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**Review of Techniques for
Monitoring the Environmental
Degradation of Polymers**

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ABSTRACT

The increased utilisation of plastics in more exacting applications and the pressure for increased life expectancy are imposing a requirement for improved inspection and characterisation of polymeric materials. The challenge this presents is to develop monitoring techniques that can detect signs of degradation prior to actual failure. The following report covers two of the most common forms of failure in polymeric materials, environmental stress cracking (ESC) and weathering. The report describes the mechanisms responsible for these two forms of failure, the accelerated test methods that can be used to assess long-term performance and the monitoring techniques that can be used to detect the first signs of degradation.

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1 Introduction

Polymeric materials are increasingly being used in high performance applications, where if failure occurs the consequences can be catastrophic, these applications include: aerospace components, medical implants, offshore installations and the transport and storage of hazardous chemicals. Whilst in the past failure of polymers in cheap, non-critical applications could be tolerated, their increased use in critical applications and the pressure for increased life expectancy is forcing companies to improve the monitoring and characterisation of these materials.

Environmental stress cracking (ESC) is the single biggest cause of failure in engineering plastics (Figure 1), accounting for approximately 30% of all failures and is estimated to cost UK industry over £100 million per annum [1], not including the cost of lost production and litigation. ESC occurs due to the combined effect of stress and chemical exposure that results in brittle failure at stresses far lower than those expected in air. The chemicals responsible for ESC may be present by design as in chemical storage tanks but are more often present as secondary fluids such as cleaning agents or lubricants. ESC also requires mechanical stress this can be either an applied load or from residual stresses produced during manufacture.

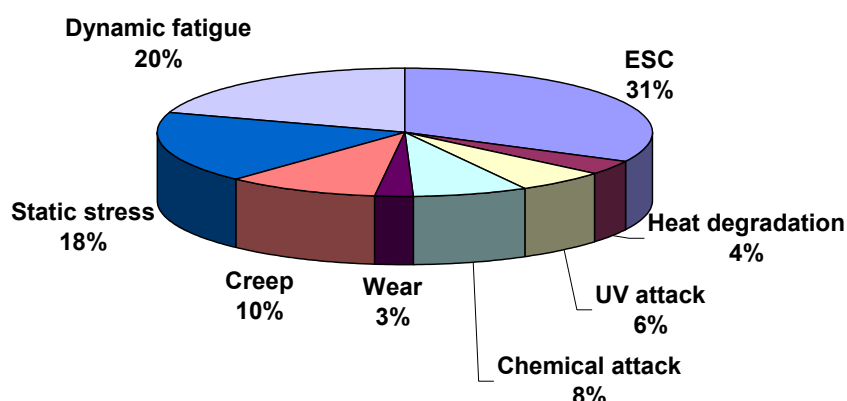


Figure 1 Cause of premature failures that are observed in polymer during service [1].

Weathering of polymers due to atmospheric exposure is the main cause of failure for plastics used in outdoor applications such as: construction and transport. The interaction of ultraviolet radiation, oxygen, moisture, temperature and stress, all result in complex photochemical reactions that degrade the physical, mechanical and chemical properties of the polymer. In addition, the presence of degraded material in itself can accelerate the degradation process leading to “auto-acceleration”. Failure may be due to fracture of the component, but can also result from the loss of transparency, gloss or colour.

The aim of this review is to evaluate measurement techniques for identifying environmental degradation due to both ESC (chapter 2) and weathering (chapter 3). Each chapter describes: the mechanisms responsible for failure, the accelerated test methods that are used to assess long-term performance and the monitoring techniques used to detect the first signs of degradation.

2 Environment stress cracking

2.1 Mechanism

Despite extensive studies ESC remains one of the most common causes of failure in polymers. The main reason for this is the complexity of the phenomenon, with aspects such as chemical compatibility, liquid diffusion, craze formation and crack development all playing their part. While crystalline and amorphous polymers are both susceptible to ESC, amorphous polymers are particularly susceptible due to their relatively open structure that leads to easy fluid penetration. Once the fluid has penetrated the polymer it becomes locally dissolved promoting cracking and crazing in the polymer. Cracking is normally preceded by the formation of crazes initiated at sites of stress concentration or at regions of local microstructural inhomogeneity. Crazes are expanded regions that are held together by highly drawn fibrils, which bridge the void allowing the craze to transmit stress and preventing the craze from propagating. The mechanism of crazing in chemical environments is essentially identical to that in air [2-5]. In general terms [6,7] craze initiation is considered to evolve from microdeformation processes in localised regions about 30 nm in diameter. As the deformation region develops, further localised deformation is induced. The growth and coalescence of such deformed nuclei create a narrow plastic zone. In the presence of dilatational stress, voids develop. This voided structure is considered the precursor of the fibrillated craze structure that ultimately leads to the formation of cracks and subsequent failure [8].

The presence of an ESC agent accelerates the formation of crazes [3-5] by a process of local plasticisation that increases the molecular motion of the polymer chains enabling the crazes to develop more rapidly. The particular stage at which the formation of the craze precursors is accelerated by the environment and the influence that different polymer types have on this process is less clear. Arnold [5] has proposed that the role of the environment is to determine when the voided precursors break down to form crazes. It has been suggested also that the environment is important in void stabilisation through surface energy reduction.

Stress concentrations can be important not only in developing localised deformed zones but also by producing a more open structure that will increase the concentrate absorbed molecules into the deformed zone.

It has been suggested [5,9,10] that the rapid acceleration in growth of the craze precursor to a visible craze occurs at a critical level of inelastic strain, which is independent of both environment and temperature. This has significant implications for ESC testing as in certain polymer-fluid combinations plasticisation-induced toughening may occur that will delay the formation of crazes. The method by which a polymer is exposed to the environment is therefore extremely important for if it is fully immersed in a solvent before it has been exposed to stress the polymer may swell reducing its tendency to craze. Likewise, very rapid stress cracking may occur if the polymer is exposed to the environment for a relatively short time but has been under stress for a much longer period of time.

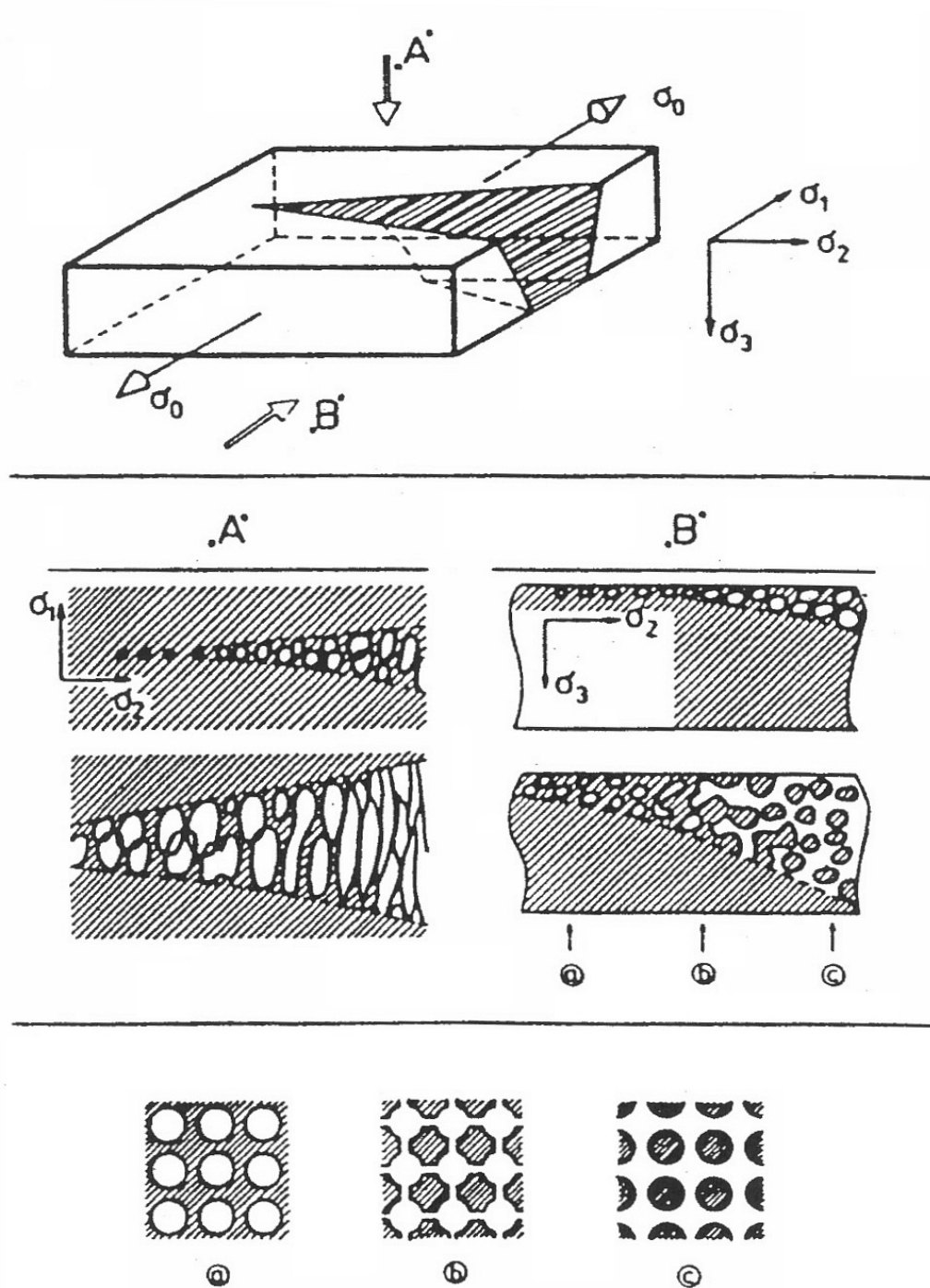


Figure 2 Transformation of a craze nucleus into a craze [8].

2.2 ESC susceptibility testing

2.2.1 Introduction

One of the main requirements to prevent failures is to assess whether a particular polymer / environment combination is susceptible to ESC. Preferably ESC susceptibility tests should be conducted prior to service examining all the chemicals the polymer is likely to come into contact with. However, due to the vast range of different chemicals this is extremely difficult and as a consequence it is found that most ESC failures are due to unintended exposure to secondary fluids such as cleaning agents or lubricants. ESC susceptibility tests are therefore vital to the monitoring of ESC and subsequent failure analysis. The evaluation of ESC in thermoplastics is covered by a number of national and international standards [11]. These test methods can be divided roughly into two groups those that are based on an applied deformation and those based on applied load. The main international standards for testing ESC resistance are:

Constant deformation tests

- Bent strip [12]
- Bent strip test for flexible materials [13]
- Ball and pin impression [14,15]
- Constant tensile deformation [16]
- Slow strain rate testing [17]

Constant load tests

- Constant tensile stress [18]
- C-ring tests [19,20]

The following section gives a brief overview of the ESC test methods that have been standardised. More detailed information about these and other non-standard test methods can be obtained from a recent technical review on ESC test methods produced by Turnbull and Maxwell [11]. It should be noted, that there are no standards for testing ESC resistance under either cyclic or biaxial stresses. Previous work has shown that fluctuating loads can actually improve ESC resistance by relieving residual stresses in the polymer [21]. However, recent work indicates that ESC resistance can be significantly poorer when biaxial stresses are used rather than uniaxial stress [22].

2.2.2 Bent strip tests

The bent strip test (ISO 4599) [12] involves clamping the test specimen to a semicircular former to apply a known strain to the specimen. The radius of curvature of former can be varied to induce different levels of stress in the specimen. This strain may be calculated using the following equation:

$$\varepsilon(\%) = \frac{d}{2r + d} \times 100$$

where d is the thickness of the specimen and r is the radius of the former.

Once the specimen has been strained it is brought quickly in contact with the chemical environment. After an agreed time the specimen is removed from the apparatus and

either visually inspected for crazing or mechanically tested to assess their residual strength.

This test is most commonly used for assessing the ESC susceptibility of amorphous polymers. It is not suitable for semi-crystalline polymers, which are susceptible to rapid stress relaxation, as the stress applied to the specimen will decrease during the test.

2.2.3 Bent strip for flexible materials

This test was developed by Bell laboratories in the USA and has since been standardised as ASTM D1693 [13]. The technique is suitable for flexible polymers such as polyethylene but should only really be used for quality control purposes. An illustration of the type of apparatus used in this test method is shown in Figure 3. The specimens used in this test are notched rectangular strips ($38 \times 13 \times 3$ mm) that are clamped in a jig so that the sample folds over on itself at an angle of 180° to produce stress within the specimen. Once loaded into the jig the specimens are immediately exposed to the chemical environment at the required test conditions. The specimens are then inspected either visually or using an automatic inspection technique [23] at agreed time intervals and the time required for 50% of the specimens to fail is noted.

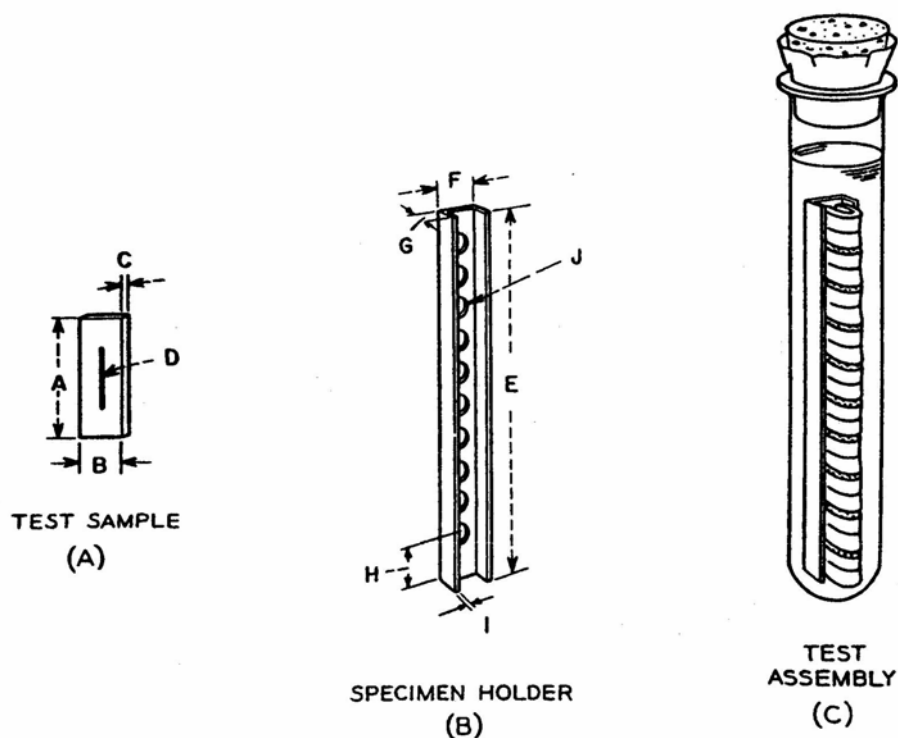


Figure 3 Bent strip technique for flexible polymers [13]

2.2.3 Ball and pin impression

The ball and pin impression test [14] is used primarily for complex finished components. The method involves drilling a series of holes of a specific diameter into the polymer. A series of oversized balls or pins are inserted into the holes to induce a

range of different stresses. One hour after the pins have been inserted the specimens are immersed in the environment for 20 hours. The specimens are then dried and visually examined for crazes. The smallest ball to cause visible crazing is used to determine the ESC resistance of the polymer.

2.2.4 Constant tensile deformation

The constant tensile deformation test is a relatively new test that is currently being developed as an ISO standard as ISO DIS 22088 part 5 [16]. The test method involves applying a constant deformation to the specimen and monitoring the stress relaxation that occurs while it is immersed in the chemical environment. The test is repeated using progressively smaller levels of deformation until the stress relaxation curves of consecutive tests superimpose on one another (Figure 4). The applied stress required to produce this level of deformation is defined as the critical stress. The ESC resistance of the material is determined by comparing the critical stress obtained in the environment to that obtained in air.

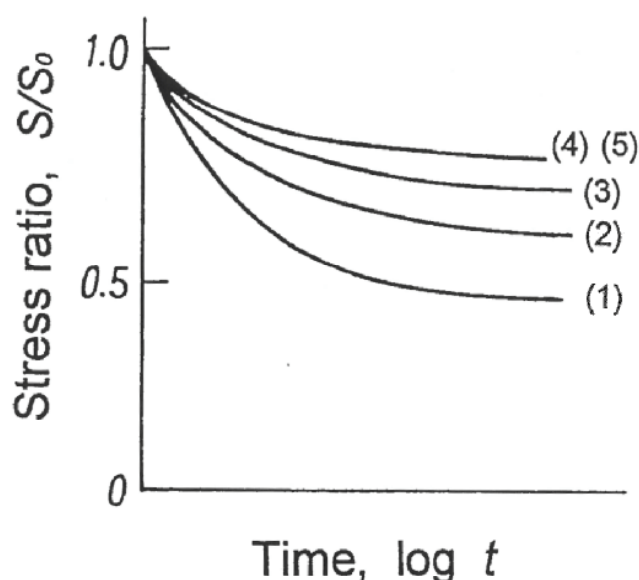


Figure 4 *Stress relaxation curves obtained using progressively smaller levels of deformation ($1 > 5$) until consecutive curves superimpose on one another (4 and 5) [16].*

Note: S_0 is the initial stress and S is the stress at time t .

2.2.5 Slow strain rate testing

The slow strain rate method has been used only comparatively recently for characterising the performance of plastics although it is a well established for metals and it is now currently being developed into a standard [17] as ISO DIS 22088 part 6. The test method involves subjecting a specimen to a gradually increasing strain at a constant displacement rate whilst it is exposed to the chemical environment. The tests are conducted under uniaxial tension at low strain rates to enhance the influence of the

environment on the specimen. Load and displacement are monitored continuously to enable stress-strain curves to be produced. The development of crazes within the specimen causes the strain to be taken up locally at the crazes such that the stress required to deform the specimen is reduced compared to that in an inert environment. The onset of craze initiation can therefore be detected by the departure of the stress-strain curve in the chemical environment from that in air Figure 5. The main advantages of the slow stain rate test are that it is relatively rapid, requires few specimens and can be automated.

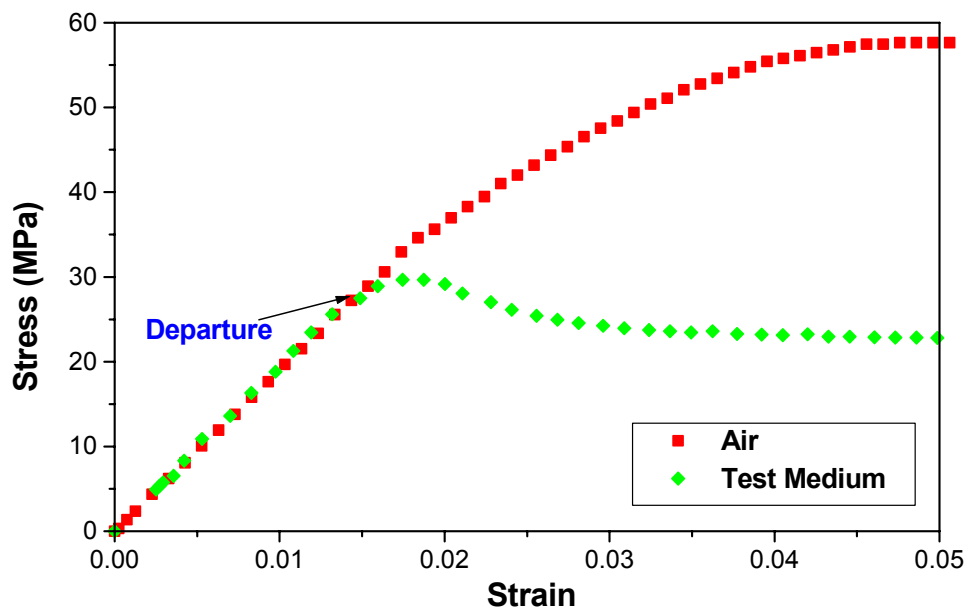


Figure 5 *Typical stress-strain plot showing difference in stress/strain profile for material exposed in air and in the test medium [17].*

2.2.6 Constant tensile stress test

The distinctive feature of this test is that a constant load is applied to the specimens, thereby avoiding the problem of stress relaxation that is found in the constant strain test methods [18]. An illustration of the type of apparatus used in this test method is shown in Figure 6. The technique involves subjecting the specimen under investigation to a constant tensile stress at a stress below the tensile yield stress of the polymer. This is usually achieved using a dead weight that is suspended from one end of the specimen. The specimen is then immersed in the stress-cracking agent and inspected at regular intervals to establish the onset of crazing. The time required for crazes/cracks to appear after the specimen has been exposed, or the threshold stress below which no crazes appear in a specific time period (typically 100 hours) can be used as a measure of the ESC resistance.

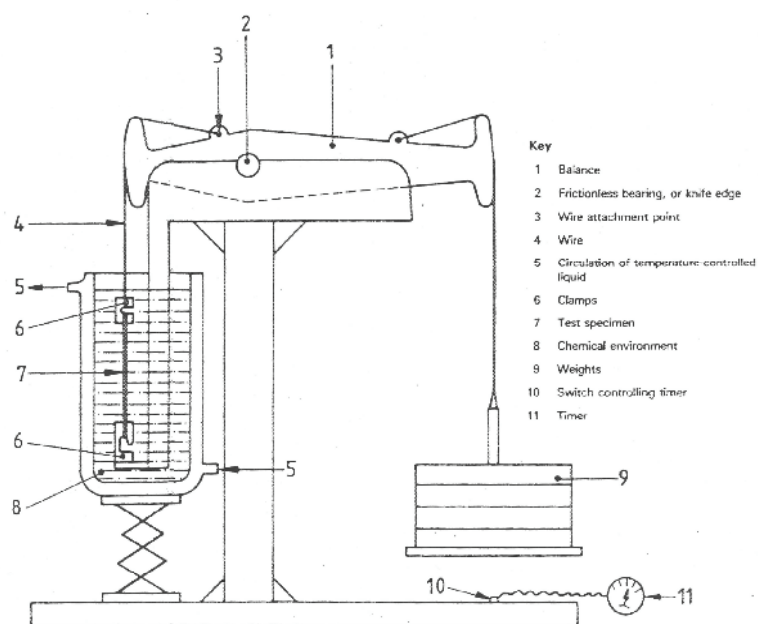


Figure 6 *Illustration of typical apparatus used for a constant load test [18]*

2.2.7 C-ring tests

C-ring specimens are often used for the testing of tubing and pipes and have been standardised for the testing of polyethylene pipe in ASTM F-1248 [19]. Typical apparatus for testing C-ring specimens is shown in Figure 7. Circumferential stress is of principle interest and this stress varies around the circumference of the C-ring from zero at each bolthole to a maximum at the outer surface of the middle of the arc opposite the stressing bolt. C-rings can also be stressed in the reverse direction by spreading the ring and creating a tensile stress on the inside surface. An almost constant load can be developed on the C-ring specimen by placing a calibrated spring on the loading bolt. This enables the C-ring to be self-loading particularly important for monitoring degradation in inaccessible places as they can be used as in situ test coupons.

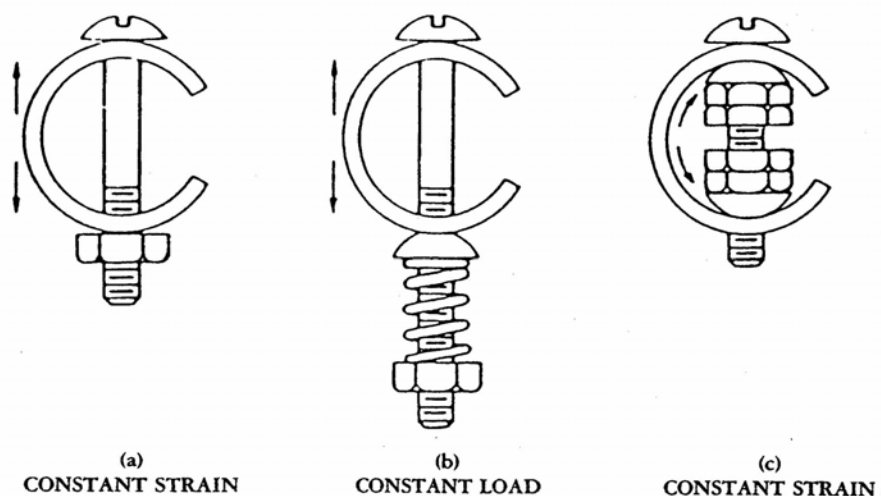


Figure 7 *C-ring test methods for assess ESC in pipe-sections[20].*

2.2.8 Self-loading tests

Self-loading tensile tests are not common in the testing of plastics and have not been standardised. However, they are extremely useful for the monitoring of plastics as they can be placed in the same environment as the material under investigation, for example in a polymer pipeline and then removed at regular intervals for testing. There are various means by which specimens can be self-loaded, the most common of which is to produce a constant stress in the specimen by using a compressed spring to apply a known load. An example of this type of jig is shown in Figure 8. The specimen is held within the tube and the stress applied by turning the bolt at the end of the tube to compress the spring. The advantage this arrangement over the c-ring tests is that it produces a simple, uniform stress pattern within the specimen.



Figure 8 Self-loading tube for environmental stress cracking of plastics

2.3 Monitoring of ESC

Once a polymer has entered service the monitoring of ESC becomes more difficult as the techniques used must be either non-destructive or the specimen removed so small that it does not compromise the functioning of the component. The monitoring of ESC in-service can be achieved at different stages of the degradation process (Figure 9), either before the craze has formed by detecting property changes that may subsequently result in ESC, or by the detection of crazes before they have developed into cracks. The first indication that a polymer may be susceptible to ESC is if it starts to absorb fluid, this can be detected either by weight gain (section 2.3.1) or softening of the polymer due to plasticisation (section 2.3.2). If solvent uptake is identified it is necessary to identify the solvent (section 2.3.3) and then to conduct ESC susceptibility tests, as described in the last section (section 2.2). If the polymer is found to be susceptible to ESC it is necessary to assess the risk of failure and its consequences. A vital part of this assessment must be to determine the levels of stress the component is likely to be exposed. If the component remains unstressed throughout its service life it will not fail. However, this assessment must take into

account all forms of stress [24-26], as most materials will contain significant levels of residual stress, which are introduced during the manufacturing process. If the decision is made to leave the component in service it is necessary to continue inspecting for the first sign of crazing (section 2.3.4).

The following section describes the different techniques that can be used to monitor ESC in plastics: by monitoring solvent absorption and localised plasticisation, by identifying solvents on the polymer surface and by detecting the onset of crazing.

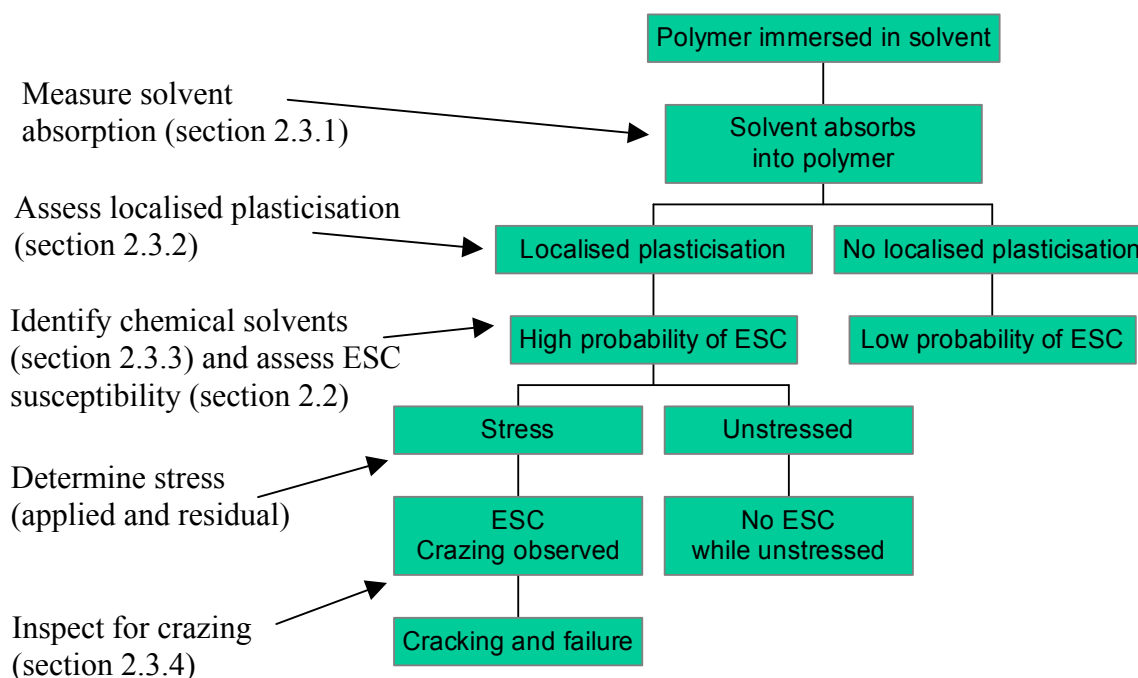


Figure 9 *Different stages at which the development of ESC in a plastic can be monitored*

2.3.1 Monitoring solvent absorption

2.3.1.1 Weight gain measurements

Monitoring the absorption of solvents in a polymer can be achieved by measuring the increase in mass as the solvent is absorbed [27]. ISO 175 [28] covers the absorption of chemical liquids into polymers and ISO 62 [29] the absorption of water. In each of these tests standard sized samples are weighed and then immersed at constant temperature in the test liquid. After an agreed time period the samples are removed from the medium and surface liquid wiped off using a dry cloth before weighing. Samples can then be returned to the medium for continuing exposure provided that the time out of the medium is minimised. The balance used should have a resolution of 0.1 mg or better, which can be relaxed to 1 mg if water absorption is greater than 1 %. The increase in mass divided by the initial mass, measured at regular time intervals, is plotted against time in order to define the absorption curve. Results can be reported either as the mass gain after a particular period of immersion or as the mass at saturation (m_s) defined as the weight gain from 3 successive measurements that differ in value by less than 1% of the overall weight gain.

2.3.1.2 Thermogravimetric analysis (TGA)

TGA can be used to monitor weight changes in samples as a function of temperature. The technique involves measuring the mass of a specimen continuously while the temperature is increased at a constant rate [30, 31]. Weight losses that occur when absorbed solvent in the polymer is driven off give a direct measurement of the mass of the absorbed solvent. The advantage of the TGA technique over conventional weight measurement techniques (Section 2.3.1.1) is that it can determine moisture content in localised areas of a component such as close to the surface. The disadvantage is that it requires a specimen to be removed and is therefore destructive. However, the specimens required are relatively small and would not compromise the functioning of larger components. TGA equipment can also be used in combination with mass spectroscopy to assist in identification of the volatiles driven off at different temperatures.

2.3.2 Localised plasticisation

2.3.2.1 Microindentation

Absorption of solvents into the polymer surface can significantly reduce the modulus of the polymer due to a reduction in the glass transition temperature (T_g) of the polymer. This is difficult to detect using conventional tensile methods, as changes to the mechanical properties will normally be confined to the surface of the material. However, changes in the polymer surface can be detected using indentations [32, 33]. The technique most commonly used is microindentation, as the indents are relatively small preventing deformation in the bulk of the material. Wright et al [33] have shown that microindentation can be used to identify the initiation of ESC in UPVC in a wide range of different fluids. Softening was detected in the UPVC prior to ESC enabling microindentation to be used as a predictive tool. However, in PMMA it was found that the softening process was disrupted by the loss of surface material preventing ESC being detected.

2.3.2.2 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) [30] can be used to measure changes in the T_g due to plasticisation. The DSC technique involves increasing the temperature of the polymer at a constant rate while measuring the power input compared to a reference specimen (Figure 10). When physical changes occur in the polymer such as the glass transition there are changes in the power required to maintain the temperature enabling transitions such as T_g to be identified. In some cases the solvents may also promote crystallisation by enhancing the mobility of the molecules in the amorphous phase of the polymer. It should be noted that solvents may induce crystallinity in semi-crystalline polymers such as PBT that have a tendency to undergo secondary crystallisation. Solvents may also induce irregularities into the baseline of the DSC trace due to the outgassing of solvent [34]. Standard methods for the measurement and analysis of polymeric materials using DSC are given in ISO 11357 [35].

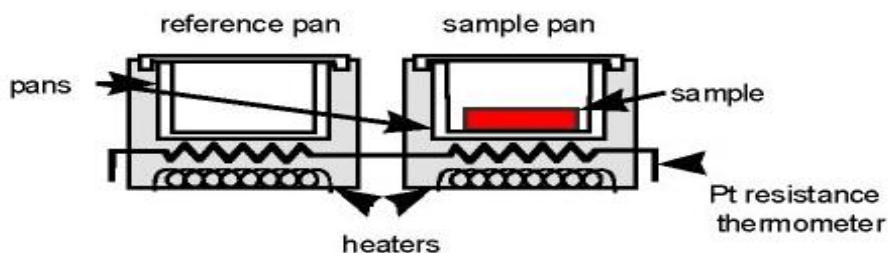


Figure 10 *Schematic diagram of the reference and specimen pans used in DSC testing*

2.3.2.3 Dynamic mechanical thermal analysis (DMTA)

Another technique for measuring changes in the T_g of polymers is Dynamic Mechanical Thermal Analysis (DMTA) [30,36,37,38]. This technique involves applying a small sinusoidal displacement to a specimen and measuring the resulting load (Figure 11). By continuously measuring of load and displacement it is possible to calculate the storage modulus E' , the loss modulus E'' and the loss tangent $\tan \delta$ of the polymer. Taking measurements over a range of different temperatures it is possible to identify a peak in the loss modulus E'' corresponding to T_g .

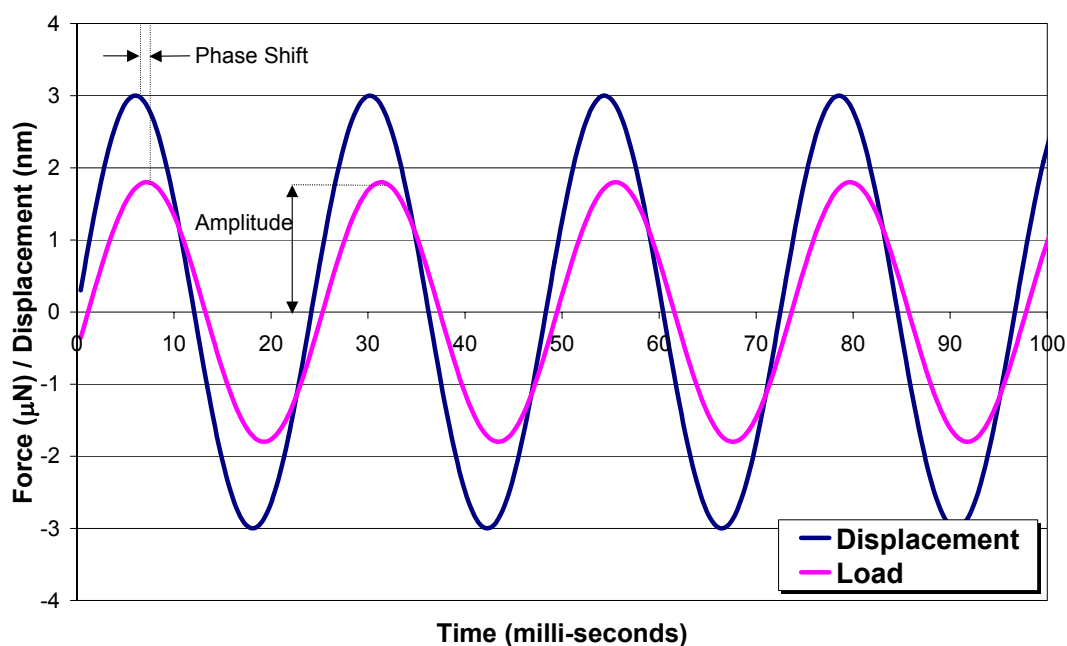


Figure 11 *Schematic diagram of the type of sinusoidal displacement that is used in DMTA tests and the phase shift ($\tan \delta$) that occurs between load and displacement.*

The main advantage of DMTA over DSC is that it is considerably more sensitive, able to detect secondary relaxations as well as the main T_g peak (Figure 12) [39]. These secondary relaxations can be extremely important as they relate to the motion of shorter segments that can influence the toughness of the polymer. Interpretation of

secondary relaxation is, however, a highly specialized activity requiring considerable skill [40]. The main limitation of DMTA is that specimens of particular dimensions have to be extracted from the component. This means that the technique is destructive and also that it is difficult to detect localised changes in T_g that occur at the surface of the polymer.

A possible method of overcoming the difficulty of detecting localised changes in the mechanical properties of the polymer is to use depth-sensing indentation [41,42,43]. This technique uses a fine indenter that can examine the material in the nanometre range allowing mechanical data to be obtained that is specific to the surface of the material. The apparatus consists of a fine indenter with a dual force and displacement measuring system. During a test the indenter is pressed into the surface of the material whilst the load and displacement are continuously measured. The load and displacement data obtained can be used to calculate the hardness and modulus of the surface. By applying a small sinusoidal load to the indenter tip and measuring the displacement it is also possible to determine the loss tangent $\tan \delta$ of the material [44]. The recent introduction of a nanoindenter hot-stage by MicroMaterials [45] also introduces the opportunity of obtaining $\tan \delta$ data as a function of temperature. Enabling the glass transition temperature and secondary relaxation peaks to be determined close to the polymers surface.

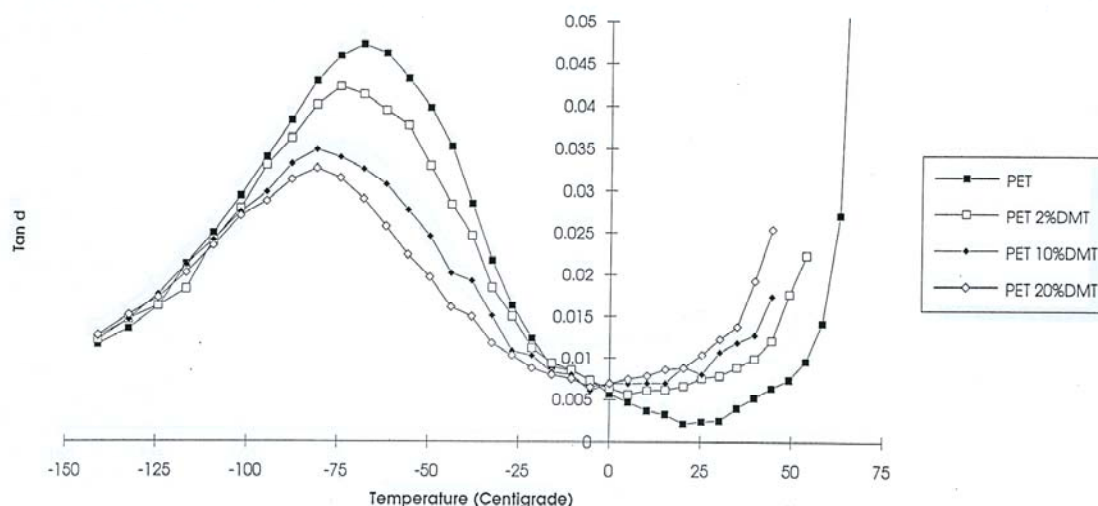


Figure 12 *Shift in the glass transition temperature and secondary relaxation peaks of PET due to the presence of a low molecular weight solvent dimethyl terephthalate [39].*

2.3.2.4 Dielectric thermal analysis

Dielectric thermal analysis can be used to determine the T_g of a polymer by measuring the complex electrical impedance of the material [30]. When a polymer is placed in an electric field dipoles within the polymer will attempt to align with the direction of the field. However, at temperatures below T_g realignment of the dipoles can be significantly retarded by neighbouring segments within the polymer. The capacitance of the polymer is thus dependent upon molecular relaxations and is therefore analogous to DMTA. By applying an alternating electric field across the polymer and

measuring the resulting capacitance it is possible to calculate the storage component, the loss component and $\tan \delta$ of the dielectric constant. Again like DMTA it is possible by taking measurements over a range of different temperatures to identify a peak in $\tan \delta$ corresponding to T_g .

In addition, to determining the T_g of polymers dielectrics can also be used to detect the absorption of small polar molecules, such as water. As the dielectric constant of the polar water molecules is considerably higher than that of the polymer absorption of these molecules into the polymer will increase its electrical permittivity. Dielectric sensors can be either placed on the surface of the specimen [46,47] or embedded into the polymer. The use of dielectrics to sense liquid has been used in a wide range of different applications [46,47] including measuring the fat content of fish, the water content of coal and an earlier DTI project on moisture in adhesive joints [48].

2.3.3 Solvent identification

2.3.3.1 Infrared spectroscopy

Infrared (IR) spectroscopy [49, 50] is one of the most widely used techniques for the identification of organic chemicals. It involves identifying the specific frequencies in the infrared region of the electromagnetic spectrum at which the bonds in the chemical vibrate. This involves exciting the chemical bonds and then analysing the frequencies that they absorb. The technique can be used to analyse a wide range of chemicals that can act as ESC agents including gases, liquids and solids. Both qualitative and quantitative chemical analysis data can be obtained.

By directing infrared light at a polymer surface and measuring the absorption (or transmission) of the various frequencies, it is possible to characterise, or "finger-print", any chemicals on the surface, since they will have specific frequencies at which they will absorb strongly. This "finger-print" of the various frequencies at which the chemicals absorb is referred to as the IR spectrum. Computerised databases of spectra for common chemicals are available to enable characterisation of molecular structure by observing spectral differences between known materials and the test sample. Some quantitative analysis is possible by analysing the magnitude of these characteristic absorption peaks.

IR spectroscopy is not inherently a surface analysis technique but can be modified to examine surfaces using an attenuated total reflectance technique. This involves using a prism in optical contact with the sample so that total internal reflection occurs after the IR light has penetrating a small way into the sample surface. Analysis is possible to within 0.5 to 3 μm of the surface. There are various ways of performing IR spectroscopy on a material, and probably the most widely used is known as Fourier transform infra-red or FTIR.

2.3.3.2 Raman

Raman is a surface analysis technique based on the inelastic scattering of monochromatic light [49,50]. A laser excites the material, which is usually in the visible region of the spectrum. The frequency of scattered light is analysed by comparing it to the incident spectra. The technique is similar to IR spectroscopy in determining the nature of molecular structures and is a complementary technique to IR spectroscopy when characteristic frequencies are weak or for highly absorbing

materials. Samples require minimal preparation, but need to be stable to high intensity light and contain no species that fluoresce when excited by visible radiation.

2.3.3.3 X-ray photoelectron spectroscopy (XPS)

XPS is an analytical technique that measures the energies of photoelectrons emitted from atoms of a sample when it is irradiated with soft (or low energy) X-rays. XPS is surface sensitive and is frequently used for quantitative elemental analysis of fracture surfaces. The technique, which is capable of detecting all elements with the exceptions of hydrogen and helium, can provide information on chemical structure (e.g. oxidation states) and element distribution present on the surface of any solid material. The technique is surface-sensitive with a maximum operational depth of less than 10 nanometres. XPS can be used to determine the effect of solvent and chemicals on surface chemistry and it can be used in conjunction with inert gas ion sputtering to determine the variation in chemical composition with depth (NB. Many polymeric material samples are sensitive to ion beam damage).

2.3.3.4 Secondary ion mass spectrometry (SIMS)

In SIMS, the surface is bombarded with a beam of high-energy ions resulting in the ejection of molecular fragments, atoms and ions from the surface, which are subsequently analysed [51]. It is capable of providing surface elemental analysis and depth concentration profiles on areas from several mm to sub micron. SIMS can detect all elements and isotopes including hydrogen and hydrogenated compounds with very high sensitivity (parts per billion). It is, however, not readily amenable to quantitative analysis as it is complex and requires reference standards. The depth resolution is under 200 nanometres and areas of up to 500µm can be studied. Whilst SIMS is suitable for all materials, flat sample surfaces are required to give the best spatial and depth resolution. There are a number of different variants of the technique including static SIMS (sub-mono-layer elemental analysis), dynamic SIMS (depth composition profiles) and imaging SIMS (elemental mapping) analysis.

2.3.4 Craze detection

2.3.4.1 Visual inspection

Visual inspection is the most commonly used technique for the early detection of crazing in polymers and composites and its importance should not be overlooked. Increasingly visual inspection may involve the use of CCTV or video cameras to aid access and enable a permanent record of the inspection to be made. For the best results visual inspection of transparent or translucent polymers should be conducted using backlighting. This causes diffraction of light from the sides of the craze allowing them to be observed more clearly (Figure 13). However, this technique does depend on whether access can be gained to both sides of the component to allow backlighting to be installed. If backlighting cannot be installed subsurface defects are extremely difficult to observe.

Enhanced visual inspection of surface cracks can be achieved by the use of dye penetrants (Figure 14). This involves applying a brightly coloured liquid penetrant to the surface of the polymer and allowing capillary action to draw the liquid into the cracks. Excess penetrant can then be removed and a developer applied. The developer draws the dye out of the cracks on to the surface. As the dye covers a larger area of the surface than the actual flaw it is considerably easier to see the defects. Dye

penetrants are widely used for failure analysis. However, care should be taken when using them for monitoring a component that is to remain in service as the penetrant can act as an ESC agent.

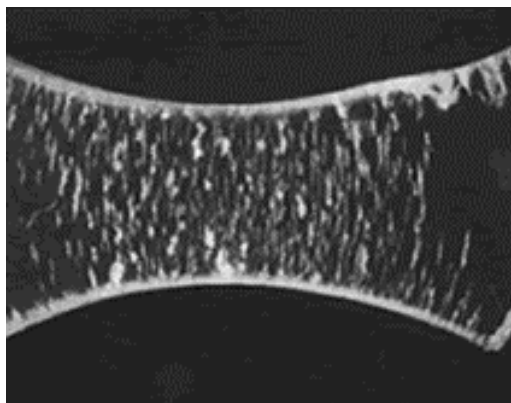


Figure 13 *Diffraction of light from the sides of the craze enable them to be observed in transparent polymers with the use of backlighting.*



Figure 14 *Red dye penetrant used to expose hairline cracking around bolthole in a plastic moulding*

2.3.4.2 Radiography

In complex components where it might be difficult to use other techniques radiography may be employed. Radiography uses localised differences in attenuation under x-ray illumination to provide a cross-sectional picture of the density of a component. Images are typically recorded on film and increasingly digital or real-time recording systems are being used. Radiography is best suited to large volumetric defects and it can sometimes be difficult to detect the small crazes.

Enhanced resolution can be achieved by using an x-ray absorbing penetrant. This involves applying a penetrant to the polymer that will absorb x-rays more readily than the polymer. When the component is illuminated the x-rays are absorbed more by the penetrant in the cracks than it is elsewhere (Figure 15). However, this technique is not particularly popular because of health and safety issues although new low intensity systems are now available, which reduce the environmental hazards.

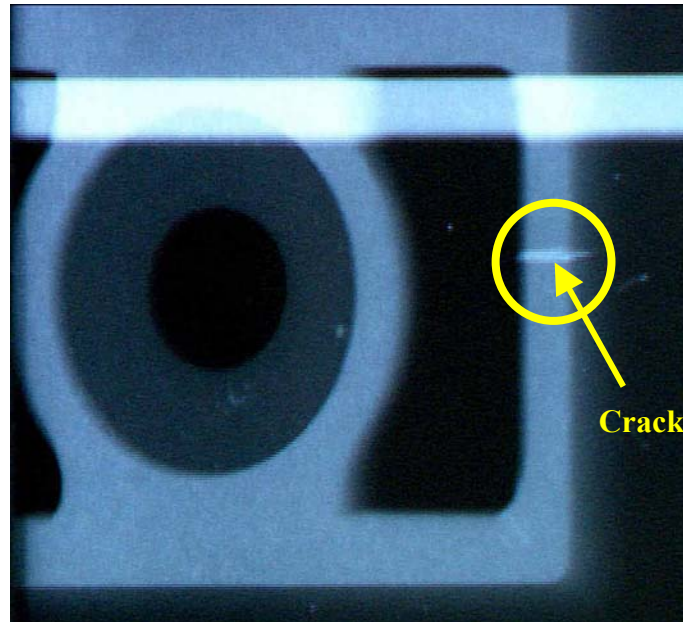


Figure 15 *X-ray image obtained using an absorbent penetrant to identify a crack in a plastic moulding*

2.3.4.3 Thermography

Thermography is a non-destructive technique that involves studying the heat radiated from the surface of an object in order to reveal the presence of surface or sub-surface flaws. It involves observing the temperature distribution on an object's surface as the object is subjected to a pulse of heat and then allowed to return to ambient temperature. Any flaws present are detected as abnormalities in the surface temperature distribution observed during this thermal transient. When a short pulse of heat is applied to the surface of an object, the presence of a sub-surface flaw inhibits the flow of heat from the heated surface into the bulk of the material. If the surface of the object is then observed with an infrared camera an apparent build up of heat can be seen in the region of the flaw.

2.3.4.4 Acoustic microscopy

Acoustic microscopy is an ultrasound technique that uses focused ultrasonic waves (5 to 150 MHz) to image defects in components. Acoustic microscopy basically involves sending a sound wave through the component and interpreting the interaction of the wave with the component. The sound wave is generated by a piezoelectric crystal or transducer, which has been cut to provide a specific frequency. The wave travels to the specimen through a couplant, which is usually deionised water. The wave travels through the specimen with a portion of the sound being reflected back every time it hits a defect within the material.

Acoustic microscope may employ either pulse echo or through transmission inspection. Pulse echo inspection consists of interpreting echoes sent back by the component, while through transmission inspection consists of interpreting sound waves after they have been passed through the component. In the pulse echo method, the same transducer is used as sender and receiver of the sound waves. Pulses are repeated using repetition rates at which the echoes from one pulse will not interfere with those of another, e.g., 10-20 KHz. The echoes received by the transducer are converted to voltages, amplified, digitised, and presented to the user as an image. In the through transmission technique, separate transducers are used to send and receive sound waves, both of which are on opposite sides of the specimen. The absence of a signal at the receiver indicates that a defect is present.

Acoustic microscopy is the only ultrasonic technique that is sensitive enough to detect defects such as crazes. However, use of this technique is limited by the fact that the area that can be scan is relatively small.

2.4 Prediction techniques

In addition, to monitoring ESC attempts have been made to predict ESC behaviour using the intrinsic solubility properties of the polymer and the solvent. Solvents that enhance plasticisation in plastics and are therefore likely to be ESC agents are those that bond readily to the polymer chains. Depending on the nature of the solvent: dispersion forces, polar interactions and hydrogen bonding may all be important in determining the strength of these bonds. The solubility parameter is a measure of these interactive forces although it is not always easy to estimate for molecules with a range of forces, particularly in mixed solvents. When the solubility parameter of the liquid is identical to the polymer, solution occurs. If the difference in solubility parameters is small, plasticisation is localised and if there is sufficient local stress/strain, ESC can occur.

The link between the solubility parameter and ESC has led to extensive studies and attempts to correlate ESC susceptibility with the solubility parameter [4,52-54]. However, there has not always been complete understanding of the principles in drawing such correlations. Implicitly, equilibrium solubility is assumed but in a short test, diffusion may limit uptake. Indeed, a correlation [55] has been shown in some short-term tests between crazing stress and the rate of uptake of various alcohols with no correlation with the solubility parameter. A more fundamental problem is that correlation of the solubility parameter is often made with respect to a specific test parameter such as the critical strain to failure. Calculation of the impact of absorbed molecules on crazing depends not only on accounting for the solubility parameter but also the local concentration at the site where crazing initiates and this will depend in the dilatational stress. When correlating the critical strain to failure with the solubility parameter allowance has to be made for the different dilatational stress values.

Thus, a lack of correlation between critical strain to failure and the solubility parameter is likely since the comparative basis is inadequate or the wrong test parameter is being used for validation. Mai [54] demonstrated this aspect particularly well showing poor correlation with solubility parameter computed conventionally but excellent correlation when account was taken of the enhanced local solubility corresponding to the stress at failure. From the viewpoint of prediction of critical

strain to failure this is not satisfactory [54]. Nevertheless, the very nature of the good correlation when more accurate computations are made does provide some confidence that the relative ranking of susceptibility based on solubility parameters (properly accounting for the dispersive, polar and hydrogen bonding parameters) has intrinsic validity and can be explored successfully. It is the test basis for evaluating the effectiveness of the predictive tool that is not ideal.

In summary, solubility parameters can provide a basis for ranking the relative susceptibility of polymers in organic fluids provided account is taken of all the interactive forces including those associated with other molecules in mixed fluids. At the same time, awareness of the type of failure process is important, as solubility parameters are primarily a factor in the plasticisation of amorphous polymers. Other mechanisms of failure may also prevail.

3 Weathering

3.1 Introduction

Weathering of polymers or more precisely their degradation due to ultra-violet radiation (sunlight) is one of the most common forms of degradation in polymers used in outdoor applications. The consequences of weather are quite familiar and include:

- Mechanical embrittlement
- Surface micro-cracking and reduced impact strength
- Discolouration due to polymer or pigment degradation
- Loss of gloss or transparency
- Changes in molecular weight
- Accumulation of degradation products (including; carbonyls and unsaturated bonds)

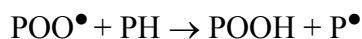
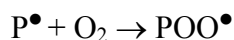
Examples of this type of degradation include agricultural polymer films that lose their flexibility and disintegrate, garden furniture that becomes brittle and stadium seats that become chalky. In the following sections the mechanisms of failure and the environmental conditions that control them will be considered. Methods of monitoring the weathering process will be discussed both in their ability to identify the onset of degradation and in their practical use.

3.2 Mechanisms

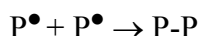
The weathering of polymers is a complex chemical process involving the photo-oxidation of polymer chains due to exposure to solar radiation [56-58]. Exposure of a polymer to solar radiation leads to breaking of the chains due to dissociation of the C-H bond in the polymer to form polymer free radicals [58].



The extent of this chemical reaction depends on the radiation exposure that is the quantity of ultraviolet light (<350nm) to which it is exposed. Once polymer radicals have been produced, reaction with oxygen generates hydroperoxides (POOH).

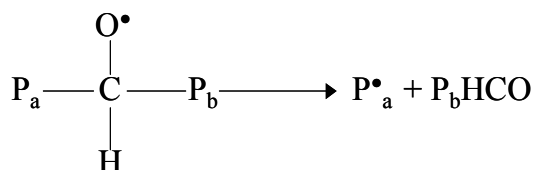


These hydroperoxides can dissociate further to produce a series of decomposition products including aldehydes and ketones. The presence of these carbonyl groups in a degraded polymer can be used as a chemical index of degradation (section 3.4.4.1). Once formed these free radicals can continue to react via propagation reactions long after the initial UV exposure has ended. Termination of these free radical reactions is normally achieved through the reaction of pairs of free radicals.



The formation and propagation of free radicals in itself does not seriously affect the mechanical properties of the polymer, as they do not significantly alter the long-chain

nature of the polymer molecules. Degradation of the mechanical properties occurs because the free radicals produced are highly unstable and readily undergo chain scission reactions. This results in the formation of two smaller polymer chains, one of which is a free radical and capable of further reactions [59].



The intensity of the UV radiation decreases with increasing depth in the material, so that the reaction tends to be a near surface process. Since oxygen is involved in the reaction process, there is an important balance between UV radiation and oxygen diffusion, and of course temperature since that will also determine the kinetics of reaction and the transport of reactive species. Under natural exposure conditions there will be wetting and drying cycles and dark periods. The significance of the latter is that some recovery of the oxygen concentration in the material can occur, which otherwise is confined to the very near surface due to consumption by reaction with the polymer radicals. Since the concentration of these radicals diminishes by termination reaction during the dark period, oxygen ingress can extend to greater depth.

3.3 Accelerated testing

For materials that have been on the market for a number of years there is often sufficient accumulated experience to permit a reasonably confident estimate of the expected lifetime of a product. However, the smallest of changes in the polymer grade, the stabilisers or the products design can significantly change this prediction. Thus while it is preferable to have actual performance data in most cases it is recognised that accelerated ageing is also required. The two main methods of achieving accelerated ageing are natural exposure and artificial exposure. The section will discuss the different types of UV exposure that can be used in accelerated testing and the influence moisture, temperature and stress have on the weathering process.

3.3.1 Natural exposure

As the ultimate aim of accelerated ageing is to improve lifetime prediction under service conditions, the most appropriate conditions are those that match the service environment exactly. These are most easily obtained by naturally exposing specimens at outdoor exposure sites. The problem with this is that the exposure period required would have to be at least as long as the life-expectance of the product. Natural weathering is therefore normally accelerated by exposure to climatic conditions that are more severe than those that are expected in service. For this purpose there are a number of established test sites in Saudi Arabia, Australia and the southern states of the USA [58]. Arizona is popular for exposure in hot dry climates and Florida for hot humid climates [58-60]. Acceleration can also be achieved by the use of Fresnel mirrors [58,61,62] that concentrate the sunlight directed on to the specimen.

Standard test procedures for the weathering of polymers in natural daylight, glass-filtered daylight and concentrated sunlight using Fresnel mirrors are given in ISO 877 [63].

3.3.2 Artificial exposure

Artificial weathering involves exposing test specimens to an artificial light source in a cabinet in which the temperature, humidity and water spray are controlled. The advantage of artificial weathering is that it is easier to accelerate the testing as all of the exposure conditions are controlled. The difficulty with this approach is to know how these different parameters interact in the weathering process. The key parameter in all accelerated weathering apparatus is the light source, which should ideally simulate solar radiation. The main types of artificial light sources that are used are: carbon-arc, xenon-arc and fluorescent tube [64].

3.3.2.1 Carbon-arc

Until the 1960's the only light source available with sufficient radiation levels was the carbon-arc source. A typical spectrum from a carbon-arc consists of a series of line emissions that are superimposed on to a continuous background (Figure 16). The spectrum is not a good match for solar radiation, particularly at the lower wavelengths (<350nm). These high-energy short wavelengths lead to such intensive damage that it bears little relationship to any natural weathering process. In spite of these deficiencies carbon-arc lamps are still in commercial use today and their use is standardised in ISO 4892: part 4 [65].

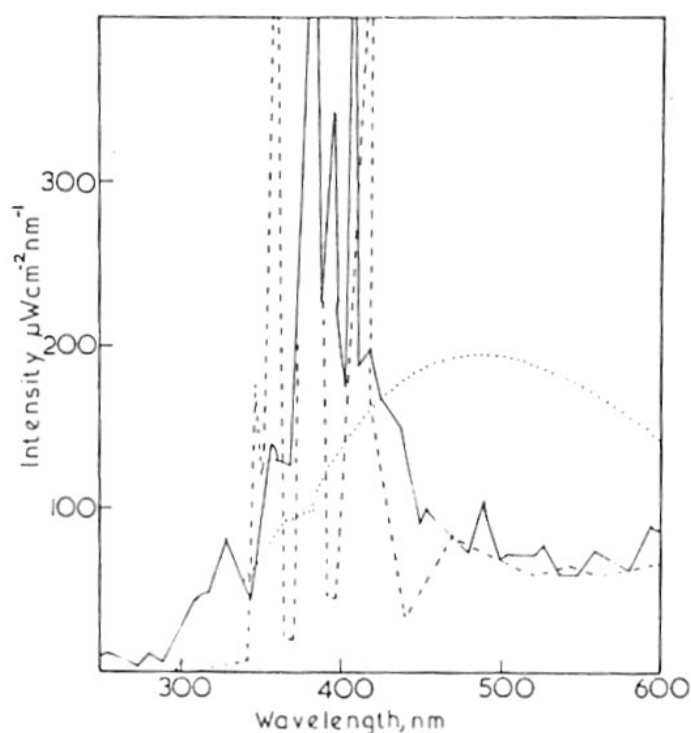


Figure 16 *Spectrum of carbon-arc lamp (—), carbon-arc lamp with a Cordex D filter (-----) and noonday Chicago sunlight (.....) [58].*

3.3.2.2 Xenon lamps

Xenon-arc lamps give a much better spectral simulation to natural sunlight (Figure 17) than other light sources but are considerably more expensive to purchase and maintain. The xenon-arc spectrum contains ultraviolet wavelengths shorter than those found in solar radiation but filters can easily remove these. Xenon lamps also emit high levels of infrared radiation, which must also be removed to prevent overheating of the specimen. Typical xenon exposure equipment such as the Xenon 1200 described by Davis and Sims [58] included water spray, light/dark cycling and humidity control. Xenon lamps are now considered to be the preferred source where the total solar spectrum is required. Test procedures for the use of xenon lamps have been standardised in ISO 4892: part 2 [66].

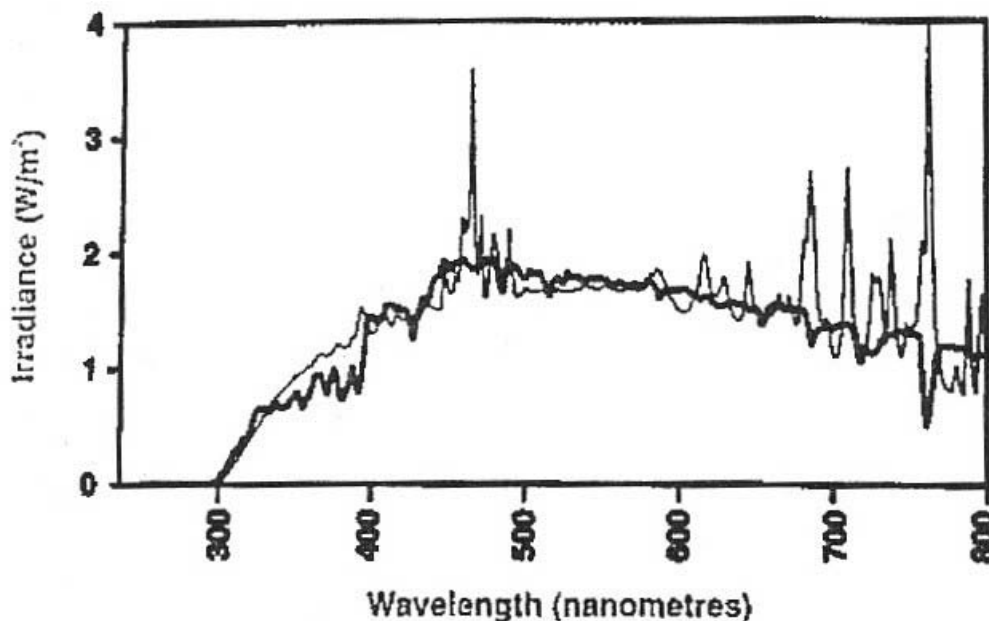


Figure 17 Spectrum of a xenon lamp (—) compared with noonday Miami sunlight (---) [64].

3.3.2.3 Fluorescent tube lamps

Fluorescent tubes are a considerably cheaper alternative to xenon-arc lamps, capable of simulating the solar spectra in the critical ultraviolet region of the spectra (Figure 18). The radiation from a fluorescent lamp is produced by re-emitting the long wavelength spectra from a low-pressure mercury vapour source. This is achieved by a phosphor coating on the inner surface of the bulbs. The spectral distribution of the light radiated by the tubes can vary depending on the type of tube used. For rapid acceleration of the tests UV-B tubes can be used. These have a strong UV peak at around 313 nm, which as a consequence accelerates the degradation process. However, they also transmit intense radiation below 270 nm, which are not found in solar radiation and can lead to degradation not found in normal service. UV-A fluorescent lamps emit radiation at a much higher wavelength producing spectra that are closer to that of solar radiation in the UV region. UVA-340 lamps manufactured

by Q-Panel have a UV spectrum (295-350 nm) that is particularly close to that of solar radiation and these are frequently used in weathering studies. Outside the UV region (>350 nm) these lamps do not emit substantial levels of radiation. As most of the degradation processes in polymers occur in the UV region this is not normally a problem. However, this characteristic does have implications for certain polymers. For example substantial degradation occurs in nylon-6 at a wavelength of 365 nm that is not well represented by fluorescent tubes. Wypych [64] gives numerous examples of other high wavelength degradation processes. Standard test procedures for the use of fluorescent tube are given in ISO 4892 part 3 [67].

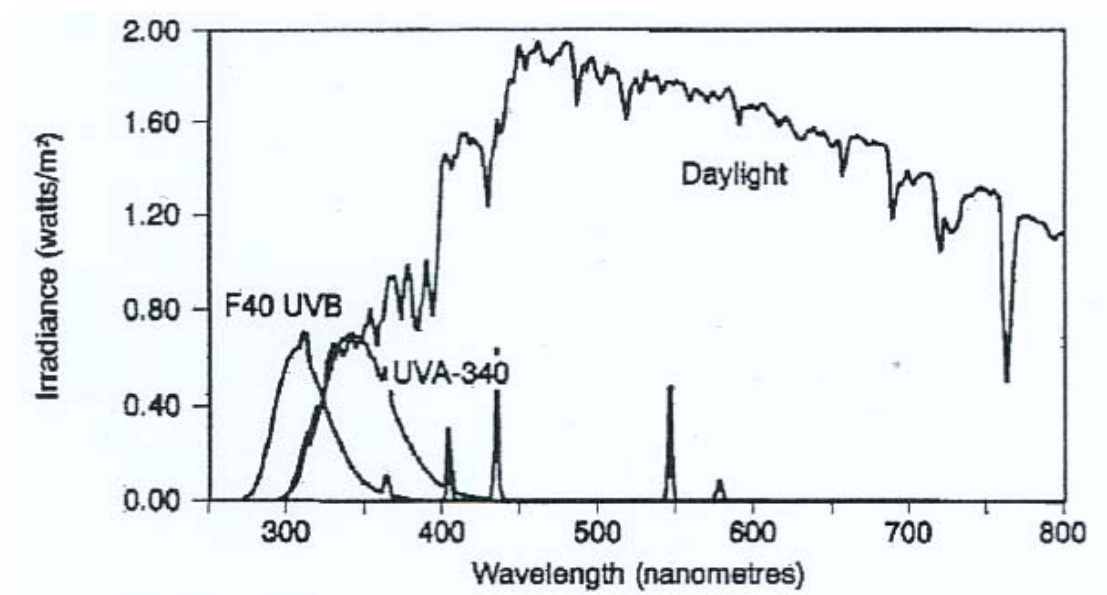


Figure 18 *Spectra of UV-A and UV-B fluorescent lamps compared to noonday Miami sunlight [64].*

3.3.2.4 Metal halide lamps

This type of lamp supplies radiation with a multi-line spectrum. The spectrum largely depends on the type and composition of the metal halide used, as well as on the type and operating conditions of the lamp. As against this disadvantage there is the advantage of 2.5 - 3 times higher radiant efficiency compared to xenon lamps. The lower heat generation linked with this, with the same effective radiant power, makes them particularly suitable for large radiation units or for equipping climatic chambers with artificial solar radiation.

3.3.2.5 Plasma treatment

Ultra-fast techniques such as plasma treatment, which induce surface damage very rapidly, have been claimed to give ranking of paints. However, when applied to PVC-U window frames, no correlation with natural or weatherometer test results was obtained [68].

3.3.3 Moisture

There are two main mechanisms by which water can influence the weathering of polymers. First there is purely mechanical stress to which the material is subjected through swelling and shrinking as a result of changing humidity and temperature [69]. Secondly there are the chemical reactions that can occur between the polymer and water, e.g. during hydrolysis (Figure 19) or in the formation of OH and HO₂ free radicals during UV exposure [70]. In both cases, the penetration of the water into the material is decisive. Due to the slow rate that water can penetrate the polymer, short humid or spray cycles do not have the same influence as longer periods of exposure. It is therefore preferential during testing to expose the specimens to prolonged spray or humidity cycles, e.g., 102 minutes dry, 18 minutes wet. In special cases, wet and dry periods in the order of magnitude of several hours can be employed.

To adjust the humidity during a weatherometer test the relative humidity of the air during must be measured at a defined point in the test room. However care must be taken in how this data is used data as it does not give a good indication of the relative humidity on the surface of the actual sample since, as a result of the impinging radiation, the sample is warmer than the test room air.

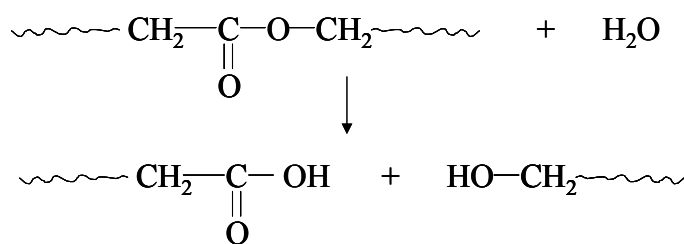


Figure 19 *Hydrolysis reaction resulting in polymer chain scission*

3.3.4 Temperature

Many decomposition processes in organic materials are temperature-dependent and as a consequence it is found that the degradation rate in weathering does increase rapidly with temperature [71]. The concept of time-temperature superposition is well established in polymer science and the effects of temperature on weathering can be predicted to a certain degree using the Arrhenius equation. Plotting curves of degradation against time for different temperatures, T , it is possible to superimpose the curves onto one another by displacing the curves along the time axis using a shift factor a_T given by the following expression:

$$a_T = \exp\left(\frac{E(T_{ref}^{-1} - T^{-1})}{R}\right)$$

where, T_{ref} is the reference temperature chosen to match the service temperature, E is the activation energy for the process and R is the gas constant. This expression has been shown to work successfully in many cases [72,73]. However, it is likely to breakdown if the temperature is shifted by a factor of 10 or if the polymer passes

through the glass transition temperature T_g . This is due to the rapid increase in the mobility of the polymer chains and free radicals above T_g , as well as increased diffusion of oxygen through the polymer.

Measuring the actual temperature of specimens during exposure tests is difficult to achieve so the temperature is normally measured using a blackened flat plate as a substitute. This gives a good approximation of the temperature of a black-coloured plastic plate during weathering and allows temperature comparisons to be made with other sites. Care should, however, be taken as on highly structured surfaces, such as textiles, as the temperature in the deeper toughs can be above the black standard temperature.

3.3.5 Stress

The presence of a tensile stress whether applied or residual within a polymer can accelerate the degradation processes and should be taken into account when testing the weatherability of polymers [74,75,76]. Furthermore, it has been shown that cyclic loading during UV exposure can significantly increase the degradation processes in a wide range of polymers including, polystyrene, polypropylene, polyethylene and nylon 6 [77-80]. The presence of cyclic stresses during outdoor exposure is particularly common as exposure to the sun can generate large thermal gradients in the plastic during daylight hours. Attempts have been made to quantify the effect stresses have on a polymer during weathering. A common approach [81] is to attribute the effects of stress to thermally activated events that are assisted by stress. This can be modelled using an Arrhenius style equation by subtracting a quantity that is proportional to the stress, σ , from the energy barrier term, ΔG . This allows the rate of degradation, r , to be given as follows:

$$r = A \exp\left(\frac{-(\Delta G - B\sigma)}{RT}\right)$$

where, A and B are constants; A is a frequency factor and B has the dimensions of volume.

3.3.6 Reprocessing

The final consideration that must be taken into account when studying the weathering of polymers is whether the material has been recycled. Much of the research conducted into the recycling of plastics has been concerned with the effects that recycling has on the immediate mechanical properties of the polymer and has not considered the effect it may have on its subsequent photo-stability. However, studies by Sadrnaghagheh and Scott [82] have shown that repeated recycling of low molecular weight polyethylene does increase the materials sensitivity to UV degradation and that alternative cycles of processing and UV exposure can significantly increase the levels of damage. The reason for this is that the degradation products can act as pro-degradants accelerating the degradation process, a process known as “auto-acceleration”. The consequences of this could be extremely serious raising quality issues regarding the vulnerability of recycled material to UV degradation.

3.4 Monitoring of weathering

3.4.1 Introduction

The magnitude of degradation that is observed in a polymer will depend on the properties that are monitored. Ideally a range of different properties should be monitored, however, this can be prohibitively expensive and in practice only one or two techniques may be used. The factors that influence the choice of techniques include:

- Relevance to service conditions and the failure criteria
- Applicability to non-destructive testing
- Relationship to fundamental mechanism
- Sensitivity and reproducibility
- Cost

As degradation due to weathering is normally highly concentrated at the surface of a polymer the ability of a technique to detect changes at or near the surface is highly desirable and in recent years full depth profiling of the material properties has been pursued using techniques such as nanoindentation [83], for modulus and hardness measurement, and FTIR with attenuated total reflectance for chemical analysis. Such techniques reveal more details of the properties of the degraded surface layer [84] and in principle, may improve quantification of the rate of material degradation as a function of time in the proximity of the surface.

The following section examines the physical, mechanical and chemical techniques that can be used to monitor the weathering of polymers. Characteristics of the polymer that can be used include physical properties such as the glass transition temperature (using DSC) and molecular weight (using GPC); mechanical properties, using microhardness, nanoindentation and DMTA; and changes in chemistry using FTIR (e.g. carbonyl index), loss of volatiles (using TGA) and the usual surface analytical techniques such as visual inspection, haze and gloss.

3.4.2 Physical techniques

3.4.2.1 Visual inspection

The visual appearance of a polymer surface can change significantly due to weathering and often in itself can render a product unsuitable for service. Moreover changes in surface appearance may indicate that the extent of the degradation has reached a point at which mechanical failure is imminent. Procedures for the precise measurement of light transmission, haze, gloss and colour changes are given in standards: ISO 13468 [85,86], ISO 14782 / ISO 2813 [87,88] and ISO 7724 [89] respectively. These techniques are particularly useful for the monitoring of degradation as in most cases they are non-destructive. The effect that weathering can have on the gloss and colour of a polymer is demonstrated in Figures 20 and 21 for UPVC that has been exposed to ultra fast weathering using oxygen plasma treatment [68]. For a more in-depth inspection of polymer surfaces light microscopy may be used. This technique again is simple to use and non-destructive but does require more highly skilled interpretation of the results [30,90-92]. The most common features of interest on a degraded polymer surface are small cracks and crazes. These are easily within the resolution and depth-of-field limitations of most light microscopes. More

powerful techniques such as Scanning Electron Microscopy (SEM) are of invaluable for use in failure analysis as they have the depth of field that is required for examining fracture surfaces. However, the specimen chamber in an SEM is normally relatively small requiring all but the smallest specimens to be cut. Polymer specimens also need to be coated with a conductive coating to prevent charging of the surface that will prevent an image being observed [30,90,92]. This coating will nearly always prevent the specimen going back into service.

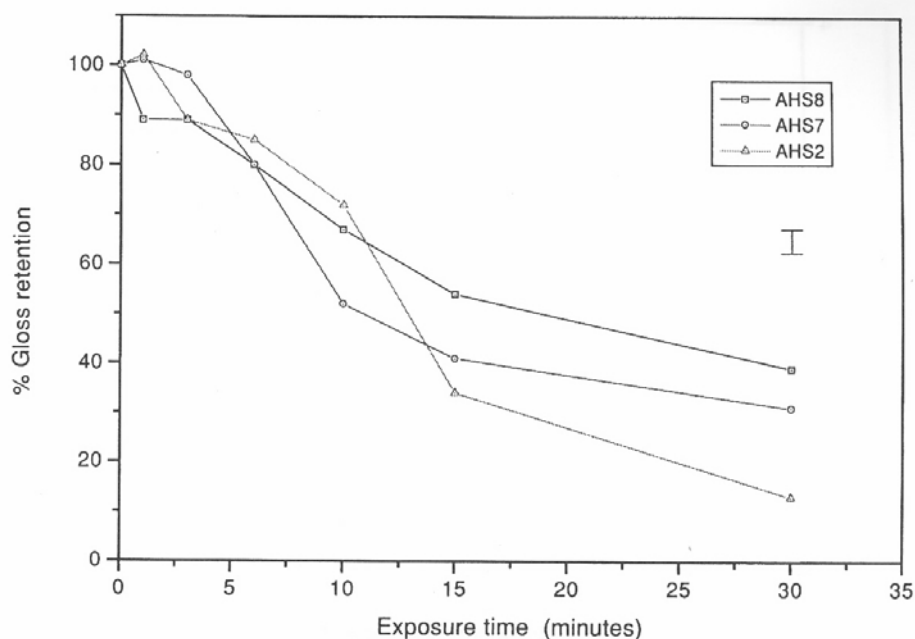


Figure 20 *Reduction in gloss during the artificial weathering of UPVC measured using a Rhopoint Labgloss Instrument [68]*

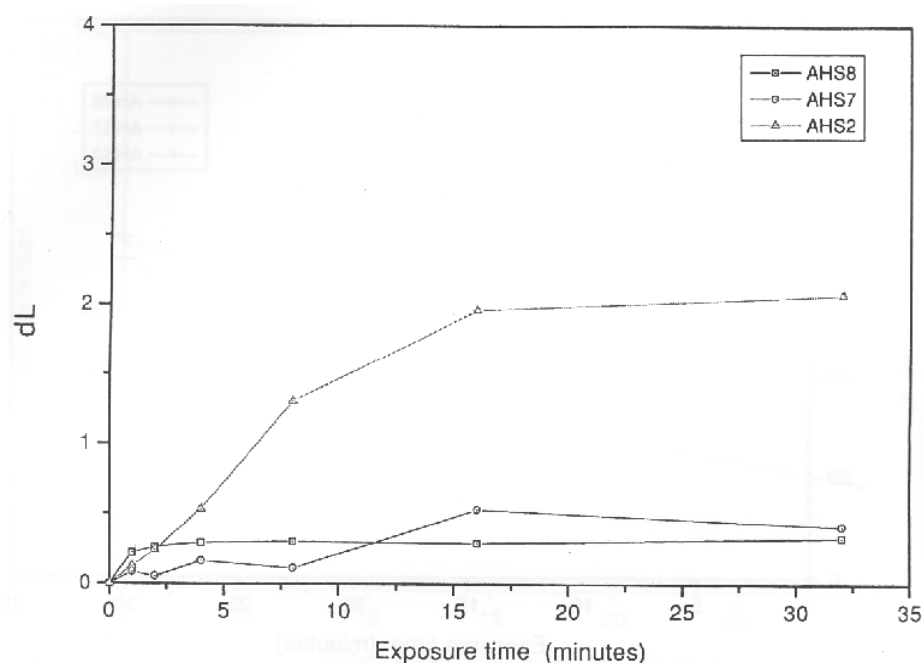


Figure 21 *Change in colour during artificial weathering of UPVC measured using a Spectrogard colour system [68]*

3.4.2.2 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is an extremely useful tool for monitoring the weathering of polymers (ISO 11357) [93,94]. Changes in the glass transition temperature (T_g), loss of stabilisers and increases in crystallinity can all be detected. A description of the DSC technique is given in section 2.3.2.2. The effect of weathering on T_g is particularly noticeable, after one year of outdoor exposure in Jeddah the glass transition temperature of PVC and polystyrene were both observed to fall by over 20°C [95]. The glass transition temperature can, however, be difficult to resolve using DSC, particularly for semicrystalline polymers.

Weathering also significantly increases the crystallinity of a polymer as a consequence of the breakdown of polymer chains increasing molecular mobility. Crystallinity can be measured using DSC by dividing the exothermic peak for the heat of fusion required to melt the crystals in the polymer sample by the theoretical heat of fusion for a 100% crystalline specimen, as follows:

$$\% crystallinity = \left(\Delta H_{sample} / \Delta H_{100\% crystalline} \right) \times 100$$

3.4.2.3 Gel permeation chromatography (GPC)

Gel Permeation Chromatography (GPC) [96] is one of the most useful techniques for determining the molecular weight distribution of polymers. As chain scission is generally considered to be the main cause for the observed decrease in the mechanical properties of weathered polymers, molecular weight is a convenient parameter to follow the degradation process. The advantage of GPC over other techniques is that it provides the entire molecular weight distribution of the polymer, which can provide valuable information about the underlying degradation process. Specimens may be taken at different depths from within a specimen offering the possibility of obtaining depth profile of degradation within the polymer. The two main limitations of the technique are that it is destructive and that despite many improvements over recent years GPC still requires highly skilled staff to operate.

3.4.3 Mechanical Techniques

3.4.3.1 Tensile testing

The most common test method used to examine the mechanical properties of all materials is the tensile test. This simply involves stretch a test piece to breaking point using constant crosshead displacement, whilst measuring the load and displacement (ISO 527) [97]. Performance can be judged using the tensile strength, modulus or elongation to break. There are, however, two main limitations using these tests for assessing weathered polymers. The first is that the results obtained are not specifically those of the weathered material but are an average of the whole test piece. The second problem is that the tests are destructive and therefore can only be used after material has been taken out of service.

3.4.3.2 Hardness / microhardness

The measurement of hardness is a cheap, simple and almost non-destructive method of determining the mechanical properties of a polymer. It is essentially a measure of a materials resistance to indentation and therefore relates specifically to the layer into which the indenter penetrates. Standard test methods for the measurement of hardness

are the Shore test (ISO 868) [98] the Ball indenter test (ISO 2039 Part 1) [99] and the Rockwell test (ISO 2039 Part 2) [100]. These techniques are not, however, suitable for measuring the properties of the thin degraded surface layers that are found on weathered polymers as the indenters will normally penetrate beyond the degraded region. Microhardness is a more suitable technique for weathered polymers, as the indenter does not penetrate as deeply into the polymer surface [83,101]. This allows changes in the hardness of the polymers surface due to weathering to be detected (Figure 22) however it is still too insensitive to accurately determine the hardness as a function of depth.

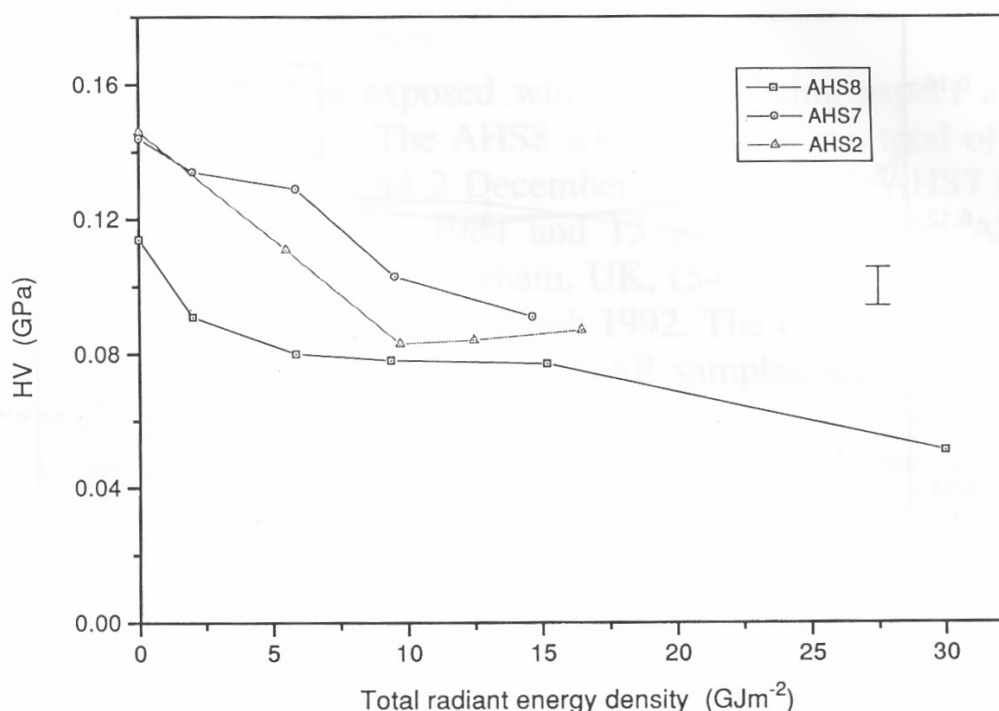


Figure 22 *Change in Vicker's hardness of naturally weathered UPVC measured using a microhardness instrument [68].*

3.4.3.3 Depth-sensing indentation

Conventional measurements of microhardness are obtained by optically measuring the indent that is left behind after the indenter tip has been removed. As a consequence, the measurements obtained using this technique exclude any elastic recovery that occurs during unloading and therefore relate purely to the yield and plastic properties of the polymer. However, information related to the elastic properties of the polymer can be obtained using depth-sensing indentation [41,42,43]. This involves monitoring both the load and the displacement throughout the indentation process allowing the modulus of the polymer to be determined while the polymer is still fully loaded ($h_{\max}$) from the load-displacement curve (Figure 23). Depth-sensing instrumentation has allowed the development of significantly finer indentation test machines that are capable of measuring the mechanical properties on a much finer scale enabling modulus depth profiles to be achieved [83].

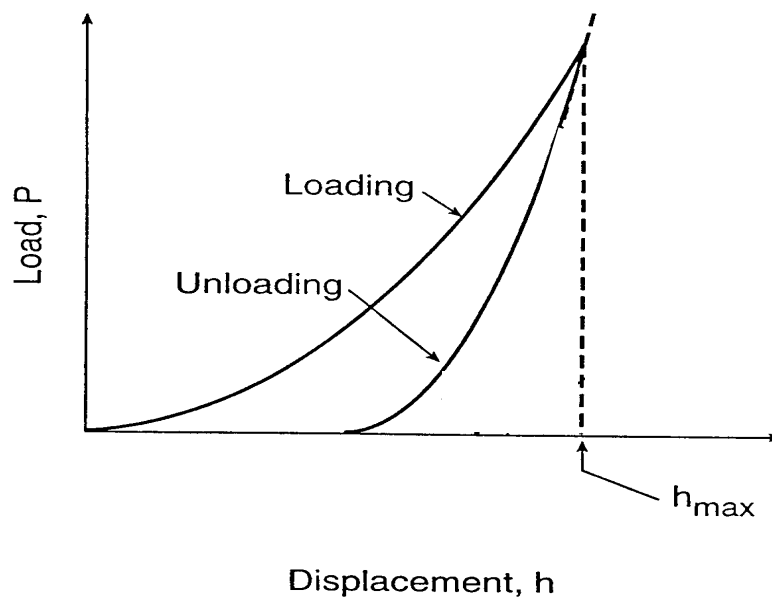


Figure 23 *Schematic diagram of the load-displacement curve obtained from depth-sensing indentation. Values for modulus and hardness are obtained while the specimen is still loaded at its maximum indentation depth ($h_{\max}$), enabling both the elastic and plastic properties of the polymer to be measured.*

3.4.3.4 Dynamic mechanical thermal analysis (DMTA)

The best technique for monitoring changes in the stiffness (E' and E'') and the glass transition temperature (T_g) of a polymer is DMTA, details of which are given in section 2.3.2.3 [30,36-38]. The main limitation to DMTA is that it is difficult to assess degradation through the thickness of the specimen. A series of thin specimens may be extracted from different layers below the surface to obtain a depth profile through the material. However, the thinnest section that can be practically taken is around 0.2mm thick. This severely limits the ability to determine changes through the thickness of the polymer. An alternative approach is to measure the modulus of the entire cross-section and then to repeatedly machine away thin layers repeating the measurement each time [102]. A depth profile of the modulus through the entire specimen can then be obtained. However, repeated machining may cause further damage to the polymer and is extremely time consuming and costly.

A more effective method of measuring T_g through the thickness of a specimen would be to use depth-sensing indentation with continuous stiffness [44]. The use of a depth-sensing instrument (section 3.4.2) enables the mechanical properties of the material to be examined in the nanometre range allowing depth profiling to be conducted. The use of continuous stiffness (section 2.3.2.3) also makes it possible to determine the loss and storage moduli (E' and E'') over a range of temperatures [45]. This raises the possibility that depth-profile of the glass transition temperature and secondary relaxation peaks could be obtained using this technique. However, further work will be required to establish whether this can be achieved in practice.

3.4.4 Chemical techniques

3.4.4.1 Infrared spectroscopy

The most commonly used chemical technique for monitoring weathering in polymers is infrared spectroscopy [30,49,50]. This makes use of the fact that chemical species can be identified from the infrared frequencies they absorb (section 2.3.3.1). The main degradation products that occur due to weathering are the carbonyl groups that produce intense absorption peaks at wavelengths between 1710-1740 cm^{-1} . By measuring the intensity of these peaks and normalising them with the signal from another part of the spectrum well removed from the carbonyl peaks it is possible to monitor the weathering process. This technique is known as the carbonyl index and is widely used. The peaks in polyethylene that are most commonly examined for the carbonyl index are 722, 1465 and 1895 cm^{-1} , these correspond to methylene rocking [103], methylene stretching [104] and C-H deformation [105], respectively. The carbonyl index can give a good overall idea of the extent of weathering in a polymer. However, it does have its shortcomings, particularly as there is no universal agreement as to how to measure this quantity or how the results relate to the loss of mechanical properties [106].

As degradation due to weathering is normally highly concentrated at the surface of the polymer the ability to detect changes at or near the surface is highly desirable. This can be achieved using an attenuated total reflectance system (section 2.3.3.1). Examination of the polymer at different depths can be achieved by examining thin sections taken from the surface of the polymer. However, this is extremely time-consuming, requires considerable skill and is of course destructive.

3.4.4.2 Thermogravimetric analysis (TGA)

The best technique for monitoring the loss of volatile chemicals, such as stabilisers and plasticisers, during weathering is TGA [30,31]. This involves heating the specimen at a constant rate whilst continuously measuring the weight of the specimen. Weight losses that occur as the temperature is increased are used to determine the quantity of different volatiles present in the polymer. The chemical composition of these volatiles can also be identified by examining the effluent from the TGA using either infrared spectroscopy (TGA-FTIR) or mass spectroscopy (TGA-MS).

TGA-FTIR is a relatively simple technique to set up and is particularly useful at identifying volatiles with simple IR spectra, such as CO_2 and HCl. However, there are many limitations to this technique as it cannot detect gases that have little or no IR absorbance such as oxygen, nitrogen and H_2S . Furthermore, it is extremely difficult to distinguish between hydrocarbons higher than propane. In such case mass spectroscopy (TGA-MS) is preferred.

3.4.4.3 ATD-GC/MS

ATD-GC/MS [107] is a multiple-technique that is capable of characterising the volatiles that are present in a polymer due to oxidation. The technique involves three main steps: Automated thermal desorption (ATD); Gas chromatography (GC); and Mass spectroscopy (MS). First volatiles are extracted from the polymer by passing a continuous stream of gas over the specimen and collecting the volatiles in a cryogenic trap (ATD). These are fed through the GC/MS system that separates out the different components, characterising them using the mass spectrometer. The spectrum

produced allows a compositional analysis to be made of the different volatiles. The technique has been shown to distinguish between different polymer grades, manufacturing routes and the effects of thermally ageing. The main drawback of the technique is that the spectra can be extremely difficult to interpret. This could be overcome by comparing the weathered polymer to unexposed material.

3.5 Prediction techniques

Prediction techniques in the context of weathering are predominantly centred on the correlation of artificial weathering with natural exposure. The principle requirements for a meaningful accelerated test are that ranking of materials should be successfully predicted and that a basis should be established for long-term prediction in service. A damage-function based on laboratory tests that takes account of the range of weathering parameters and can be applied to a wide variety of locations and, hence, exposure conditions seems unrealistic [108-111]. A more realistic goal is to focus on predicting degradation for a particular climatic condition. The prediction of long-term performance in service depends on the ability to predict the rate of degradation due to natural weathering from laboratory tests. It is insufficient to demonstrate that 2 months in a weatherometer with a specified weathering cycle is equivalent to 2 years say in natural conditions, for which data may be known as a reference point, unless for example there is a framework for predicting the extent of degradation at 15 years. If the trends in the degradation rate are quite different its significance is questionable. A detailed comparison of artificial and naturally weathered UPVC window frames [112] showed that the rate of change of damage with dose was so sensitive to the exposure conditions that quantitative prediction was untenable.

For ranking of materials, it is necessary to demonstrate that the relative performance of the different materials, in terms of the extent of degradation, is consistent with that observed in natural conditions. Turnbull et al [112] concluded from a detailed study of UPVC material with three different formulations that the ranking of these materials was consistent for the natural and artificial weathering provided that the artificial weathering was not too extreme. In that context, it is important that a reference formulation, for classes of material, which is well characterised in terms of outdoor exposure should be adopted for laboratory testing. This would provide a basis for quality control, for comparison of different weathering apparatus and a basis for relative life prediction. There are challenges because of the ageing aspects of polymers and it may be necessary to have different reference materials for different classes of material but in principle these can be overcome.

Fundamental modelling to predict degradation presents a major and possibly insurmountable challenge given the complexity of modern polymers with the numerous additives and stabilisers and the input data requirements. The minimum data are required are the rate constants for all of the reactions and the diffusion coefficients of all of the species including reactants such as oxygen and low molecular weight stabilisers, and the products of the reaction. The model would have to account for the concentration of all these species with respect to time and position and have to allow for the attenuation of UV level as a function of distance from the exposed surface, the nature of which is evolving with time as degradation proceeds.

4 Concluding remarks

4.1 *Environmental stress cracking*

1. Numerous test methods have been developed for assessing ESC susceptibility using constant stress and strain. The use of an applied stress rather than strain is often preferred for ESC testing as stress relaxation can significantly influence the results obtained from constant strain tests.
2. Standard ESC test methods almost all involve full immersion of the polymer in solvent. There are, however, concerns that full immersion for extended periods of time may inhibit ESC by swelling the polymer and blunting crack tips.
3. The ability to detect localised property changes at the surface of the polymer is essential for the monitoring of ESC. To aid the monitoring of ESC in inaccessible structures such as pipelines and storage tanks there is a need to develop protocols for the use of self-loading test coupons for plastics.
4. Solubility parameters have been successfully used to predict ESC susceptibility in simple screening tests. However, considerable work would be required before life-time assessments could be made, particularly in relation to the influence stress has on the diffusion of solvent within the polymer.

4.2 *Weathering*

1. A number of ultra violet exposure systems are available for the accelerated weathering of polymers. The instrument that most closely simulates the solar spectrum of light is the Xenon system, however, this is also the most expensive.
2. As weathering damage is normally highly concentrated at the surface of a polymer the ability to monitor degradation at or near the surface is required and full-depth profiling of the material properties is highly desirable.
3. The degradation processes that occur during weathering are complex and modelling has proved extremely difficult. Correlation of accelerated test results to natural weathering is therefore normally achieved by ranking the results to a material with a known in service performance.
4. A key issue that requires further study in weathering is the effect that degraded material has in accelerating the weathering process. The consequences of this could be extremely serious for the use of recycled material raising quality issues regarding its vulnerability to UV degradation.

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