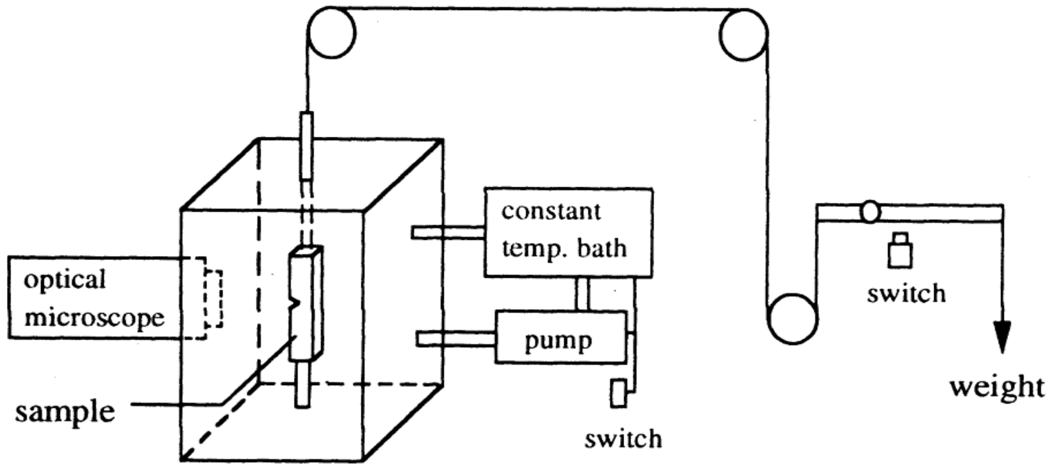

Figure 3.4 Apparatus for the test at constant load.[51]

The value of the applied stress depends on the testing temperature. The recommended value is that which produces brittle failure as fast as possible. Based on extensive investigations by Lu and Brown[24, 52, 53] on many different polyethylenes, the constant load test is usually carried out in 10 vol.-% Igepal solution at load of 4.2 MPa , and temperature of 50°C.

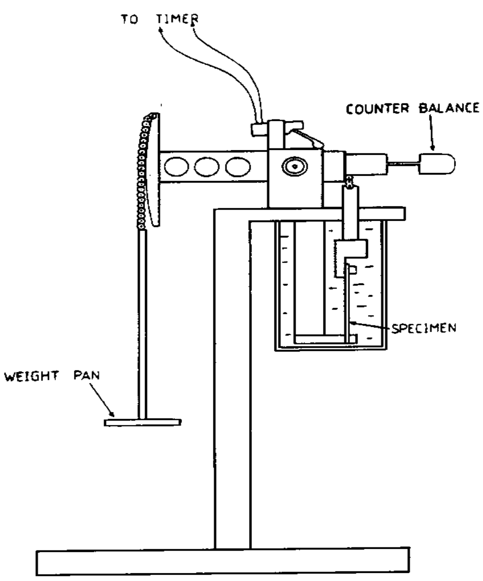

Figure 3.5 Rapra high temperature tensile creep rupture set-up.[2]

Figure 3.5 shows Rapra high temperature tensile creep rupture testing device which is quite similar to the common test at constant load. It involves application of a tensile stress and the recording of the time to rupture.

3.2.2 Monotonic Creep Test

Hough and Wright[3] developed a monotonic creep testing machine for assessing the ESC of amorphous thermoplastics. This is similar to the slow strain rate testing technique used for many years by the metal industry to assess the stress corrosion cracking and the hydrogen embrittlement.[54] However, here the strain response to a constant stressing rate is monitored. The method as shown in Figure 3.6 employs a tensile creep machine with the weight pan replaced by a blow moulded vessel. Specimen strain is monitored via a Moirè fringe extensometer which is shown in Figure 3.7.

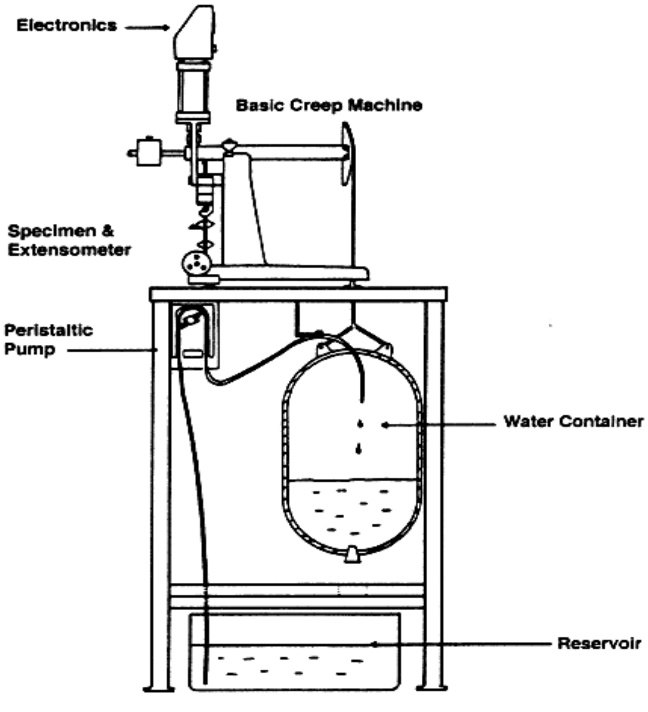

Figure 3.6 Monotonic creep testing machine.[3]

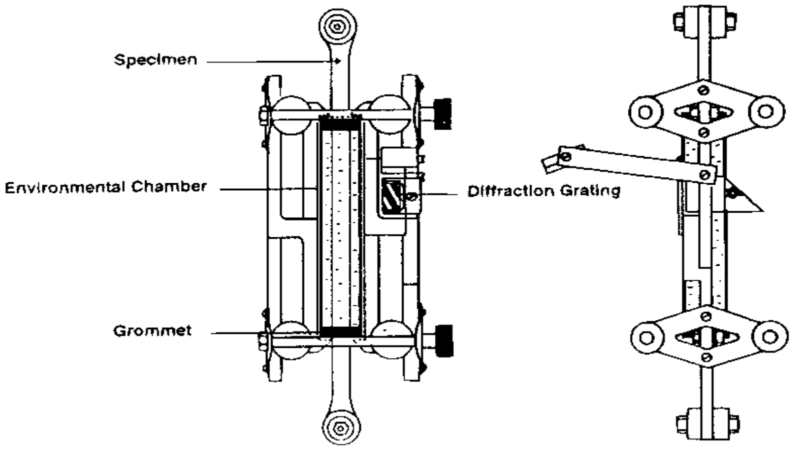

Figure 3.7 Rapra Moirè fringe extensometer with environmental chamber attached to the specimen.[3]

The monotonic creep method is capable of high resolution and discrimination. The fact that the method generates critical time, critical stress and critical strain proposes the use of the method for investigating the criterion for initiation of the ESC phenomenon.[2]

3.2.3 Test Method for Determining ESCR of Ethylene Based Plastics

BTT has been the method most commonly accepted by industry as a measure of the ESCR of ethylene based plastics. While BTT is attractive from the point of view of simplicity, it has been criticized on several counts. There are a few variables that can affect reproducibility of the test results: the curvature of the bent specimen depends on the stiffness of the polymer material; the strain is not maintained constant during the test; it is difficult to assure a sharp notch that is reproducible from specimen to specimen. Crissman[55] developed a new method for determining the ESCR of ethylene plastics under different stresses and temperatures (Figure 3.8). A strip specimen is bent around a metal cylindrical form having a specified radius of curvature. This ensures that all the specimens conform to the same geometry during the test. Typically the specimens are unnotched strips. The stress cracking agent is a 10 vol.-% Igepal solution in water. The stress-cracking behavior of different polyethylenes is investigated in the temperature range from 23 to 90°C and constant applied stress. A set of conditions was determined that can be applied to polyethylenes having widely different densities and molar masses. The optimum test conditions are as follows: a nominal specimen thickness from 1 to 1.25 mm, a bend radius of 5.5 mm, applied stress of 5 MPa, and a temperature of 75°C.

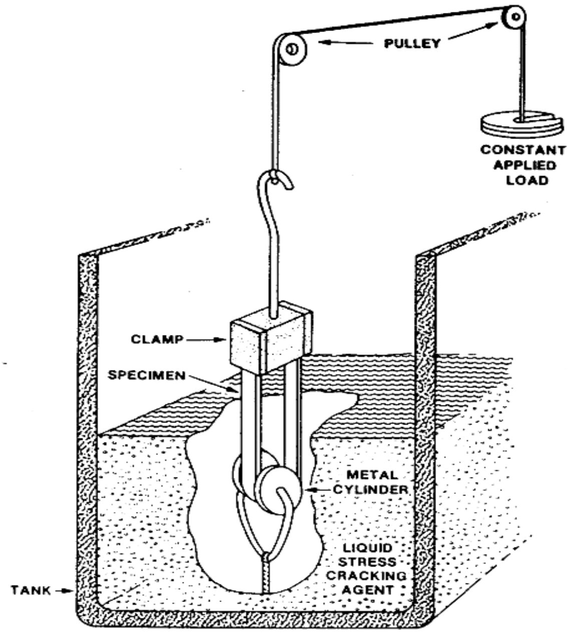

Figure 3.8 View of the device for testing ESCR of ethylene based plastics.[55]

3.3 Bottle ESCR Test

Unfortunately, the data obtained by bent strip methods do not necessarily correlate with those results obtained for bottles made from the same polymer. A bottle ESCR test has been developed for assessing the ESCR of plastic bottles. In this technique, the bottles are filled with a stress cracking solution which fills 10 vol.-% of the bottle. The capped bottles are then placed in an oven at 60°C and a stress is generated by the increased internal pressure.[1] Bottles that do not fail after 7 days are considered adequate.

It can be concluded that the constant strain methods are widely used for examination of the ESCR of plastics due to their simplicity and cheap equipment necessary for the tests. But the reproducibility of the results is not so good because of human error (failure is detected visually), the curvature of the test specimen depends on the stiffness of the polymer material and strain is not maintained constant during the test. The stress will decay with time due to stress relaxation. Tests at constant load are more accurate because an optical microscope is usually used for detecting of the notch opening and crack opening displacement. The time to complete failure is directly proportional to the time for crack initiation[15, 55] and that makes it possible to predict time to failure in the initial stage of the slow crack growth process. And therefore, the test procedure is shorter than the one at constant strain.