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Practical Guide to Selection of Environment Stress Cracking Test Methods for Plastics

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Environment Stress Cracking of Polymeric Materials.

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ABSTRACT

A range of test methods for assessing the resistance of polymeric materials to environment stress cracking (ESC) exist in the form of international and national standards. In addition, there are a wide variety of in-house test methods with various specimen geometries and loading configurations. Such a proliferation of methods presents difficulties when developing a rational test protocol for selecting materials for service applications. The objective of this document is to provide assistance in adopting an appropriate test strategy for evaluating ESC of plastics. The guide identifies the parameters that influence ESC and the main failure criteria. Preliminary materials selection test methods are discussed and the development of integrated test programmes for the acquisition of design data.

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Content

Glossary

$\frac{da}{dt}$	Crack growth rate,
$\frac{da}{dN}$	Crack growth rate per cycle,
ε_c	Critical strain,
ΔK	Stress intensity factor range,
σ_{th}	Stress threshold,
K	Stress intensity factor,
K_{IESC}	Threshold stress intensity factor for ESC,
S_N	Fatigue strength at N cycles,
t_f	Time to failure

1 Introduction

Environment stress cracking (ESC) describes the accelerated failure of a polymeric material in a brittle mode as a consequence of the combined action of environmental exposure and stress. The likelihood of failure depends on the characteristics of the material, the environmental exposure conditions and the nature and magnitude of the stress, as illustrated in Figure 1. ESC of plastics is most commonly associated with exposure to liquids, usually organic, and occasionally gases at low temperatures, but may be induced also by outdoor exposure to weathering. Failure occurs often due to inadvertent exposure to secondary fluids rather than the design fluid, for which extensive testing has usually been undertaken.

About 30% of failures of engineering plastics have been attributed to environment stress cracking[1] and the estimated cost to UK industry has been put at a value of £100m pa. The increasing utilisation of plastics in more exacting applications and the pressure for increased life without uneconomic overdesign are imposing a requirement for improved characterisation of performance.

There is a wide range of test methods and specimen geometries for evaluating ESC. Hence, the judicious selection of the most appropriate methods is not always easy but that are usually chosen based on the following criteria: the purpose of testing, the characteristics of the service application, the consequences of failure and various ancillary factors.

2 Purpose of testing

Testing is carried out for the following reasons:

- materials development;
- materials selection;
- plastic product testing;
- chemical product testing (assessment of aggressiveness of a fluid to various plastics);
- design information/data;
- quality assurance/control (QA/QC);
- research.

Ranking or screening type of tests may be sufficient in materials development, preliminary selection, chemical product testing and in QA/QC testing. These tests can be severe (usually in terms of the stress/strain) to ensure confidence in the low probability of failure although, for materials selection, there may be a risk of excluding otherwise acceptable less costly materials. Plastic product testing, where practically possible, is the final stage of evaluation of the product for the application and should simulate as closely as possible service conditions (e.g. bottle tests) or be designed to be more severe. QA/QC tests will usually have the same generic form as for product testing but be more severe.

For the purpose of final materials selection and design, the tests should reflect the key features of the service conditions.

2.1 Characteristics of service conditions

The three interactive variables in defining the likelihood of ESC cracking in service are stress state, environment exposure conditions, and material characteristics, as illustrated schematically in Figure 1. The service conditions may be categorised with the aid of the following questions.

2.1.1 Stresses

- are residual stresses present[2];
- are fabrication stresses significant (may need to assume near-yield for fasteners etc);
- are applied stresses static or dynamic (e.g. fluctuating pressure, start-up/shut-down routines);
- are cyclic stresses well characterised in relation to frequency, waveform, stress amplitude and stress ratio;
- are there stress concentrators inherent in the design;
- are thermal stresses important;
- what is the probability of unintentional excursions in stress;
- can we compute the stresses using finite element analysis.

2.1.2 Environment

- what is the design environment;
- is the environment constant and relatively pure;
- is the plastic exposed to weathering conditions;
- is the plastic designed to be exposed to a range of environments (possibly unknown at the design stage);
- what temperature range will the product be exposed to;
- what secondary environments might the plastic reasonably be exposed to;
- are the projected materials chemically resistant to the possible environments.

2.1.3 Material

- is the material in sheet form;
- are fabrication or processing defects likely;
- are knit lines present;
- has there been exposure of the product prior to use (e.g. to weathering);
- has there been significant ageing prior to service application.

2.2 Failure criterion/consequences

- can crack initiation be tolerated;
- is the fracture toughness high;
- what is the critical crack size;
- are crack arrest features built into the design;
- what are likely initial defect sizes;
- is the crack growth rate low;
- what is nominal design life;
- is “leak-before break” relevant;
- what are the consequences of failure: economic, safety, environmental impact;
- are there specific design codes for the application;
- what are the NDT limits.

2.3 Ancillary factors

- availability of equipment;
- cost of testing;
- rate of data generation;
- familiarity/experience, e.g. is there a known relationship between specific test data and field experience;
- existence of standards;
- legislative requirements.

Modern plant design and duration now encompasses the various factors just discussed in terms of Risk Based Management computations[3,4].

3 Planning a test strategy

In view of the wide ranging and interactive nature of the factors which affect the choice of test method, it is not possible to be prescriptive about a test programme. Development of an expert system which pursues the various possible paths in a logical way is feasible but beyond the remit of this project. Nevertheless, we can examine the key elements in the strategy in relation to the broad test categories, as demonstrated by the flow diagram in Figure 2.

It should be emphasised that for most applications, there is seldom reliance on one specific test method. A hierarchy of testing is usually undertaken as part of an integrated test programme. Also, consideration of factors such as orientation and knit lines[5,6] is essential (Section 2 ESC Test Method Review[5]).

4 Ranking and screening tests

Ranking or screening tests are essential in preliminary materials selection. They may also be used to evaluate the potential aggressiveness of a particular chemical product to a range of plastics. The tests should be rapid, simple and cheap to perform, but not misleading.

In principle, constant total strain, constant load and slow strain rate are candidate test methods, in most cases using very simple test pieces unless focused on specific products[5].

4.1 Constant strain tests

Constant total strain methods (Figure 3) 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. The more meaningful tests are when the threshold/critical strain to crazing or fracture is measured, albeit that the critical strain is based somewhat arbitrarily on a limited exposure period. This usually involves testing over a range of applied strains, which adds to the cost but, since jigs can be immersed in simple baths and multiple specimen test rigs (Figure 4) can be employed, the overall cost is not great. Ranking of materials performance should be considered carefully as comparison based on the critical initial stress may show a different ordering if the modulus of the various materials differs significantly. Indeed, with any ESC test, the basic mechanical properties in the reference environment (usually air) should be measured and recorded so that the results from ESC testing are put in context. All straining jigs should be checked by strain gauging reference specimens (preferably with a non-contacting method) to ensure that the strain is similar from one jig to the other for nominally the same applied strain.

The use of elliptical jigs (Figure 5) for determining the critical strain from one specimen should be considered primarily as a basis for obtaining a first estimate prior to bent beam tests, as the relaxation induced by craze development elsewhere on the specimen may affect the value of the critical strain. Otherwise, a modification as proposed by Bergen[7] should be undertaken.

Of the different type of bent beam tests undertaken, there is a virtue in the use of 4-point bend testing for the determination of the critical strain as there is a greater region of uniform stress and, accordingly, greater allowance for the impact of microstructural or surface inhomogeneities.

4.2 Constant load testing

Constant load testing tends to be more expensive because of the more complex apparatus (Figure 6), including the need for environmental cells. Since numbers of parallel tests have to be conducted to measure a threshold stress, the cost of testing is not trivial. It is used less commonly as a ranking or screening test primarily for that reason.

4.3 Slow strain rate testing (or slow rising load)

Slow strain rate testing (Figure 7) is often the first test to be conducted in ranking and screening for stress corrosion cracking of metals. Its development and utilisation for testing of plastics has been less marked. However, it has the specific virtue that testing is relatively rapid and always produces a result; i.e. if there is no ESC, the material will yield and ultimately be pulled to failure. Test times are usually a few hours unless there is particular interest in testing to final fracture which could then extend to about 24 hours or more for some materials. However, the apparatus is relatively expensive, and the setting up time and dismantling of the test system is not trivial. At the same time, computer-based monitoring of the stress-strain curves and manipulation of the data can reduce the effort of analysis markedly.

The slow strain rate method is very effective in ranking the aggressiveness of different environments. However, it is important that all the test are conducted at the same strain rate as the test results are strain rate dependent. When comparing different materials or different grades, the output, in terms of departure stress or departure strain, should be quoted in the context of other mechanical properties since two materials of similar departure stress could have markedly different departure strains, and vice versa. The effective modulus can be modified by the environment and the value should be quoted.

4.4 Comparison of results from different techniques

Comparative measurements have been made with all three techniques for two materials (ABS and polycarbonate) in several environments[8]. In all cases, the ranking was consistent although the data for 4-point bend testing of ABS were limited because of marked stress relaxation in the particular environment.

Although a limited study, the indications are that the selection of the particular test method for ranking purposes may not be so critical provided testing is conducted in an intelligent way and the data are interpreted with awareness of the limitations of the techniques. Nevertheless, there is some preference for the use of slow strain rate testing because of the rapidity of generation of test data.

The slow strain rate technique is considered a severe test and often the assumption is made for metals that no environment assisted cracking in this test can mean no cracking in service. This may not always be a valid assumption since testing is done usually at only one strain rate. Accordingly, whilst an appropriate method for ranking and broad screening, greater care must be exercised if it is intended to demonstrate, for example, that a chemical product will not cause cracking in a wide range of plastics. In relation to issues concerning plasticisation by the environment and the importance of loading for a period prior to exposure, it is unclear whether slow strain rate testing would have demonstrated cracking susceptibility if testing was conducted at only one strain rate.

5 Design data

When considering testing a material for design purposes in relation to ESC the fundamental question that should be answered is:

“under what conditions will ESC occur and how likely is it that such conditions might prevail in service, even if just transiently.”

In other words, what are the boundaries for cracking of the material (i.e. safe operating limits) for the application (i.e. in terms of material/environment/stress combinations) and are the service conditions well within those boundaries. Risk analysis depends largely on this framework. For some systems there may be specific design codes imposed by legislative authorities and these would be the primary basis for design.

The reason for posing the question above is because, too often, failures in service occur due to excursions from perceived design conditions or unexpected factors introduced during installation. At the same time, the data forming the basis of design are obtained mostly from very limited test conditions. Accordingly, the degree of conservatism in the design data may not be fully known, i.e. the risk has not been evaluated, and failure comes as a surprise. Of course, the situation may be compounded further by ignorance of the end-user who may mis-use the product.

The development of a test programme is intrinsically linked to the design philosophy which itself will be based on characterising the service conditions and upon the consequences of failure, as detailed above. It would be ideal if the boundary for cracking could be mapped out comprehensively with intelligent restraint based on insight into the possible range of conditions. This can be expensive and so the challenge is to combine the minimum of testing with a clear evaluation of risk.

The test programme can be sorted initially in terms of whether design is based on no initiation of crazes/cracks or on a damage-tolerant perspective and acceptable lifetime.

5.1 Initiation-dominated design and testing

Testing here provides pass/fail information or quantitative parameters such as a threshold stress.

The effectiveness of pass/fail data depends on establishing a test which is considered to be sufficiently severe for the application. This is coupled usually with some established history of application of the test for service prediction.

Typical of pass/fail tests might be a constant load test conducted at about 90% yield in the appropriate environment. Whilst the design stresses may be lower, it is usually necessary to assume that some feature of the system may be loaded to near yield at least transiently.

The recent work of Arnold[9] in highlighting, for some systems, the greater test severity associated with pre-loading followed by exposure (compared with simultaneous exposure) indicates the need for incorporation of such a test into a test programme.

Slow dynamic straining can be used as a severe test. This can accommodate to some extent the possibility of an uncontrolled transient in stress, e.g. slow movement of a pipe due to inadequate or failed fixings or support. Testing should be conducted at a range of strain rates (gauge length strain rates), typically from 10^{-6} s^{-1} to 10^{-4} s^{-1}. The range is chosen to allow for time-dependent effects. For example, susceptibility might become apparent with increasing strain rate although not at lower strain rates if there is the potential for significant time-dependent surface plasticisation or swelling. More research in this area is required. Any departure stress *below* yield over the range of strain rates would constitute a failure. At the same time, a small *plastic* strain to fracture in the environment might also be a concern as it would indicate an intolerance to a transient overload.

In other applications, the test may be configured to the nature of the product as in the bottle tests (ESC Test Method Review Section 3)[5], with the stress increased beyond likely service conditions and with the temperature increased to increase the severity of the environmental exposure conditions. In this context, where the design and application are relatively simple, establishing conservative boundaries for cracking is straightforward as the stresses are well known. At the same time, the consequences of an individual failure due to inadvertent exposure to other chemicals would be considered of small significance. Hence, the need for more extensive testing would be limited.

Design based on the concept of a threshold stress seems an attractive prospect in principle, with an appropriate conservative allowance. This assumes that crazing and cracking can evolve but only above a certain stress level. However, there would have to be very considerable confidence in the range of service stresses and in fabrication and installation, where appropriate, to enable such an approach to be undertaken. A materials engineer may be disinclined to take such a risk unless there were other compelling factors.

The potential role of cyclic loading has to be considered in appropriate circumstances. This may be induced by a variety of sources such as start-up and shut-down operations, fluctuating pressures or temperatures. The frequency need not be high; diurnal fluctuations in load may be sufficient[10]. Under cyclic loading, failure will eventually occur. Testing of plain specimens is often considered to represent a situation of initiation-dominated life. For a metal, the time for fatigue crack initiation is only about 5% of life when initiation is viewed from the perspective of high resolution SEM studies of cracks. It is likely that plastics will behave in broadly the same way. Most of the life in plain specimens is spent in the growth of very small crazes/cracks which are not often readily detectable. Hence, the definition of initiation is linked to the method of crack detection. For this reason, fatigue from plain specimens is often considered to be initiation-dominated; thus the inclusion in this section. With plain specimens, the design is based on S-N curves and the desired fatigue strength to give a certain fatigue life. The major problem is to represent the form of the cyclic loading in service and either to accelerate the testing by increasing the frequency or to establish a basis for extrapolation of limited test data derived from testing at the service frequency. A combination of both is the most effective approach although high frequency testing should be avoided due to thermal degradation problems.

Much of the emphasis in this discussion has been in relation to mechanical stressing. As indicated for the bottle tests, increasing the temperature in an intelligent way can be used to increase the severity of the environment. This cannot be generalised because there are some environment-plastic combinations for which the increased diffusivity at the elevated temperature could result in more significant surface plasticisation or swelling compared to ambient temperatures.

More generally, the effect of temperature should be investigated if it is a service variable, as it usually is to some extent. Indeed, testing at very low temperatures, as experienced by plastics components in motor vehicles in some climates, may be necessary.

5.2 Propagation dominated design and testing

The perception here is that crack-like defects will be introduced in processing or fabrication or developed early in service. Design is then based on a threshold stress intensity factor for cracking or more usually on the assumption of a finite life. For simple products, design may be based on the principle of no through-thickness cracking in a severe test, e.g. the bottle test.

Measurement of K_{IESC} is probably best approached using fracture mechanics specimens such as compact tension specimens (ESC Test Method Review Section 7)[5] subject to very slow rising displacement. The indication from studies in metals is that measurement under these conditions can be more efficient than testing under constant load conditions and may be more conservative depending on the strain rate. The problem of design on the basis of threshold is again the concern that excursions in stress may lead to crack development from the defect.

Accordingly, the safer approach is to assume that the threshold will be exceeded and to derive crack growth laws from laboratory experiments. The lifetime can then be predicted by integrating the crack growth law from the assumed initial crack size up to the critical crack length. This is a commonly used approach for metals but there are important distinctions with respect to plastics. Crack growth laws applied in service are usually intimately connected with an inspection protocol, the inspection intervals being governed initially by the assumed growth laws and initial defect size and information from inspection fed back to condition future intervals. Crack detection in plastics is more difficult. The other distinction is the long-term change in properties of plastics with age and this can raise uncertainty about the value of growth laws derived from short-term laboratory studies.

In addition to these specific concerns, it is less clear how effective the life assessment process is in predicting service life particularly in situations where multiple crack sites exist, crack coalescence is important and short crack growth can be significant. Most laboratory studies also accelerate the growth process by testing at elevated temperatures.

Recent research on polyethylene[11] is focusing not on crack growth kinetics but on the fibril creep processes in the craze zone which are considered the rate determining step in growth. This may provide a new and more effective approach to predicting crack growth kinetics based on short term accelerated tests.

6 Quality assurance / control testing

These tests are essential to ensure that products or fabrications conform to design standards and may be introduced in a random way to check production quality or the quality of a fabricated system, e.g. the quality of a welded joint.

Specific product tests such as the bottle test or the impression test for finished components (ESC Test Method Review Section 3)[5] may be used. Testing of welds poses more problems. Non-destructive tests[36] are required that can identify susceptible welds, where microstructural changes or residual stress may increase the probability of ESC failure.

7 Summary

The information obtainable from the different types of tests and the potential engineering usage are summarised in Table 1 and Table 2.

Table 1. Nature of results from ESC tests

Type of test	Test result	Test time
constant total strain : *elastic* *plastic-elastic*	ε_c, σ_{th}, t_f craze/no-craze	variable
constant load	σ_{th}, t_f, departure strain	variable
slow strain rate	departure strain/stress	Function of strain rate - usually a few hours
fracture mechanics based: *increasing K specimens* *decreasing K specimens* *constant K specimens*	da/dt v. K, K_{IESC}	variable
fatigue: *smooth/notched* *precracked*	S_N da/dN v. ΔK, ΔK_{th}	function of cyclic frequency, range of data required

Table 2. Application of ESC test results

Test result	Engineering usage
ε_c	classification of susceptibility; screening; design criterion
σ_{th}	classification of susceptibility; screening; design criterion
departure stress/strain	ranking of materials/aggressivity of environments
da/dt v. K	life prediction; inspection intervals; design
K_{IESC}	classification of susceptibility; design criterion
S_N	classification of susceptibility; screening; life prediction;
da/dN v. ΔK	life prediction; inspection intervals; design
ΔK_{th}	design criterion

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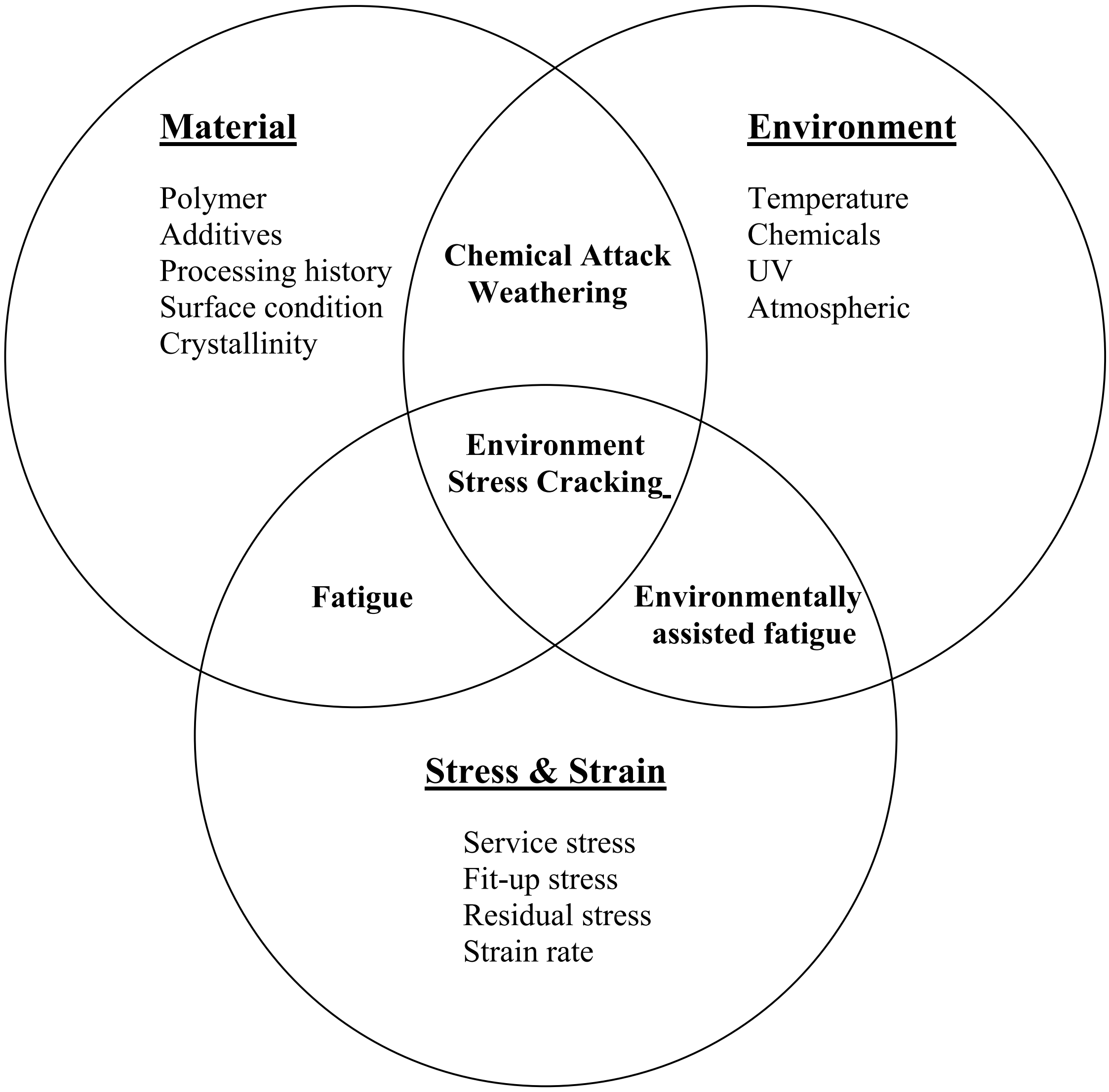

Figure 1 Interaction of material properties, environment and stress/strain on environment stress cracking.

Selection of Materials for Service

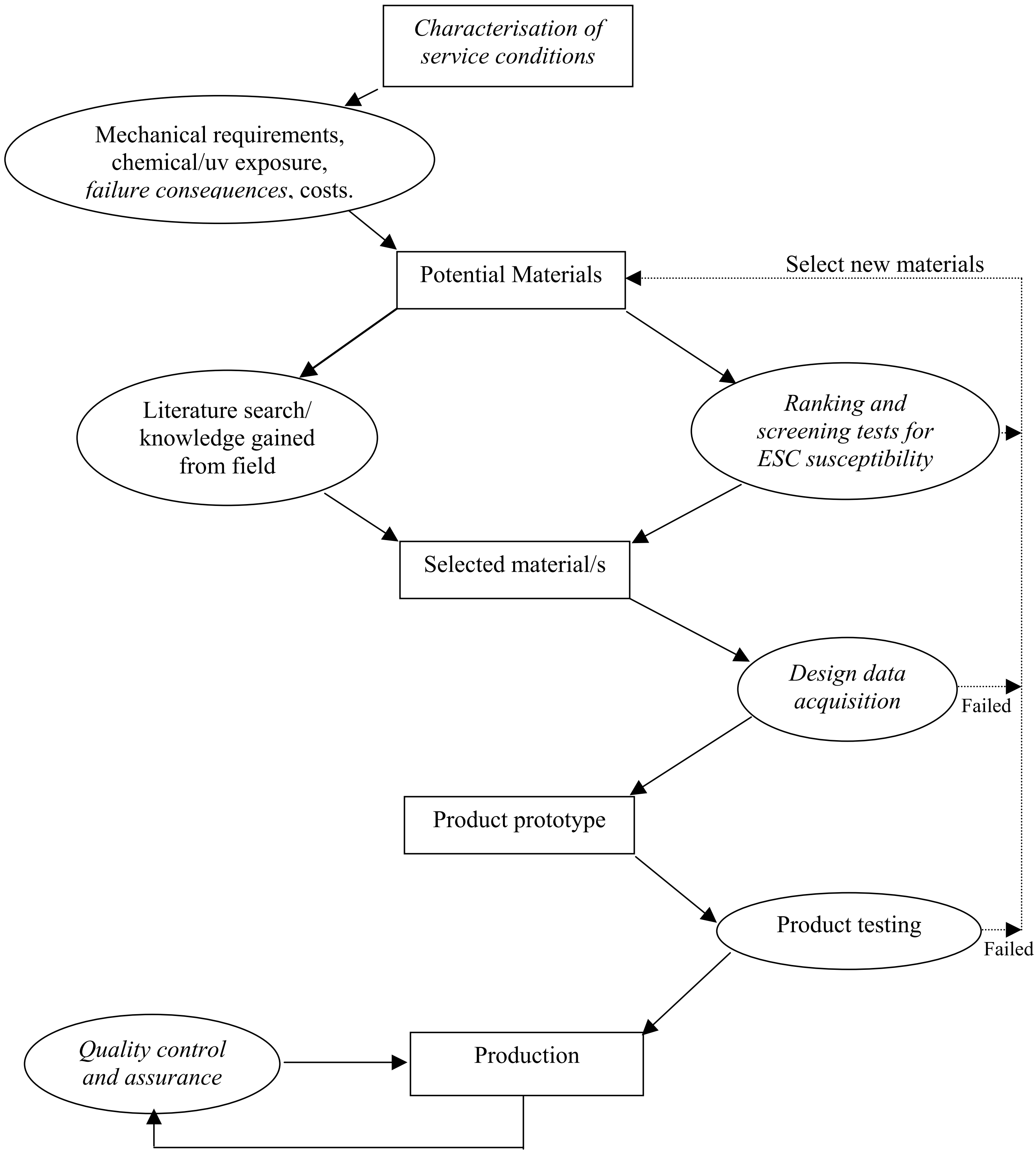

Figure 2 Flow chart illustrating a typical test strategy employed in materials selection. ***Italic headings*** **refer to particular sections of the report.**

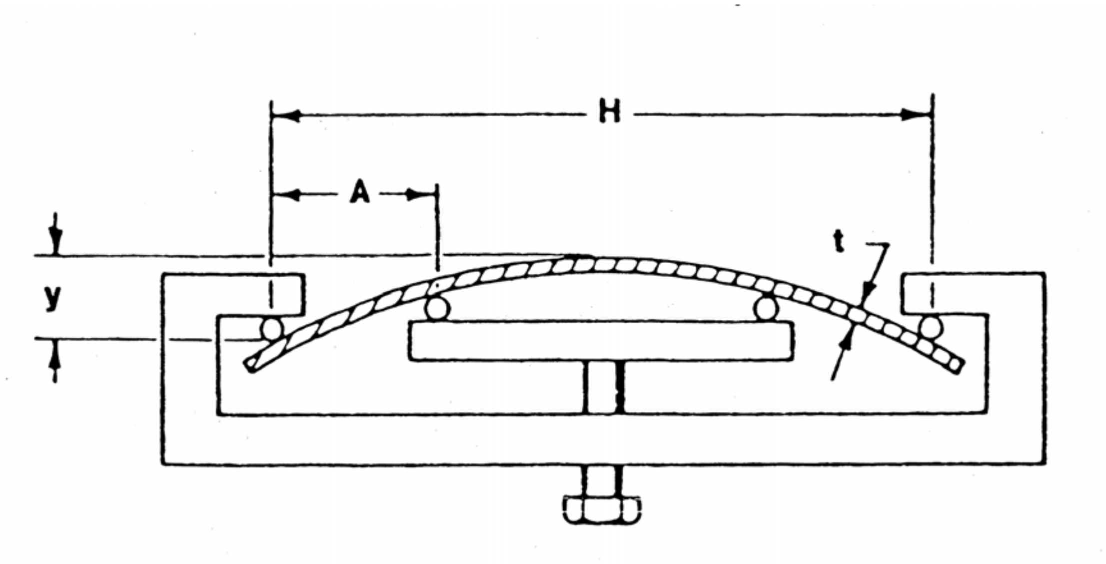

Figure 3 Schematic illustration of 4 point bend constant strain apparatus, where H distances between the outer supports, A distance between inner and outer supports, t thickness of specimen, y deflection of specimen.

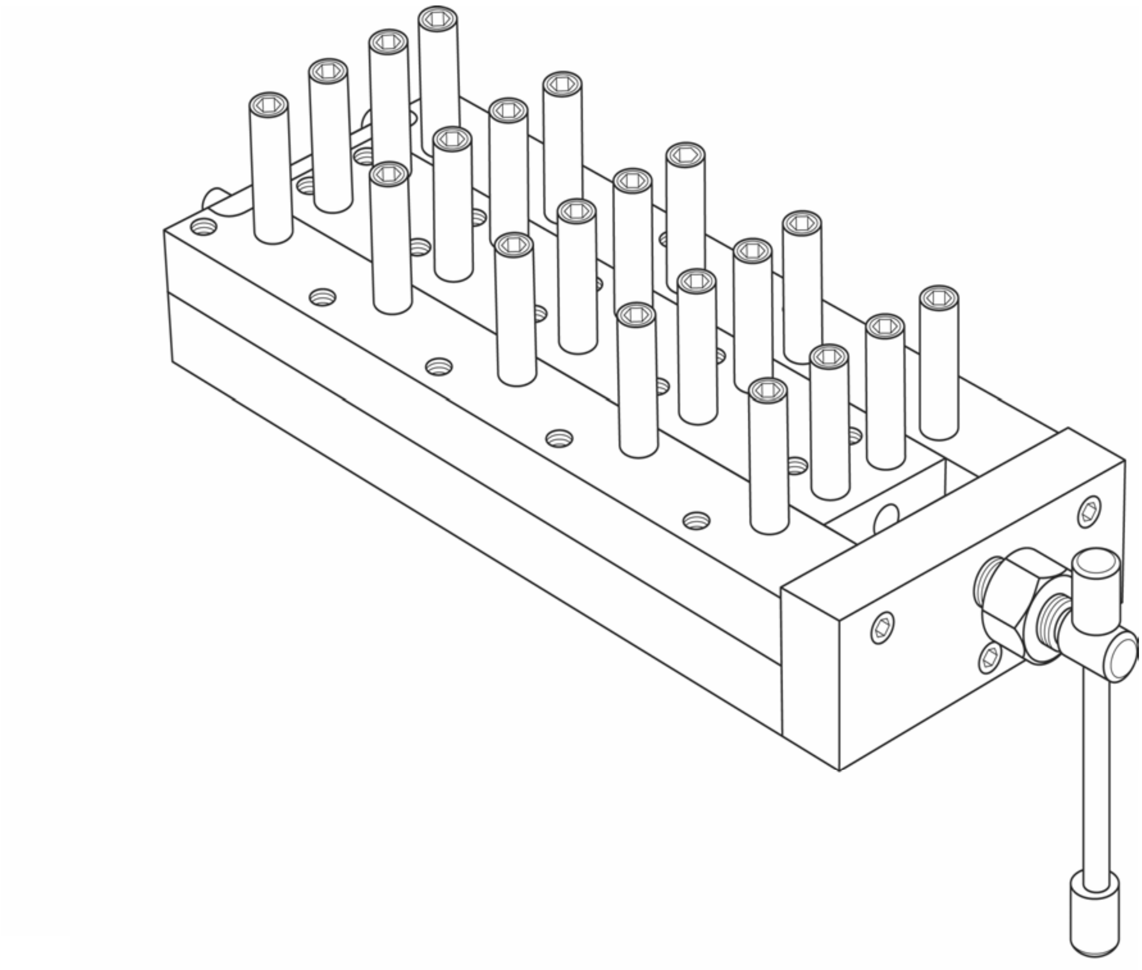

Figure 4 Illustration of a multiple four-point bend jig capable of simultaneously testing five specimens.

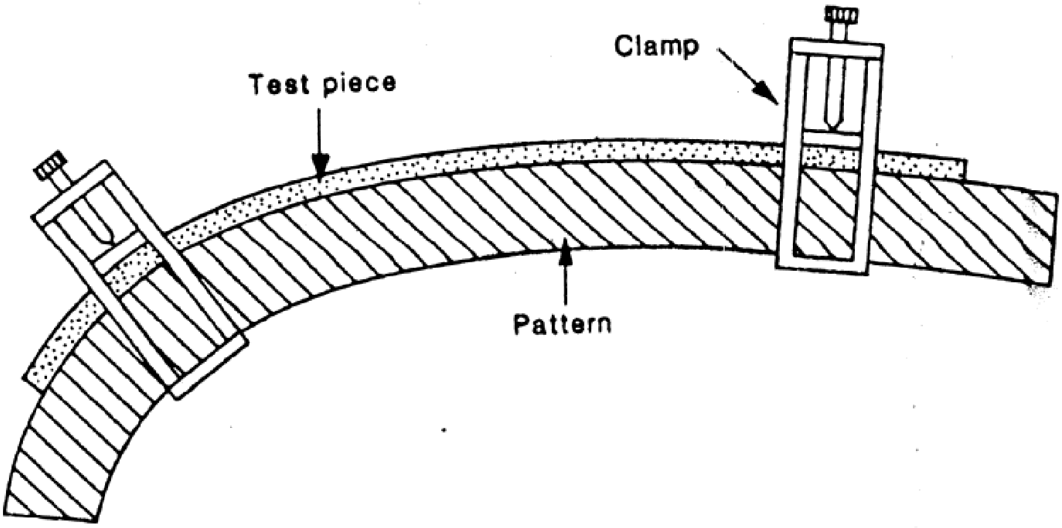

Figure 5 Elliptical jig with a former of variable radius used to develop variable strains along the length of the specimen

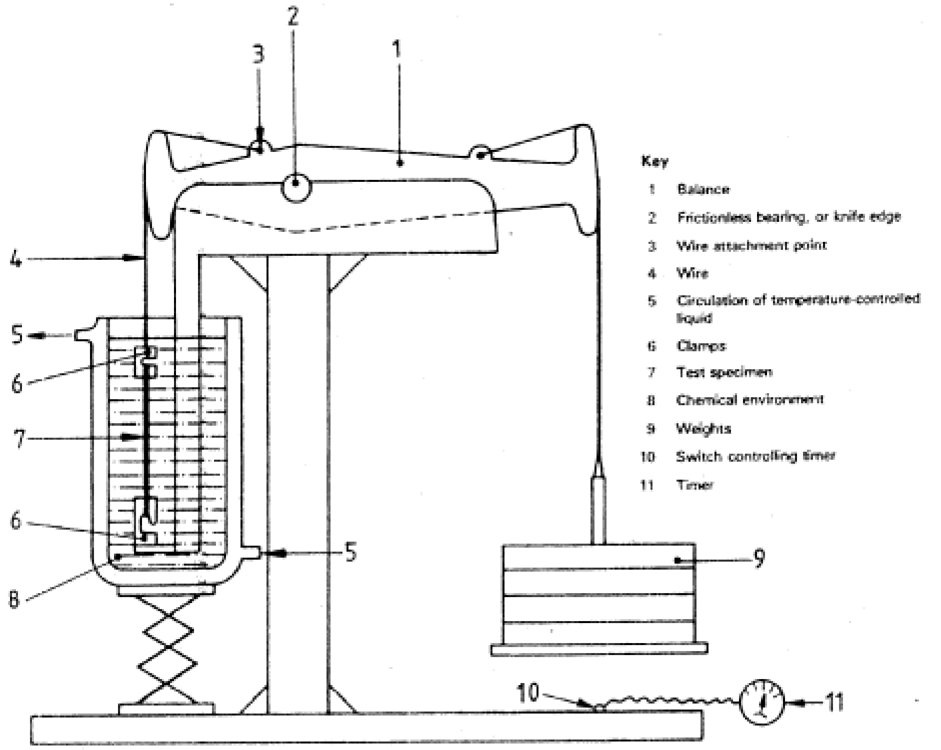

Figure 6 Illustration of typical apparatus used for a constant load test.

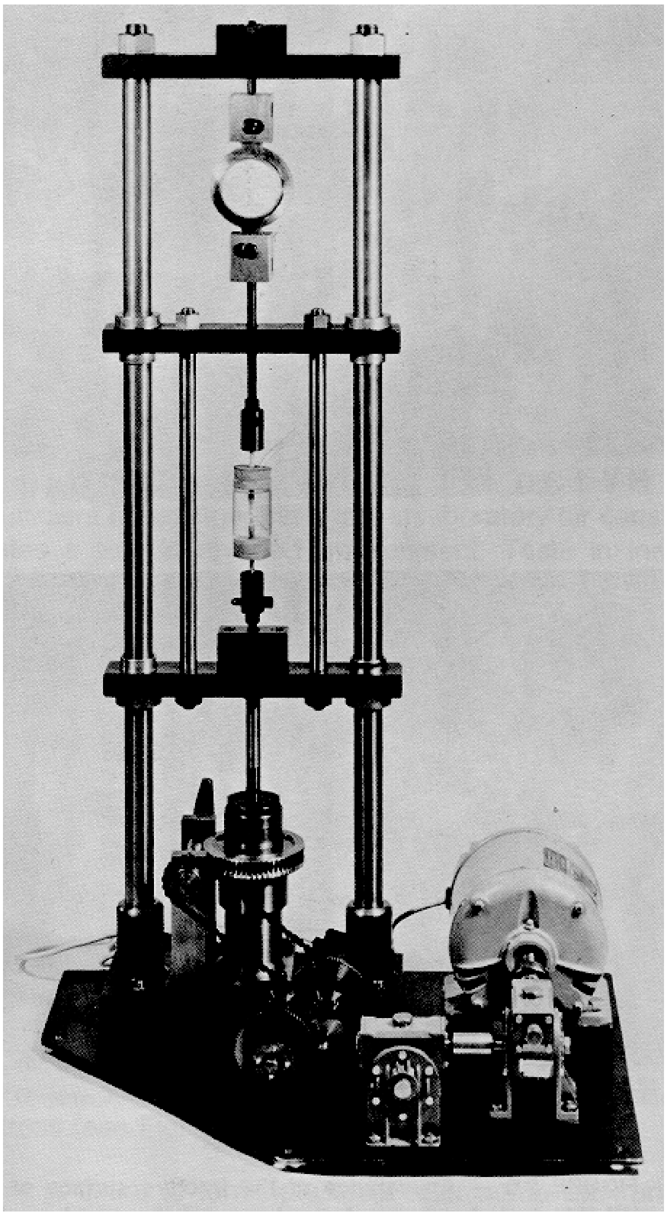

Figure 7 Typical apparatus used for slow strain rate testing of plastics (courtesy of University of Newcastle upon Tyne, Newcastle upon Tyne, UK).