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Review
Weathering of polymers: mechanisms of degradation and stabilization, testing strategies and modelling

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The weathering of polymers is reviewed with attention concentrated on the mechanisms of degradation and stabilization, the methods of testing weatherability, and the predictive modelling of weathering behaviour. An introduction to the chemical mechanisms of degradation and stabilization is given and reference made to some of the many reviews available in the literature. Significant emphasis is placed here on engineering aspects, such as the way that weathering influences fracture mechanisms. The difficulties associated with relating accelerated laboratory tests with outdoor service behaviour are discussed. The complexities of the degradation processes limit modelling of the rate of degradation to rather specific systems and the predictions cannot be generalized.

1. Introduction

Degradation of components made from polymeric materials occurs in a wide variety of environments and service conditions, and very often limits the service lifetime. Degradation occurs as the result of environment-dependent chemical or physical attack, often caused by a combination of degradation agents, and may involve several chemical and mechanical mechanisms. For example, many polymers are prone to degradation caused by weathering in which photochemical reactions, involving ultraviolet solar photons and atmospheric oxygen, lead to chain scission. The chemical reactions may be accelerated by elevated temperatures caused by the warming effect of the sun. Alternatively, or additionally, the chemical reactions may be accelerated by the presence of stress that may be applied externally, or may be present in the form of moulding stress, or as the result of a temperature gradient or of differences in thermal expansion coefficient at different locations within the moulding. Failure is often simply taken as the fracture of the component, but degradation of some other property, such as the transparency or surface gloss, may render a component unserviceable.

In broad terms, the majority of failures that are the consequence of polymer degradation can be attributed to one of three types of source:

(a) Molecular degradation caused during processing, usually due to elevated temperatures (as in melt processing) and often in combination with an oxidizing atmosphere.

(b) Degradation in service caused by the natural environment, as in the example in the first paragraph above.

(c) Attack by an aggressive chemical, again during the service lifetime.

The type of degradation referred to in (c) includes as the major problem environment-sensitive fracture, in which contact with a liquid chemical leads to craze initiation and growth. This can be a particular problem with consumer goods, where the service conditions are not under the control of the supplier; the end-user may employ an inappropriate cleaning fluid, for example. Significant research has been conducted in this area over the past 20 years and several test procedures have been developed. The present review is focused primarily on area (b), in which degradation is caused by the natural environment. Molecular degradation that occurs during fabrication may render the polymer more vulnerable to further damage during subsequent natural weathering, however, and some consideration is given to area (a).

Thus the main concern of this review will be to examine the causes of degradation of polymeric components from the completion of fabrication to ultimate failure. It will be necessary to examine the mechanisms of failure and the features of the environment that control them, and then to look for possible

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remedies. The methods of testing are discussed with reference to their application in establishing ranking orders for plastics with respect to their weather resistance; in determining the effectiveness of additives such as anti-oxidants; in providing data for lifetime prediction; and in research into the mechanisms of failure and the development of improved materials. There are elements of degradation behaviour that are common to all polymers and elements that are peculiar to a particular polymer. Much research has been conducted on the important commodity polymers poly (vinyl chloride) (PVC), polyethylene and polypropylene, and these materials are used by way of example in this review.

2. Mechanisms of degradation

2.1. Chemical mechanisms of degradation

In an aggressive chemical environment polymer molecules may break (chain scission), cross-link, or suffer substitution reactions. Substitution is the least common and causes the smallest property changes and will not be considered further in this review. Scission and cross-linking both occur under natural weathering conditions, and molecular degradation can also take place during processing. There is general agreement that molecular degradation occurs almost exclusively at defects in the molecule. Much research has been conducted into the chemical reactions involved and there are many papers and several reviews on this topic [1–7].

2.1.1. Photo-oxidation

Of major importance is the process of photo-oxidation. This proceeds by a radical chain process initiated either by dissociation caused by the collision of a photon with sufficient energy with a polymer molecule, or as the result of some impurity present, for example trace metals from the polymerization catalyst. Once initiation has occurred, converting the long-chain polymer molecule, PH, into a radical, $P^{\bullet}$, the reactions are as listed by Davis and Sims [8]:

(i) Propagation:

$$P^{\bullet} + O_2 \rightarrow POO^{\bullet} \qquad (1)$$

$$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet} \qquad (2)$$

(ii) Chain branching:

$$POOH \rightarrow PO^{\bullet} + HO^{\bullet} \qquad (3)$$

$$2POOH \rightarrow POO^{\bullet} + PO^{\bullet} + H_2O \qquad (4)$$

$$PO^{\bullet} + PH \rightarrow POH + P^{\bullet} \qquad (5)$$

$$HO^{\bullet} + PH \rightarrow P^{\bullet} + H_2O \qquad (6)$$

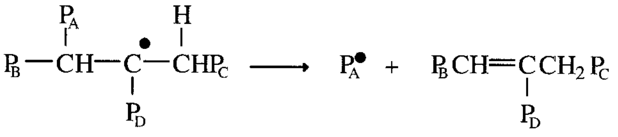
Some alternative reactions are given by other authors [9, 10] as

$$POOH \rightarrow P^{\bullet} + {}^{\bullet}OOH \qquad (7)$$

$$POOH + PH \rightarrow PO^{\bullet} + P^{\bullet} + H_2O \qquad (8)$$

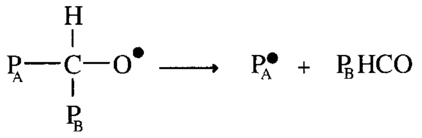
Termination is then normally through the reaction of pairs of radicals. The reaction schemes are affected by trace metal impurities such as polymerization catalyst residues or contaminents from processing machinery, for these may catalyse some of the degradation reactions, for example Reaction 4 [11]. Degradation can still occur slowly in the dark through the formation of hydroperoxides through intramolecular back-biting hydrogen abstraction by peroxy radicals [12].

The reactions listed above would not cause serious degradation of the engineering properties of the material as they stand because the long-chain nature of the polymer molecules is preserved almost unchanged. Degradation occurs because the radicals are unstable and may undergo scission reactions. For example, alkyl radical decomposition is as follows:



$$P_B{-}\overset{P_A}{CH}{-}\underset{P_D}{\overset{\bullet}{C}}{-}\overset{H}{C}HP_C \longrightarrow P_A^{\bullet} + P_BCH{=}\underset{P_D}{C}CH_2P_C \qquad (9)$$

Two smaller molecules are produced, one of which is a radical and may participate in further reactions of the kind shown above. β-scission of alkoxy radicals produces a similar result:



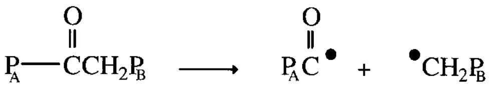
$$P_A{-}\underset{P_B}{\overset{H}{C}}{-}O^{\bullet} \longrightarrow P_A^{\bullet} + P_BHCO \qquad (10)$$

Discussion of scission reactions for polypropylene is given in a recent paper by Severini *et al.* [13].

Hydroperoxides produced by Reaction 2 or by other means can be decomposed by u.v. radiation with wavelength below 360 nm giving a $PO^{\bullet}$ radical, as shown in Reaction 3. The decomposition of hydroperoxides is generally acknowledged to be a key feature in the degradation of polyolefins, though their behaviour in polyethylene, in which they do not accumulate during photo-oxidation, is different to that in polypropylene, in which they do accumulate [14]. (Note that hydroperoxides accumulate both in polyethylene and polypropylene on thermal oxidation [15]).

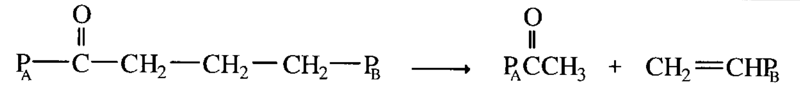
The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also warns that the material is vulnerable to further deterioration because they are photo-labile. Aldehyde and ketone carbonyl groups are common products during processing and the effect of processing on the subsequent degradation behaviour has been identified as of significant importance [15]. Two important photolytic decomposition reactions for aliphatic ketones are:

(i) Norrish type I:



$$\mathrm{P_A{-}\overset{O}{\overset{\|}{C}}CH_2P_B \longrightarrow P_A\overset{O}{\overset{\|}{C}}{}^{\bullet} + {}^{\bullet}CH_2P_B} \qquad (11)$$

(ii) Norrish type II:



$$\mathrm{P_A{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CH_2{-}P_B \longrightarrow P_A\overset{O}{\overset{\|}{C}}CH_3 + CH_2{=}CHP_B} \qquad (12)$$

Although most studies of photo-oxidation have centred on u.v. radiation, the need for information on the behaviour of polymers for insulation (polyethylene) and jacketing (PVC) in nuclear installations has stimulated study of the effect of γ-radiation. Clough and Gillen [16, 17] found that radiation dose and temperature act synergistically in promoting degradation.

2.1.2. Thermal decomposition and oxidation

Thermal degradation is of relevance here because damage suffered by the polymer during processing at elevated temperature can lead subsequently to further deterioration under the conditions of photo-oxidation. Thermal degradation is a serious problem with PVC and has been the subject of much research. The initial step in the process of degradation is dehydrochlorination, with hydrogen and chlorine atoms on adjacent chain carbon atoms stripping off to form HCl and leaving behind a double bond in the polymer backbone. Adjacent sites become less stable, more HCl may be stripped off, and a conjugated polyene structure develops. This causes yellowing of the material. HCl catalyses the reaction which is therefore auto-accelerating unless steps are taken to remove the HCl. The process is accelerated in oxygen but can occur in the absence of oxygen at temperatures above 120 ° C [18]. Troitskii and Troitskaya [19] conclude that abnormal unstable fragments have a major influence over thermal degradation of PVC.

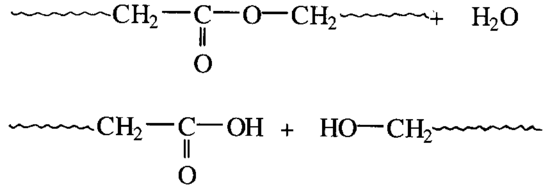
Mechanico-chemical degradation may occur during processing, producing free radicals that may then initiate dehydrochlorination in PVC [20, 21]. It is expected that dehydrochlorination will initiate at pre-existing defect sites in the polymer, though there is evidence that it may not be restricted exclusively to them [20]. The small amount of oxygen present during processing allows the formation of hydroperoxides by reaction with radicals. After thermal degradation the polymer will suffer further degradation during later stages in processing, or under other conditions favouring thermal oxidation, or under conditions of photo-oxidation [22]. Even though the shearing action during processing is generally believed to promote molecular damage, the inclusion of lubricants to reduce the viscosity during processing does not produce any significant reduction in the vulnerability of the product PVC to oxidation [23]. The susceptibility to further degradation will depend on the amount of HCl present, the degree of unsaturation and on the hydroperoxide content [20].

Although generally regarded as a lesser problem than with PVC, degradation of polyolefins occurs during processing as well. Mellor *et al.* [24] found that the lifetime under u.v. exposure was very sensitive to the degree of oxidation that took place during processing on a two-roll mill and that the rate of u.v. degradation was related to the increase in melt flow index that occurred in the material.

Billiani and Fleischmann [25] used the weight-average molecular weight, M_W, to assess molecular degradation during injection moulding of polypropylene and found that it was more sensitive to increases in melt temperature than to increases in shear rate. There was no significant difference between the molecular weight of material taken respectively from the skin and the core, and they deduced that degradation occurs in the plasticizing system and/or in the sprue. Amin *et al.* [26] claimed that processing low-density polyethylene (LDPE) at 160 ° C produces hydroperoxides that have a photo-initiating effect, whereas those produced by thermal oxidation in the range 85–95 ° C do not [26]. This has been examined further by Lemaire and co-workers [27, 28] and by Gugumus [29] who discuss the chemistry of oxidation and the nature of the oxidation products. Gugumus further claims that the mechanisms may be adapted to other polymers including non-olefinic polymers such as polystyrene and polyamides [29], though this may not be so because Ginhac *et al.* [27] report that hydroperoxides which initiate new oxidation reactions form in polypropylene under thermal oxidation conditions that do not cause the formation of active hydroperoxides in polyethylene.

2.1.3. Hydrolysis

Hydrolytic attack can cause chain scission in some polymers, leading inevitably to a deterioration in properties. A general hydrolysis scheme can be summarized as follows:



$$\mathrm{\sim\sim CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2\sim\sim + H_2O \longrightarrow \sim\sim CH_2{-}\underset{O}{\underset{\|}{C}}{-}OH + HO{-}CH_2\sim\sim}$$

Polymers susceptible to this kind of attack include polycarbonate. The reaction can be unacceptably fast at elevated temperature and can be a problem with articles that need to be sterilized. Some polymers absorb water, leading to other problems. Nylons become plasticized and their Young's modulus can fall by as much as an order of magnitude. Some relevant references are given in a recent paper by Paterson and White [30]. When water is absorbed in polycarbonate in sufficient quantity it can form disc-shaped defects that act as stress-concentrating flaws and cause a serious fall in toughness. A review of the literature and some new results have been presented recently by Qayyum and White [31].

2.1.4. Attack by pollutants

The attack of polymers by pollutants has been reviewed by Rånby and Rabek [32]. Some of the pollutants themselves are photolytic, leading to further products that may cause degradation. For example, SO_2 photo-oxidizes and reacts with water to produce H_2SO_4.

2.2. Mechanical degradation

If a chemical bond is placed under sufficient stress it will break. It may not always be easy to apply such a stress because deformation mechanisms intervene. For a polymer chain bond to be broken, the segment in which it is contained must not be able to uncoil (i.e. it must be extended between entanglements or cross-links already) nor slip. Such constraints may be present in a cross-linked polymer, where the short chain segments become fully extended at fairly low extensions, or in a highly oriented polymer, or possibly at the tip of a growing crack. Molecular fracture has been shown to occur in this way using electron spin resonance to detect the free radicals that are produced when chain scission occurs (see section 6.5 below).

2.3. Stress-aided chemical degradation

The phenomenon of mechanico-chemical degradation (or sometimes more specifically "mechanico-oxidative" degradation) has been known to occur in rubbers for many years [33]. The effect of stress on the rate of chemical degradation in a much wider range of polymers has been reviewed by Terselius *et al.* [34] and Popov *et al.* [35]. Unlike the case of mechanical degradation dealt with in the previous section in which very high stresses are needed to break a chain bond, a more modest stress may accelerate scission caused by chemical reaction. The most highly stressed bonds will still be the most likely to react [36, 37] so that bonds contained within short segments or highly strained bonds near entanglements will be most vulnerable. Highly oriented polymers are generally more resistant to this type of attack than when in more randomly oriented form because the molecules tend to share the load evenly, so that the chance of overstressing is much less. Nevertheless, the rate of oxidation of oriented polypropylene at 130° C was found to increase with load at high loads [38, 39].

Rapoport *et al.* [40] argue that the bond rearrangements required in the oxidation reaction are more easily achieved in a coiled molecule so that an oriented polymer will oxidize more slowly. Another reason is that diffusion of oxygen is generally lower in an oriented polymer [35]. A further relevant factor is that the diffusion rate of stabilizer is lower in an oriented polymer [35]; this may be either beneficial or detrimental, depending on the exact mechanisms of degradation and stabilization in operation (see section 3). Although many of the laboratory experiments upon which these conclusions were based were conducted on mechanically drawn samples, similar improvement in stability was found for low-density polyethylene blown film [41]. The majority of the studies found in the literature are on polypropylene or polyethylene, but Bellenger *et al.* [42] reported that orientation actually increases the sensitivity of PVC to photodegradation, suggesting that stretching gives rise to conformations that are especially prone to hydrogen abstraction by radicals.

Stress can alter the effective activation energy for a chemical reaction [43] and much of the quantitative analysis of the effect of stress is based on the equation usually attributed to Zhurkov [44] in which the rate of degradation r is given by an Arrhenius-type expression modified by subtracting from the energy barrier term, ΔG, a quantity that is proportional to the stress, σ. Thus the rate of degradation can be expressed as

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

where A and B are constants; A is a frequency factor and B has the dimensions of volume. Essentially the same equation was derived by Bueche [45–47] but his work has received less attention, possibly because he attempted to derive expressions for A and B and so disguised somewhat the basic simplicity of its form.

Stress may cause a change in the diffusion rates of the various mobile molecules and this may alter the reaction rates [35]. Popov *et al.* [35] note that residual stresses have exactly the same effect as externally applied stresses [32–34]. They emphasize that internal stress/residual stress and molecular orientation are not the same thing, and that there is a regrettable tendency in the literature to confuse them, a point made elsewhere by White and co-workers [48, 49]. Popov *et al.* [35] further observe that the oxidation may induce stresses locally and that these stresses may influence subsequent reaction. They claim that whereas tensile stresses generally accelerate degradation, compressive stresses will often retard it [35, 50]. This has been observed by DeVries and Hornberger [51] who found that residual compressive stresses formed at the surface of polycarbonate and polystyrene by rapid quenching improved the resistance to pollutant gases. Stresses may alternatively arise as the result of absorption or desorption of water [31, 52–57] or of secondary crystallization [58, 59]. Secondary crystallization may even be promoted by changes that occur as the result of weathering. For example, entanglements in the amorphous phase may be released as the result of scission [60] which occurs preferentially at distorted bonds, freeing chain segments to crystallize on neighbouring crystallites; this is known as "chemi-crystallization" [61–63], or sometimes "oxidative crystallization" [35].

2.4. Effects of processing: morphology

Much of the discussion of thermal degradation in section 2.1.2 is related to the problem of molecular degradation during processing, when the temperature required to produce the desired flow properties for a moulding operation is often high enough to promote significant degradation, especially if oxygen is present. Sometimes the forces on the melt are sufficient to cause mechanical scission (section 2.2). There will often be circumstances during processing operations in which stress-aided chemical degradation will occur; section 2.3 addresses this problem in the formed product, but some degradation of this kind may have already occurred during processing.

There is a further aspect of processing that has not yet been dealt with and that is the morphology of the moulded or formed polymer. The rate of cooling is often quite high in moulding operations and varies considerably from one position within the moulding to another. As a consequence the morphology of a semi-crystalline polymer varies substantially within an injection moulding, which normally contains equiaxed spherulites in the core and an oriented structure near to the surface. This is discussed further in section 6.9. The important point to note here is that degradation reactions occur almost exclusively in the amorphous phase because it takes up oxygen much more readily than the crystal phase [64] and that there can be a strong influence exercised by the morphology. It is further suggested that oxidation may occur preferentially at the crystal–amorphous boundary where the effects will be most damaging [65–67]. Nishimoto *et al.* [68] found that the crystal structure of their polypropylene samples varied with the quenching conditions and that there was a marked variation in property deterioration even though the (γ –) radiation-induced oxidation did not differ. The diffusion rates of the various reactants are very different in the crystal and non-crystal regions of most polymers.

Another morphological feature is molecular orientation, which can occur in either crystalline or amorphous regions. There have been several studies of the effect of orientation on the degradation of polymers and some of them are referred to in section 2.3, in which the effect of orientation on stress-aided chemical degradation was discussed. Photo-degradation is slower in oriented polyethylene in the unstressed state as well as when an external stress is applied [69]. Some of these topics are discussed further by Slobodetskaya [70], who observed that hydroperoxides accumulated at a lower rate in oriented polypropylene than in unoriented material.

2.5. The engineering perspective

The ultimate goal is the development of materials with indefinite lifetime. This may never be achieved, but it would be almost as valuable if methods could be developed that would permit an accurate prediction of component lifetime, either from the time of manufacture, or from the time of an in-service inspection.

Studies of degradation mechanisms of polymeric materials have concentrated largely on the chemical reactions that are involved. As a consequence, the understanding of the chemical mechanisms of degradation is quite advanced. The spectacular improvement in polymer lifetime made possible by anti-degradation additives, many of them commercially available and in widespread use, bears testimony to this. Nevertheless many review and research papers on this topic claim that more research should be done in this area. The successes of the past, in combination with the recognition that indefinite lifetime is still far from being realized, signals that in some respects this is a reasonable point of view. It is evident, however, that some of the engineering aspects of weathering-related failure of polymers are not as well understood as the chemical mechanisms of degradation. Many examples are to be found in the literature in which a chemical characteristic (such as the carbonyl index) is used to monitor the progress of degradation reactions and is found to correlate fairly well with the deterioration of engineering properties (such as the elongation to break in a tensile test), yet there is very little known about the links between chemical changes and the consequent mechanical changes. Furthermore there are many examples in which such correlation is not found. It seems that to be able to predict lifetimes of polymeric components a more comprehensive appreciation of the engineering aspects of failure is required and that more insight is needed into the relationship between chemical and mechanical degradation. Only then can predictions of lifetime, based on chemical kinetics and other physico-chemical properties such as diffusion, be developed with confidence.

It is generally accepted that with most polymers the surface becomes embrittled during outdoor exposure. Although it is not completely evident why this should be so, it is usually dismissed as being the consequence of chain scission. In some cases the deterioration appears to be more rapid than would be expected simply from the standpoint of molecular weight reduction. This could be explained if the key load-bearing bonds, such as those with the greatest strain (especially tie molecules in semi-crystalline polymers and segments close to entanglements) are attacked preferentially, as discussed in the previous section. It has even been suggested that preferential attack at irregularities, including chromophores, may lead to stress concentration and the formation of microcracks [71, 72].

Cracks form easily in the embrittled layer, sometimes apparently without any external applied force. These cracks can then act as stress raisers and facilitate the failure of less seriously degraded material nearer to the centre of the section [73–80]. Bucknall and Street [74] showed that the application of a brittle layer of glassy polymer to rubber-toughened polymer caused a reduction in impact resistance. A more comprehensive series of model experiments was conducted by So and Broutman [75, 76] who applied thin brittle polystyrene coatings to rubber-modified polymers (high-impact polystyrene and acrylonitrile–butadiene–styrene (ABS)). They showed that the critical flaw size given by linear elastic fracture mechanics correlated well with the coating thickness.

Although this is of direct relevance to the case of an embrittled layer at the surface of a weathered polymer component, analysis of the fracture mechanics in this case is less straightforward because of the variation of properties through the depth of the wall. Young's modulus may change as a function of depth from the surface, and if this is the case then the strain energy density for a particular applied strain will vary with depth. Even if an apparently discrete embrittled surface layer is present it is still likely that some degradation occurs at greater depths and that the fracture toughness is itself a function of depth. Schoolenberg [77, 80] discusses the fracture processes and notes that the depth of embrittlement does not necessarily equal the depth of the surface cracks. Schoolenberg and Vink [78] found that the spontaneous growth of surface cracks in polypropylene in artificial u.v. exposure was slower in injection mouldings than in compression-moulded samples. This may be because of the orientation expected to be present in an injection moulding or because of compressive residual stresses at the surface. Galli *et al.* [81] also observed that surface cracks formed in polypropylene under u.v. exposure and claimed that they were promoted by "frozen-in moulding stresses", though they do not present any measurement of frozen-in stress nor do they define precisely what they mean by this term. Karpukhin [82] observed that the depth of cracks that developed in the surface of polyethylene cable insulation equalled the calculated oxidation depth. He claimed that the driving force for their formation was shrinkage stress in the oxidized layer, corresponding to a shrinkage strain of 1–2% [82]. This shrinkage, if present, may be caused by chemicrystallization [83].

Schoolenberg and Meijer [79] found that exposure of polypropylene in a Xenotester (an artificial weathering cabinet using a xenon lamp ultraviolet radiation source) caused the fracture energy to drop, but that after prolonged exposure it partly recovered. This may be related to a similar observation made by Sherman *et al.* [84] in which the surface layer of their polycarbonate samples became so fragile that it flaked off. Presumably partial recovery occurs when the degraded surface layer becomes too weak to transmit stresses into the interior when it is strained. Wolkowicz and Gaggar [85] showed that the impact resistance of thermally aged ABS recovered significantly if the degraded layer was scraped away using a microtome knife. Magnus [86] describes degradation of PVC as repeated cycles in which an embrittled surface layer forms and then a few micrometres are removed after cracking (possibly promoted by stresses caused by oxidation), accompanied by partial recovery of coloration and mechanical properties and a loss of gloss. Magnus calls this process "multilayer weathering". This tends to be observed in severe weathering conditions, whereas in temperate climates the more modest rate of degradation may not give rise to cyclic behaviour unless the exposure period is very long. Other factors may influence surface failure, and Davis [87] suggested that perspiration products, transferred to the surface of polycarbonate during handling, may accelerate crack formation.

Degradation due to weathering develops much more slowly in the interior but if the surface becomes too weak for fracture to instigate there then the damage in the interior may influence the fracture mechanism [87]. Damage accumulating around a pre-existing flaw in the interior may lead to it becoming the critical flaw in preference to a surface crack [88]. If the same surface always faces the sun then the degradation rates at different surfaces will be widely different. When degradation at the surface facing the sun becomes so advanced that fracture cannot nucleate there, then failure may nucleate at a less degraded surface [89].

Finally, when assessing the results of long-term conditioning tests, it is important to recall that polymers change their properties during ageing even in the absence of chemical reaction [90, 91].

3. Stabilization

3.1. Introduction

The inclusion of stabilizers can produce a spectacular improvement in the lifetime of a polymer component. Although a basic understanding of the mechanisms of degradation was needed before effective stabilizing systems could be chosen, the study of the effect of these stabilizing systems has led to a more detailed understanding of degradation mechanisms and so to improved stabilizing systems.

3.1.1. Photo-stabilizers

The methods that offer protection against photo-oxidation are u.v. screening, u.v. absorption, excited state deactivation, free radical scavenging and hydroperoxide decomposition. These are all discussed in a review by Allen *et al.* [92].

3.1.1.1. U.v. screening. Screening is provided by pigments or by a reflective coating [8]. Carbon black is very effective and is used to stabilize many outdoor grades of polymers. Bigger and Delatycki [93] found that carbon black provided effective protection for high-density polyethylene under laboratory photo-oxidation, even at a level of only 0.05 wt %, and that further increases of carbon black content up to 5% produced still better performance. Damage is confined to the surface regions because u.v. penetration is restricted to very short distances. Compounds containing carbon black are themselves black and this restricts the applications mainly to products for the construction industry. Other chemically inert pigments that block u.v. also often give an unattractive appearance; chalk, talc and short glass fibres give greys and browns that are generally unappealing. Some pigments actually photo-sensitize the polymer, as was found to occur with cadmium sulphide in low-density polyethylene [94]. TiO_2 is another common additive which may act as a screen [95–98] but may occur in different forms, some of which are chemically active and can promote photo-degradation [52, 99]. A quest to find ways of reducing the reliance on TiO_2 to provide weatherability in PVC formulations has been described by Conroy and Wursthorn [100].

3.1.1.2. U.v. absorption. This can be provided by additives that are transparent to visible light and do not alter the appearance of the product. Transparent compounds can be made; ideally the transmittance should be 100% in the visible range and zero at wavelengths below the visible limit of about 400 nm, and there exist stabilizers that come remarkably close to this specification [92]. The most common u.v. stabilizers are the hydroxybenzophenones, the hydroxyphenylbenzotriazoles, the hydroxyphenyltriazines and derivatives of phenyl salicylates; their chemical formulae and the trade names of some of the commercial compounds are listed elsewhere [8, 92]. The act of absorbing u.v. is not the only requirement of a molecule to contribute to stabilization; it must also dissipate the energy absorbed without damaging the polymer it is meant to protect. Some discussion of how this may happen is given by Allen *et al.* [92]. As with screens, the presence of u.v. absorbers causes the u.v. intensity to drop more rapidly as it penetrates into the material and degradation is concentrated even more sharply near the surface [101]. It would be most economical if these additives could be concentrated at the surface [102].

3.1.1.3. Excited state deactivation. Deactivation or quenching provides an alternative method for the dissipation of energy absorbed by a polymer chromophore to the damaging scission reaction. The tendency for carbonyl photolysis to lead to backbone cleavage can be reduced by deactivating excited carbonyl species using transition metal chelates. Allen *et al.* [92] cite studies in which it was shown that the quenching process can operate over a distance up to 19 nm, so that protection can be provided by a very low concentration of additive if uniformly dispersed. It should be noted, however, that the studies referred to were made on a solution and that the separation of 19 nm of the quencher from the excited molecule was only an average value [103]. As with u.v. absorbers, the quencher must be able to dissipate the acquired energy. Excited hydroperoxides are thought to be too unstable to allow deactivation to occur [92].

3.1.1.4. Radical scavengers. These break the oxidation chain, so limiting the damage. Allen *et al.* [92] discuss the "chain-breaking donor mechanism" and the "chain-breaking acceptor mechanism", giving details of the chemical structure of the stabilizers and of the reactions involved in the stabilizing processes. In the chain-breaking donor mechanism a hydrogen atom is donated to an alkoxyperoxyl radical to form a hydroperoxide. The donor is a hindered phenol or, less commonly, an aromatic amine [92, 104]. Alkyl radicals are the target of the chain-breaking acceptor mechanism. There are many compounds that can be used for this purpose. Free radicals that are relatively stable and do not themselves initiate reactions with the undamaged polymer can be used, reacting with alkyl radicals when they are produced by photo-oxidation. Examples of suitable free radicals are nitroxyls and phenoxyls. Alternatively quinones react with alkyl radicals to form radicals that do not initiate oxidation of the polymer. Allen *et al.* [92] note that alkylperoxyl radical scavengers are most efficient in the presence of excess oxygen, whereas chain-breaking acceptor anti-oxidants operate best in oxygen deficiency, and that as a consequence it is an advantage if a stabilizing molecule has groups providing both characteristics. It is believed that some stabilizers act via cyclic reaction paths so that they are regenerated and can be effective at lower concentrations or for longer periods of time than would otherwise be expected. Examples include copper ions and hindered amines [92].

3.1.1.5. Hydroperoxide decomposition. Decomposition into inactive products is an important method of stabilization in polyolefins for it prevents generation of radicals by processes such as Reactions 3, 4, 7 and 8. Hydroperoxides are more potent photo-initiators than carbonyl groups [105]. Decomposition can be achieved by reaction with phosphite esters or nickel chelates, or by a catalytic action by a range of compounds listed by Allen *et al.* [92] and including dithiocarbamates and mercaptobenzothiazoles. Decomposition of hydroperoxides formed during processing is also important for the stabilization of PVC [106].

3.1.1.6. Discussion. From the brief introduction presented above it is evident that some classes of chemicals may provide stabilizing action through two or even more mechanisms. This is of great benefit but may have slowed progress in developing optimal stabilization systems because of the uncertainty attached to the true mechanism of stabilization in some cases. Combinations of stabilizers can be used to provide multi-mechanism protection, though care must be taken that no antagonism exists between the different components wherein the presence of one of them (or of its reaction products) renders the other less effective than when used in isolation. In some cases the combination of two different anti-oxidants provides better protection than would be predicted by simply adding the effects produced by them both when used alone, a phenomenon known as synergism.

Finally it should be noted that there may be physical changes associated with the presence of stabilizers and their effect should be taken into account. An extreme example is the use of carbon black as a u.v. stabilizer. The carbon black may provide some reinforcement, altering the stiffness and strength of the material. In sunlight, a black-filled polymer will heat up more than an unfilled grade or one containing stabilizer that absorbs infrared radiation less readily. Temperature gradients may develop and may lead to the modification of the residual stress distribution and this in turn may have an influence on the subsequent failure mechanism [107].

3.1.2. Thermal stabilizers

Thermal stabilizers for PVC have been discussed in four reviews in a single volume [18, 20, 108, 109]. The features required by a thermal stabilizer have been listed by Ayrey and Poller [18] and include (i) reaction with and removal of HCl liberated during the early stages of degradation; (ii) replacement of labile Cl atoms or other structural weaknesses by more stable entities; (iii) interruption of chain reactions such as "unzipping" or the auto-oxidation production and decomposition of peroxides; (iv) interruption of conjugated polyene sequences (to reduce colour deterioration); and (v) reaction with pro-degradant products of the stabilization process. The main classes of thermal stabilizers are listed below.

3.1.2.1. Organo-tin stabilizers. These compounds are effective in preventing chromophore production during processing and may provide some photo-stabilization in addition [18, 110], though Cooray and Scott [20] claim that some compounds may act as pro-oxidants due to photolysis of the stabilizer. Organo-tin stabilizers can be used for clear grades of polymer. High molecular weight forms must be used to prevent migration if used in contact with food.

3.1.2.2. Organo-phosphorous stabilizers. These are effective for preserving the original colour in PVC and polyolefins [109]. They decompose hydroperoxides and react with peroxy radicals to terminate kinetic chains. Pobedimskii *et al.* [109] give a glossary of phosphites suitable as candidates for this application and present some kinetic data for various phosphites reacting with hydroperoxides. They note that transition metal ion–phosphite combinations are synergistic and are effective in scavenging peroxy radicals.

3.1.2.3. Metal soaps. These and other organic compounds have been used as stabilizers for PVC for many years and have been reviewed by Guyot and Michel [108]. They discuss the mechanisms of thermal degradation and stabilization by these classes of compounds and note in particular the importance of the reaction products. A discussion of the chemistry of stabilization of various commercial stabilizers for the protection of polypropylene during melt processing is given by Henman [111].

3.2. Compatibility, diffusion and volatilization of stabilizers

Ideally, stabilizer molecules should be dispersed singly throughout the polymer matrix. This will not generally happen but compatibility with the polymer should be sufficient to prevent gross phase separation. The solubility of the popular commercially available hindered amine light stabilizer Tinuvin 770 in isotactic polypropylene is given by Spatafore and Pearson [112] as $< 0.1\%$ at room temperature; solubilities increase rapidly with temperature [113]. In semi-crystalline polymers the stabilizer molecules will generally be rejected from the growing crystals and will be located in the non-crystal phase, though this is partly influenced by the rate of cooling [114]. The preferential concentration of stabilizer in the amorphous phase is an advantage because degradation is normally much more severe there. There may be significant segregation of the various molecular species in products such as blow-extruded films in which impurities or low molecular weight oligomers tend to be carried towards the centre ahead of the solidification front [115].

Stabilizer molecules may diffuse through the polymer and may precipitate at the surface, sometimes causing a change of appearance termed "blooming" [112, 116]. Lustoň [117] concludes that loss of stabilizer is usually diffusion-controlled and gives lists of the volatility and diffusion parameters for many stabilizers in a number of common polymers. Once at the surface the stabilizer may be lost by volatilization or by dissolving into a liquid or solid which makes contact with the polymer there. This must be avoided in the case of plastic films or containers in contact with foodstuffs. On the other hand some stabilizer diffusion may be needed to maintain levels in regions, normally near the surface, in which it becomes depleted through chemical action [118–120]. This replenishment may occur during dark periods and may account for differences in behaviour in tests conducted using continuous irradiation and cyclic exposure, respectively. The rate of oxygen diffusion into the interior may limit reaction there, though Carlsson and Wiles [121] suggested that degradation in polypropylene occurs preferentially at the surface not because of this but because the chromophores that cause initiation of photo-oxidation segregate to the surface. The molecular mobility will influence the likelihood of recombination of radicals formed by molecular scission (the "cage effect") [122].

The rate of diffusion is governed largely by the molecular size and some control can be exercized by synthesizing oligomeric or polymeric stabilizer molecules. The influence of molecular weight on the efficiency of phenolic anti-oxidants in polypropylene has been studied by Tocháček & Sedlár [123] who consider both diffusion coefficients and solubilities. A mixture of high molecular weight and low molecular weight stabilizer molecules has been recommended by Gugumus [119] for some applications. Minagawa [120] suggests that a molecular weight in the range 200–2000 is required to allow stabilizer molecules sufficient mobility to reach active sites and that higher molecular weights (up to 5000 for a hindered amine light stabilizer (HALS)) are required for permanence. It is sometimes possible to copolymerize a stabilizing group onto the polymer so that it is bound to it permanently [124]; this solves the problem of migration to the surface and ensures good compatibility. This is the method used by Al-Malaika *et al.* [125], who prepared polymer-bound HALS for use in master batch compounding. Vogl *et al.* [126] have described the synthesis of such compounds and of other polymeric stabilizers. Kamińska and Kaczmarek [127] note that a copolymerized unit inserted into PVC can stop the unzipping action. Perhaps this explains the observation by Turcsánya *et al.* [128] that the thermal degradation of PVC was much reduced when copolymerized with an α-olefin. A somewhat different approach was used by He Mingbo and Hu Xingzhou [129], who photo-grafted HALS on to the surface of polypropylene. They claimed that copolymerization of the stabilizer with the monomer causes an adverse change in the properties of the material and that the later attachment by photo-grafting provides highly effective stabilization. Another example of post-polymerization reaction is reported by Crine *et al.* [130] who claim that an anti-oxidant compound can be grafted to polymer chains during crosslinking of cable-grade polyethylene. Another development is the use of polymer-bound HALS attached to a chosen part of a multiphase polymer. Hahnfeld and Devore [131] report improved weatherability in acrylonitrile–EPDM–styrene terpolymer in which HALS was bound to the EPDM (rubber) phase. If the HALS is simply blended into this polymer it tends to segregate to the matrix. The best results were obtained when HALS was present both bound to the rubber phase and blended into the polymer [131].

The stabilizer molecules should be non-volatile or else they will be lost. It is important to remember that stabilizer added to give protection against photo-oxidation at modest ambient temperatures must still survive any elevated-temperature processing operation such as injection moulding. Polymeric stabilizers will inevitably be superior in this respect. Retention of stabilizer is especially difficult with fibres and films for which high molecular weight versions of hindered amine light stabilizers are preferred [120]. In some cases stabilizer may be extracted if the polymer is in contact with hot water, leading inevitably to accelerated degradation [132].

The concentrations of the products of reaction vary through the thickness of a polymer product. Aleksandrov *et al.* [133] used infrared analysis to show that photo-oxidation of PVC was concentrated near the surface and that dehydrochlorination products were just beneath. The depth at which polyene structures were present varied with irradiation conditions [133].

3.3. Classes of stabilizer

It is beyond the scope of this review to deal in detail with all stabilizing systems, but it is valuable to consider some of the more common and effective systems. The chemical formulae and trade names of many common stabilizers are given by Gugumus [119] and by Minagawa [120].

3.3.1. Phenolic anti-oxidants

Phenolic anti-oxidants act as radical scavengers [120]. A disadvantage is that they may form coupled by-products that lead to discoloration [120]. The oxidation products may produce a photo-sensitizing action [120]. Chirinos-Padron [134] claims that hindered phenols give little or no protection to polypropylene, whereas Pospišil [104] states that they are effective during fabrication, storage and end-use. Pospišil notes that the effectiveness of phenolics is often reduced in the presence of pigments such as titanium dioxide (TiO_2) or carbon black with which they react [104]. They are often used in combination with other additives for best effect, as explained in section 3.4.

3.3.2. Hindered amine light stabilizers (HALS)

Hindered amine light stabilizers have proved to be very effective, especially with polyolefins. An example is bis(2, 2, 6, 6-tetramethyl-4-piperidinyl) sebacate, which is available commercially as Tinuvin 770 and has been referred to in some publications as HALS-1 [135, 136]. A survey of recent literature on the behaviour of polymers containing HALS indicates that the exact mechanisms of stabilization are still a matter for discussion [92, 120, 125, 134–143] though it is generally agreed that the products of reaction play an important part and that regeneration of some of the active species may occur, prolonging the lifetime of the stabilizing system. Furthermore it is generally agreed that the stabilization effect of HALS is not caused by u.v. absorption [140, 141, 143]. It is not agreed whether quencing of photo-excited carbonyl chromophores is involved [136, 139, 140].

Klemchuk and Gande [140] suggest that the primary stabilizing mechanism is the trapping of radicals by nitroxyls and that nitroxyls are regenerated from the alkoxy products of alkyl radical trapping. For example, one possible scheme involves reaction of nitroxyl radicals with polymer alkyl radicals to give alkoxy hindered amine derivatives which react in turn with alkyl peroxy radicals to regenerate nitroxyls. Klemchuk and Gande give another reaction pathway via aldehyde/acylperoxy radical/peracid; the acylperoxy radicals are trapped by HALS and lead to the regeneration of nitroxyl radicals via carboxylic acids. Other reactions involving regeneration of active species are described by Kurumada *et al.* [136]. Klemchuk and Gande [140] believe that tetramethyl piperidines and their nitroxyls can form complexes with hydroperoxides and that this will improve efficiency by ensuring that the stabilizing species are concentrated in the region in which the probability of initiation of photo-oxidation is highest, but Fairgrieve and MacCallum [139] question whether complexes form between HALS and hydroperoxide groups.

Gugumus [119], Kurumada *et al.* [136] and Vyprachticky *et al.* [141] also attribute the stabilization to radical scavenging but suggest in addition that the HALS may promote hydroperoxide decomposition. On the other hand, Klemchuk and Gande [140] claim that reactions between tetramethyl piperidines and hydroperoxides are too slow to give a significant contribution to stabilization at moderate temperatures. They further consider that reactions with alkylperoxy radicals are similarly too slow to make a major contribution. Geuskens and Nedelkos [144] found that under γ-irradiation the oxidation of HALS by peroxy radicals proceeded rapidly but that subsequent oxidation by hydroperoxides proceeded more slowly. Chmela and Hrdlovič [137] found that the photostabilizing efficiency of HALS in polypropylene differed for different substituents on the nitrogen atom, and suggest that this may depend on the compatibility of the substituent with the flexible polymer chain [137].

Another role attributed to HALS is to inhibit the catalytic action of metal impurities within the plastic by forming complexes with them [139, 141]. For example, Kurumada *et al.* [136] propose that the HALS forms complexes with transition metal ions, such as titanium from polymerization catalyst residue, to prevent the formation of metal ion–hydroperoxide complexes which initiate auto-oxidation.

The effectiveness of HALS is significantly reduced in the presence of protonic acids such as HCl and HNO_3 [145, 146]. HALS offer little or no protection against thermal oxidation, for example, during processing [141], and low molecular weight HALS are volatile and are lost during oven-ageing [119]. HALS are generally of little use as stabilizers if acids are present because they react to form salts which offer no weather resistance. As a result they are difficult to use with PVC because it tends to generate acids, though Minagawa [120] claims that new formulations have been developed in Japan that overcome this problem.

Antagonistic reactions involving HALS sometimes take place and are discussed below in section 3.4, but there is another detrimental effect that is not of this kind, namely the acceleration of hydrolysis of bisphenol A polycarbonate by hindered amines [147].

3.4. Synergistic combinations

It is common to use combinations of different stabilizers in an attempt to combat degradation through more than one process. For example, HALS may be used in combination with u.v. absorbers (such as benzophenones or benzotriazoles) to give the best performance in polyethylene films and in thicker sections of polyethylene and polypropylene [119, 148]. In many instances it is reported that there is a clear synergism, with a performance benefit in excess of expectation based on observations of the improvements caused by including the stabilizers in isolation [136]. In some cases antagonism seems to occur, and the effectiveness of one of the stabilizing additives is diminished by the presence of the other. An excellent introduction to the competing theories of synergistic action in the stabilization of polypropylene and some ideas on antagonism are given in the review by Allen *et al.* [92]. Sometimes synergistic or antagonistic reactions occur between antioxidants and other additives [149]. Chakraborty and Scott [148] describe the action of a benzophenone u.v. absorber with a peroxide-decomposing anti-oxidant (metal dithiocarbamate) and a chain-breaking anti-oxidant (hindered phenol). The peroxide-decomposing and chain-breaking anti-oxidant have a synergistic effect during thermal oxidation of low-density polyethylene but are antagonistic during photo-oxidation, possibly because of prevention of the photolytic destruction of the dithiocarbamate by the oxidation products of the phenol. Examples of both synergistic and antagonistic reactions of anti-oxidants in polyethylene with thermal decomposition products of azodicarbonamide (used for chemical foaming) are given by Latocha and Uhniat [150].

HALS are sometimes used in combination with hindered phenols [104, 134, 141, 151]. Chirinos-Padron [134] reports both synergism and antagonism in studies of natural weathering of polypropylene films containing high molecular weight additives, and suggests that both physical and chemical mechanisms may be involved [134]. He further suggests that favourable effects may be provided by reaction products of the HALS and the phenols. In another paper, Chirinos-Padrón *et al.* [152] report both synergism and antagonism of HALS and nickel complexes during thermal oxidation of polypropylene.

Hindered phenols are often used in combination with phosphites [104, 119, 120, 153]. This results in improvement in the resistance to degradation during oven-ageing or processing. The role of the phosphite is believed to be primarily to react with hydroperoxide groups formed by reaction of the hindered phenols with peroxy radicals, reducing them to alcohols [153]. Regeneration of phenolic anti-oxidants is believed to occur [104]. Synergistic effects have been observed in both oven-ageing and u.v. exposure of Ziegler-type polyethylene, whereas under some conditions antagonism was observed when a Philips-type polyethylene was tested [153]. This was attributed to the higher level of unsaturation in the Philips polymer. It is worth noting that different polyethylenes give different decomposition products even when they are additive-free [67, 154]. Minagawa [120] notes that this kind of stabilizer may have poor hydrolytic stability and may form acids that can cause corrosion of processing equipment.

Some observations are difficult to explain. Gugumus [119] reports that a mixture of low molecular weight HALS (HALS-1) and a high molecular weight HALS (HALS-3) showed strong synergism in some polypropylenes when subjected to u.v. exposure in film form. The same author notes that a combination of low and high molecular weight HALS is not always beneficial and quotes examples (in polypropylenes) in which low molecular weight HALS perform best and others in which high molecular weight HALS give the best results [119].

Synergistic and antagonistic reactions can occur between stabilizers or anti-oxidants and pigments in thermal and photochemical degradation [155].

4. Recycling and controlled degradation

There is considerable concern about what happens to a life-expired polymer article. Landfill sites for the disposal of waste are becoming scarcer and plastics are under pressure to repeal their throwaway image. Incineration is an option for they have considerable calorific value. Two other options that are related to the topics covered in this review are recycling and controlled degradation.

4.1. Recycling

Recycling is by far the most desirable way of disposing of unwanted materials but the problems attached to the collection and sorting of plastics waste are considerable and have been discussed at length in the popular media as well as in the technical literature. Of concern here is whether degradation of the material during initial processing and subsequent service renders it unsuitable for further use. The most acceptable form of recycling is that conducted in the factory, in which waste such as sprues and runners and rejects are re-granulated and used to produce new products of the same kind. With many polymers the amount of degradation during the initial processing and subsequent re-granulation is fairly modest. Normally the reground material is mixed with virgin stock, and as long as the fraction is small (say 5%, a target easily managed in a well-designed and well-run moulding operation) there is no perceptible fall-off in short-term product property as assessed by conventional procedures. Valenza and La Mantia [156, 157] prepared blends of virgin and waste polypropylene and found that virgin material usually showed the highest elongation to break but that samples made from 100% degraded stock outperformed many of the blended compositions.

A second type of recycling can be applied where a single product made from a single known polymer can be easily identified and efficiently collected. Examples are high-density polyethylene milk crates and polypropylene car battery cases. The ideal solution for recycling products of this kind is to reprocess them into new articles, possibly blending with virgin material as in factory recycling, or to formulate a new material, possibly with filler added, which is suitable for other, perhaps less critical, applications. In both cases the extent to which this is possible will depend on how much molecular degradation took place before reprocessing commenced. Sadrmohagheh and Scott [158] studied the reprocessing behaviour of low-density polyethylene and found that repeated processing caused the material to become more sensitive to u.v. degradation and that alternative cycles of processing and u.v. exposure were much more damaging than repeated processing alone.

4.2. Controlled degradation

Most of the reports in the literature on controlled degradation of polymers relate to photo-oxidation, though it would alternatively be valuable to control degradation in anaerobic conditions, or in soil, or in sea water. A combination of photo-oxidation and biodegradation is most appropriate in some cases, particularly in agricultural applications such as mulching films.

Pozzi *et al.* [159] suggested that the introduction of carbonyl chromophores into polyethylene could be used to make it photo-degradable. Chakraborty and Bowen [160], citing earlier work by Scott, described the use of metal dithiocarbamates which act as melt stabilizers and then photo-stabilizers for polyethylene and polypropylene, but which themselves degrade on extended u.v. exposure to yield products that are pro-degradent. Polymers containing this type of additive break down very suddenly once the system switches from anti- to pro-degradent and the authors claim that the timing of the switch can be predetermined if the service conditions are known. They further claim that the material is recyclable provided that it is collected and reprocessed before the photo-degradation stage commences. Despite the optimistic note of this development, two recent reviews question the desirability of controlled degradation and both suggest that recycling and even incineration may often be the best option from an environmental viewpoint [161, 162]. Klemchuk [161] warns that it is necessary to consider the possible toxicity of the small-molecule products of degradation for these may enter the water table. Some further ideas, including the use of starch as a bio-degradable filler, are given by Scott [163].

5. Exposure conditions

5.1. Natural weathering

The ultimate objective of testing is the prediction of component lifetime under service conditions. The most appropriate exposure conditions are therefore those that match exactly the service environment. The problem with direct testing is that the exposure period must be equal to or greater than the required service lifetime if the results are to be used with confidence. In an application that demands a lifetime of say 50 years this is unacceptable and some form of accelerated conditioning procedure is required. With artificial weathering, conducted in the laboratory, this is easily arranged, but the validity of predictions of service life under natural conditions based on the data from such tests is questionable, as discussed in the following section. An alternative strategy is to weather samples in extreme climates and to devise a method to relate the rate of degradation at the test site to that in the service environment. In this way "natural" conditions are preserved during testing, though the temperature and the levels of ultraviolet irradiation may be quite different from those met in service. Suzuki *et al.* [164] obtained good agreement between the mechanical degradation results for samples exposed in two different sites in Japan by plotting against the total u.v. dose rather than the time exposed. Further acceleration can be achieved by using mirrors to concentrate the solar radiation on to the test samples and to arrange that the exposure frame tracks the sun.

Marshall [165] observed in a review published in 1982 that standard procedures for studying weathering deterioration were inadequate. He criticized tests which enhanced the likelihood of ductile failure and recommended that test procedures that were biased towards the production of brittle failure should be adopted as a precaution against over-optimistic test results [165].

5.1.1. Test sites

All of the popular test sites are located in hot climates with high ultraviolet levels. Arizona is popular for studies using a hot dry climate and Florida for a hot damp climate [8, 52] but there are many reports of studies in which outdoor exposure has been conducted in other parts of the world, including Australia, Israel and Saudi Arabia. Davis and Sims [8] give details of the climatic conditions at various popular test sites and, for comparison, at locations in the UK and elsewhere in Europe.

5.1.2. *Conditioning procedures*

The exposure conditions must be carefully planned and controlled. The climate at almost all locations shows significant seasonal variations and this must be taken into account both when planning trials and when assessing the results. Advice is given both in Standards and also in reviews of this topic [8, 52, 166–168]. The samples must not be in the shade of trees or buildings. They may be mounted on open frames, but for some applications it may be prudent to test the behaviour when mounted in a backed frame or even in a box with a glass lid (to imitate conditions in the passenger compartment of a stationary car with the windows closed, for example). In the northern hemisphere the frames are normally placed facing south and the angle of exposure is often recommended in standards as 45 ° to the horizontal. For more severe exposure the frame can be tilted from the horizontal by an angle equal to the latitude of the location and this is frequently chosen in research studies. Details of sun-concentrating devices are given by Davis and Sims [8], Baum [169] and Caryl [170].

If the results of outdoor weathering are to have any value other than as an indication of the expected behaviour of the material at the test site then the climatic conditions should be monitored. The temperature and humidity should be recorded continuously and rainfall should be measured. It is important to record the pattern of rainfall, in particular the time during which rain is falling, and not simply the total precipitation [52]. If the rain follows suddenly after a period of strong solar heating then the temperature gradient that develops during exposure from one side will become reversed, causing a reversal of the thermal stresses. This topic is discussed further in the section on artificial weathering. The radiant exposure should be recorded; measurement of the full spectral distribution is preferred but if this is not possible then the irradiation versus time should be measured within chosen ranges, e.g. 295–385 nm, or at 340 nm. Details of how this information may be gathered and examples of data collected in Greece are given by Gardiner and Kirsch [171].

To complete the profile of the test site conditions it is desirable to measure pollutant concentrations, including ozone, sulphur dioxide and nitrous oxides in the air, and the pH of the rain.

5.2. Artificial weathering

The main motive for artificial weathering is to accelerate the weathering processes so that a reasonably reliable prediction of the service lifetime of a component can be obtained in an acceptably short test period. For studies of performance rating some recommended conditioning procedures are to be found in Standards. The relevant standards have been reviewed by Brown [172] who provides a useful glossary of ASTM, BS, DIN and ISO standards for testing the degradation of plastics through weathering and other causes. Particular attention is drawn to BS2782 [173] and BS3900 [174]. The conditioning parameters that can be varied are considered in turn below.

5.2.1. *Temperature*

All thermally activated rate processes are accelerated by increasing the temperature and most artificial weathering is conducted at elevated temperature. Unfortunately this may promote degradation processes that do not occur at lower (ambient) temperatures [52, 175, 176]. Even if this is not the case there can still be serious problems when several processes are involved in degradation, since the rates may not be accelerated proportionately and the various stages in the degradation process do not imitate those in natural conditions. This is particularly the case when sequential reactions involving degradation products are involved or when diffusion of one of the reactants is required to maintain adequate concentration in the reaction zone. For example, at ambient temperature photo-oxidation in the interior of a thick section may be limited by depletion of oxygen through reaction whereas at elevated temperatures diffusion of oxygen may be sufficiently rapid to maintain the reaction. It is evident from this that the section thickness is an important characteristic and must always be taken into consideration when attempting to relate the results of controlled weathering to the service behaviour of a component.

When plastics components are exposed outdoors on a hot sunny day they can reach quite high temperatures (~ 100 °C in some cases [177]). The surface that faces the sun is normally hotter than the surface facing away from the sun. A significant temperature gradient can be supported because of the low thermal conductivity of polymers and this will lead to the development of thermal stresses. These stresses may provide the driving force for the formation of surface cracks that may ultimately provide the site for initiation of a macro-crack by which the component fails. The non-symmetric relaxation of residual stresses in the temperature gradient may lead to a modified residual stress distribution when temperature equilibrium is restored [31, 178], with tensile stresses now appearing near the surface, and this may be an alternative mechanism by which surface cracks form during weathering.

Tensile residual stresses have been observed to develop during natural weathering of polystyrene and poly(vinyl chloride) [179, 180], polycarbonate [181] and to a lesser extent in semi-crystalline polymers [182]. Because of the potential importance of the presence of a temperature gradient in influencing the failure of a weathered polymeric component, consideration should be given to the provision of a temperature gradient across samples undergoing artificial weathering. This will occur if a water spray is used to simulate rainfall, but more attention needs to be paid to the conditions of spraying than has been the case up until the present. It is important that the water cools only the heated side of the test piece and does not flow around the back. The water temperature must be measured and should be as cold as possible for maximum effect.

In an investigation of the behaviour of polyethylene in a marine environment it was found that the degradation rate was lower when the samples were floating in sea water than when they were exposed out of the water [183, 184]. This was attributed to the cooling effect of the water.

The measurement of surface temperature in test conditions presents problems. The temperature of the test-piece is determined partly by the absorption of radiation and cannot be taken to be equal to the background temperature in the test surroundings or enclosure. This is true of outdoor weathering too and Davis and Sims [8] report surface temperatures more than 30° higher than the surroundings, while Clegg and Curson [177] claim that temperatures of up to 100 °C are possible for black-coloured plastics [177]. The problem is further exacerbated by the changes in absorption and emission characteristics that will almost certainly occur during exposure as a consequence of the chemical and physical changes taking place. No satisfactory method to overcome this last problem has been suggested, but to obtain a reproducible measurement of temperature suitable for comparison from test to test the use of a black panel adjacent to the test-piece was recommended. The temperature of this device was measured and taken to be characteristic of the conditions at the test-piece, but there were defects in the design, for the cooling of the thermal sensor depended on the position and the black panel thermometer has been superseded by the improved "black standard thermometer" [52, 175].

Where testing is designed to investigate thermal degradation the problems are not so severe. If the objective is to determine the likely degradation during fabrication then tests can be conducted using similar temperatures to those required by the process; the time the material is held at elevated temperature during fabrication is normally quite short and there is no great need for acceleration in this case. It is important to match the atmosphere within the test enclosure to that within the processing equipment.

5.2.2. Ultraviolet irradiation

The major hazard in natural outdoor exposure is the ultraviolet component of solar radiation. The lower the wavelength the greater is the photon energy, and one way of accelerating deterioration is to use lamps giving wavelengths below the lower limit (approximately 290 nm) of solar radiation. This may lead to reactions that cannot be promoted by solar irradiation [52] and tests based on acceleration by this means cannot be used with confidence. A more acceptable means of acceleration is to use a high intensity of irradiation. Care must still be exercised in choosing the intensity level for similar reasons to those discussed in the previous section regarding temperature. In this case the provision of an excessive illumination level may cause the reaction in the interior of a test-piece to become oxygen-diffusion-limited, even if under ambient conditions the diffusion rate is sufficient to replenish the oxygen used by reaction. This is of course opposite to the effect of an elevated temperature and there may be some scope for compensating one with the other. This should be done only if full account is taken of the effect on other reactions involved in degradation and with proper attention to the kinetics of diffusion. Some accidental compensation may well be in operation in current test procedures, providing a rather fortuitous benefit in the correlation between artificial and natural weathering behaviour.

Another way of providing acceleration is to maintain illumination at the chosen peak level for 24 h each day instead of having a diurnal variation that includes a dark period. This is probably the most acceptable method of acceleration though even this is not free from objection. Diffusion of oxygen, stabilizers and other reactants will continue during the hours of darkness so that their distribution will differ during natural weathering from that obtained in artificial conditioning without a dark period [185] (see section 3.2 above).

There are two sources of u.v. radiation in common usage in artificial weathering of polymers, based respectively on the xenon arc and on fluorescent tubes. Both sources are capable of matching the solar spectrum reasonably faithfully and have largely replaced earlier sources such as carbon arc and mercury vapour lamps which will not be considered further here. The xenon arc contains u.v. wavelengths shorter than the cut-off level of solar radiation and these must be removed by filters unless the advice to avoid them is ignored. Xenon lamps also emit a high intensity of infrared radiation and this must also be removed to avoid overheating the samples. The layout of the xenon source with the associated filters and water cooling arrangement in the commercially-available Xenotest 1200 is given by Davis and Sims [8]. The Xenotest 1200 offers water spray, light/dark cycling and humidity control and has gained quite wide acceptance in industry but is expensive to run. The xenon burner and the filters deteriorate with use and their performance must be checked regularly or a suitable strategy must be developed to compensate for this ageing effect [175].

Fluorescent tubes are much cheaper to run and do not have the disadvantage of producing unwanted heat. Tubes are available with several different spectral outputs. The intensity of UV-B tubes peaks strongly at around 313 nm and the output is very high throughout the lower wavelength end of the solar spectrum. As a consequence they provide strong acceleration, but the output is also high at wavelengths below the solar radiation cut-off (within the range 270–295 nm) and may lead to unwanted reactions. UV-A tubes do not have this problem and a lamp manufactured by the Q-Panel Co. for their Q–U–V artificial weathering chamber [8] and designated UVA-340 gives a very close match to solar radiation up to approximately 350 nm. Ultraviolet fluorescent tubes emit low levels of visible radiation and no infrared; the heating effect is negligible and a separate source of heat is required to maintain temperature levels at or above those experienced outdoors. This is not really a disadvantage because the provision of independent control over illumination and heating is a desirable feature in a testing rig. The spectral output from fluorescent tubes changes with use and the tubes should either be checked regularly for spectral output or should be taken out of service after 1600–2000 h [8, 186]. When an array of tubes is used they should be rotated and withdrawn according to a systematic programme designed to ensure constant illumination throughout the conditioning period [186].

It has been suggested by Kockott [52] that filters can be used to isolate narrow wavelength bands for exposure to determine which part of the spectrum is detrimental, and that this information may assist in the design of suitable stabilizing systems.

5.2.3. Water spray and humidity control

The provision of a water spray allows the simulation of rainfall which may promote degradation for a variety of reasons. The impingement of water droplets may cause (mechanical) erosion; some polymers undergo hydrolysis reactions that may lead to chain scission; the thermal shock produced when cold water falls on a previously warmed surface may cause surface cracking [187]; some polymers are swollen by water, causing residual stresses to form when water is unevenly distributed, as during the initial exposure to water, or soon after the source of water is removed if desorption occurs.

An effective method of providing a suitable spray is to use an atomizer or modellers' airbrush. An alternative method of wetting the sample is by condensation. In the Q–U–V artificial weathering chamber a trough of heated water provides a humid atmosphere and condensation occurs on the samples because they are cooled naturally through the exposure of the unexposed surface to laboratory air [8, 186]. Condensation may occur in natural weathering, and these conditions may be faithfully reproduced by this method. The condensation method is not expected to produce the same degree of thermal shock as a cold water spray and may produce a temperature gradient quite unlike that caused by rainfall, so it may not provide an adequate test of the resistance of a material to natural exposure to water.

Some polymers absorb water when exposed to moist air and it is necessary to monitor the humidity within the artificial weathering chamber and preferably to control it as well. The absorption of water is a particular problem with polymer composites [188].

5.2.4. Oxygen pressure

The rates of oxidation processes involved in weathering are sensitive to the partial pressure of oxygen at the gas–solid interface [185] and some acceleration can be achieved by increasing the partial pressure of oxygen within the conditioning chamber above ambient [6, 10, 34, 37, 38, 189]. This approach has been confined to research studies and there is not enough knowledge of the effect to adopt it for routine testing at present.

5.2.5. Pollutants

The introduction of pollutants into the conditioning chamber permits investigation of their effect and the use of concentrations higher than those found in field conditions provides acceleration, but the level of knowledge is not adequate to formulate meaningful routine tests [52, 175]. The common atmospheric pollutants in industrialized regions are sulphur dioxide, oxides of nitrogen and carbon, and ozone. There is a significant photochemical contribution to their activity, though laboratory experiments by DeVries and co-workers [51, 190] have shown that accelerated degradation occurs in nylon 6 when exposed to SO_2, NO_2 or O_3, even in the absence of significant u.v. intensity (presumed to be at background laboratory levels). This effect was accentuated in the presence of an applied stress [51, 190, 191]. Igarashi and DeVries [192] reported similar effects with polyethylene fibres. Ozone is produced under ionizing radiation, adding to the attack of polymer surfaces exposed to γ-irradiation [193].

Polymeric coatings do not generally provide a very effective barrier to the passage of SO_2 according to Funke and Haagen [194], and degradation reactions in which it takes part may not be restricted to the surface.

Consideration should be given to the effect of pollutants on additives as well as polymers. For example Jakubowicz and Möller [195] report that $CaCO_3$ filler in PVC was replaced by $CaSO_4$ by reaction with H_2SO_4 formed from photo-oxidized SO_2 and water.

5.2.6. Stress

Although stress is not specifically an aspect of the weather it interacts with the weathering agents, often to produce accelerated degradation, and it is advisable to include the facility to apply loads to samples during the artificial weathering process. The importance of exploring load as a parameter has been acknowledged in authoritative reviews on the strategies needed in weathering studies [8, 52]. DeVries and co-workers [51, 190, 192] showed that nylon 6 and polyethylene samples degraded more rapidly under the combined action of u.v. and stress than when exposed to u.v. unstressed or when stressed in air in laboratory lighting conditions (presumably low u.v. levels). On the other hand George and O'Shea [196] found that an applied load reduced the rate of degradation of nylon 6 exposed outdoors. They used quite high stresses and attributed their observations to orientation that was promoted by the load. Probert *et al.* [197] did not detect any significant effect of stress on glass reinforced polyester during outdoor exposure in the UK.

There are two reasons for including stress in weathering test programmes. Firstly the data obtained are of direct value since a majority of components are required to bear load in service, and secondly it appears to be a means of acceleration that has rather fewer disadvantages than the other methods. Experiments with dead-weight loading and with both static and cyclic bending have demonstrated acceleration of u.v. degradation in polystyrene, polypropylene and glass-fibre-reinforced polypropylene [198]. It would be a particularly simple task to provide static bending jigs for mounting samples in the form of bars or plaques in existing commercially available artificial weathering enclosures. A bent strip similar to that used for environment-sensitive fracture testing of polymers was recommended by Kaufman [199] for outdoor exposure 25 years ago, but has not been adopted widely.

5.2.7. Plasma treatment and other ultra-fast methods

It has been reported that the ranking of paints obtained by observing their degradation under plasma treatment agrees well with service behaviour [200]. It is evident that plasma interaction is very rapid and that strong acceleration of degradation is promoted. Some control can be exercised over the chemical composition of the gas phase at the surface with a view to reproducing the chemical reactions that control degradation in natural conditions, but it seems that in general the reactions under plasma bombardment are quite different from those prevalent during weathering [20]. Plasmas can be used to modify the surface of polymers in ways not normally found under natural conditions [202]. Nevertheless Friedrich and co-workers report that the chemical changes caused by plasma treatment of poly(ethylene terephthalate) agreed with Xenotest results [203] and with natural weathering [204]. In disagreement with the other sources cited above, Friedrich *et al.* [204] claim that the chemical reactions involved in oxygen plasma degradation of poly(ethylene terephthalate) are similar to those in thermal oxidation and photo-oxidation. Their tests were conducted on thin samples so that the expected differences in diffusion-controlled depth variations in degradation in thick samples could not be confirmed.

Ogita *et al.* [205] showed that plasma attack of LDPE occurred primarily in the amorphous regions, giving an etching effect. Vasilets *et al.* [206] compared the effect of steady and pulsed plasmas on the surface degradation of polyethylene at 77 K. They found that the thickness of the layer containing degradation products was much less in the steady discharge (~ 1.5 μm) than in a pulsed discharge (30–40 μm). They found that for steady discharges the initial accumulation rates were lower but the sputtering rates were higher; perhaps the second observation explains the first, for the products of reaction would be removed more rapidly at a higher sputtering rate. Further studies using polyethylene, polypropylene and other polymers have been presented by Grinevich and co-workers [207, 208]. As with all accelerated tests, the several chemical reactions involved in degradation will be accelerated by different amounts and will be subject to the availability of reactants whose concentrations may be diffusion-controlled.

Another ultra-fast method of degradation has been described by Sommer *et al.* [209] who used a mercury lamp source and focused the light on to their polyurethane coatings with a mirror. The exposure was conducted within the specimen cavity of an electron spin resonance spectrometer so that the concentration of radicals could be monitored throughout the exposure period (see also section 6.5). Because of the short lifetime of radicals at room temperature the sample cell was kept at ~ 140 K. Sommer *et al.* argued that the key step in degradation is radical formation and that their tests, lasting only 3 h, would give a rapid ranking of different polymers with respect to their weather resistance. Their results showed large differences between stabilized and unstabilized grades but they had no data on outdoor performance with which to compare them.

5.3. Correlation between the effects of natural and artificial weathering

There is not a uniformly-applied definition of what is meant by "correlation" in weathering. The term 'correlation' is often used even when there is no attempt to establish a quantitative relationship between degradation rates under natural and artificial conditions; it is then applied simply when similar trends are observed. There are several critical reviews of the correlation between natural and artificial weathering [8, 172, 210, 211]. There is general agreement that no correlation exists between natural and artificial weathering, and this view is even expressed in some of the Standards [174]. Even accelerated outdoor weathering using mirrors to provide enhanced exposure has been found to give contradictory information on polyolefins [212]. Marks and Butters [213] express doubt that data obtained in an extreme climate can give reliable prediction of performance in a temperate climate. Brown [172] quotes Davis and Sims [8] as follows:

> "Accelerated tests should only be considered therefore as giving a rough indication of the relationship between natural and artificial weathering. . . [Artificial weathering] is neither as perfect as its disciples claim nor as useless as its detractors state. . . The degree of correlation between natural and artificial ageing seems to be inversely related to the degree of acceleration."

In a similar manner, Gugumus [210] states:

> "Good correlation may be the result of a restricted amount of data or from data generated with closely related compositions or stabilization systems. . . Good correlation, with sufficient data on a variety of systems, can nevertheless mask a significantly differing behaviour of special compositions or additive systems."

Gugumus [210] discusses examples showing good and bad correlation. He notes that a combination of a sunlight-emulating fluorescent tube with a "black light" can often give good correlation with natural weathering but that failure times (to a chosen carbonyl index) of polypropylene films exposed in this way can differ from those obtained with a xenon arc by an order of magnitude. The results of xenon arc tests on polypropylene films did not correlate well with Q–U–V test results. Degradation of blown low-density polyethylene films exposed to a combination of u.v. and infrared lamps gave poor correlation with results obtained with samples weathered in Florida. On the other hand good correlation was found when comparing the results obtained with blown low-density polyethylene film weathered in Florida and in a xenon arc-based Weather-O-Meter when characterizing degradation by the exposure time required to cause the elongation to break to fall to one-half of the value obtained when unexposed or the time to reach a chosen carbonyl index [210]. The agreement based on the value of the carbonyl index may be fortuitous, for Akay *et al.* [214] found no simple correlation between carbonyl group concentration and mechanical properties in their study of low-density polyethylene. Not surprisingly, in another study of low-density polyethylene, Komitov [41] found no correlation between the carbonyl index and mechanical properties in samples with different thermo-mechanical histories. Good agreement was found between xenon arc and natural weathering behaviour of high-density polyethylene [210]. Gugumus [210] declares a strong distrust of tests based on fluorescent tubes, and this point of view is supported by the results of Rabinovitch and Butler [215] for PVC. It is evident that simply matching the u.v. spectrum of the artificial source to the solar spectrum is not enough to obtain good correlation with outdoor performance.

Other aspects of accelerated weathering in addition to the type of u.v. source are clearly important. Moore *et al.* [216] attribute the lack of correlation between the degradation of medium-density polyethylene in the form of (blue) water pipes exposed to natural weathering and artificial weathering using mercury vapour lamps, respectively, to the time-scale of the exposure rather than the fundamental chemical events. Bityurin *et al.* [217] found a dose-rate effect in the degradation of poly(vinyl chloride), giving a clear indication that difficulties must arise if accelerated conditioning is attempted.

Even when good correlation is claimed to exist between natural and artificial weathering the agreement is often less than perfect when assessed quantitatively, as, for example, in studies of PVC by Matsumoto *et al.* [218] and Gantcheva *et al.* [219]. In the former the experimental measurement of the acceleration obtained under the chosen artificial weathering conditions was ~ 2.9, whereas the value predicted from consideration of the u.v. exposure was ~ 11 [218].

Although most of the studies upon which the remarks above were based were made on polyolefins or PVC, similar observations have been made on other thermoplastics [220–222] and also with thermosets [223].

The reasons for poor correlation of natural and artificial weathering are evident from the discussions of mechanisms of degradation and stabilization. Gugumus [210] observes that polyethylene and polypropylene light stabilizers generally perform better in outdoor service than is predicted by an accelerated test using xenon arc exposure. This is usually because one of the ingredients in the stabilizing system (e.g. a low molecular weight hindered amine) diffuses to the surface during the dark periods to restore some of the protection. For a particular polymer system it is sometimes possible to "recalibrate" the xenotest, leading to a reasonable correlation between natural and artificial weathering performance.

5.4. Correlation between thermal degradation in laboratory tests and service performance

Although not strictly an aspect of weathering or surface degradation, the need for reliable test procedures for susceptibility to thermal degradation and for assessment of thermal stabilizing systems is similar to that for photo-oxidative degradation and stabilization. Oven-ageing at elevated temperature is the most common conditioning procedure but it is not possible to use the results to predict service behaviour when the conditions in practice are complex and involve the application of stress, as, for example, in mixing, calendering or extruding [15].

6. Characterization of weathered polymers

6.1. Introduction

Methods of assessing the changes that are promoted by weathering are of great importance. They are used to indicate the kind of chemical degradation that has taken place and can be used to determine the rate of reaction. They are required to assess the action and effectiveness of stabilizers. The most sensitive methods may indicate that degradation has occurred long before it is apparent in the engineering properties. There are many techniques available, some of which require sophisticated, expensive equipment found only in specialized research laboratories, and some which are widely available and can be applied routinely without extensive operator training. The following review of these techniques is arranged according to the characteristic that is to be monitored.

6.2. Oxygen absorption

The most common method to monitor oxygen uptake in polymers during weathering is infrared absorption [224]. Samples in the form of films can be studied in transmission, and with a solid object a thin section must be taken from the surface for use in transmission or in a cell for "attenuated total reflection" (ATR) [224]. The sectioning method requires considerable skill and is destructive but it permits study of the degradation at different depths within the sample (depth profiling). The extent of oxygen uptake is followed by measuring the carbonyl absorption at 1710–1740 cm^{-1}, normalizing the value by dividing by the signal at a part of the spectrum well removed from any strong absorption resonance from any of the components of the sample. This procedure selects the oxygen that has reacted to form carbonyl groups, often to give a ketone ($\lambda = 1712$ nm), and does not indicate the amount of oxygen reacted in any other way or simply physisorbed. With modern instrumentation using Fourier self-deconvolution of the carbonyl absorption it is possible to separate the different contributions (ketones, saturated carboxylic acids etc.) [225]. The carbonyl index is a most valuable quantity, however, because this type of modification provides a chromophore that may take part in further degradation reactions. An example of depth profiling in low-density polyethylene using the infrared carbonyl index to examine variations in the extent of reaction at intervals down to 25 μm is given by Davis and co-workers [8, 226]. Marks and Butters [213] found that ATR monitoring of carbonyl build-up was the most sensitive and reliable method for studying weathering of rigid PVC, and reported that changes were apparent before any change was detected by other techniques.

Depth profiling can also be performed by photoacoustic spectroscopy [227], exciting different frequencies to provide information from different depths, of the order of tens of micrometres. This technique has the advantage of fairly simple sample preparation and been applied to the study of natural weathering of polyethylene [228], to accelerated degradation of PVC [229] and to degradation of rigid polyurethane foam in various environments [230]. Modern infrared spectrometers with a Fourier transform data analysis facility are quite expensive but they are relatively easy to use and there is a vast amount of applications-oriented information available to assist interpretation of the spectra obtained. Many of the data can be accessed by computer, and the facility to compare spectra obtained on experimental samples with reference spectra made using standard materials is becoming fairly widely available.

To obtain a direct measurement of the total oxygen uptake a manometric method is required [8]. Davis and Sims [8] report that the sensitivity of modern apparatus allows detection of oxygen absorption rates as low as 2×10^{-5} mol O_2 kg^{-1}polymer h^{-1}. The problem with this method is that there will inevitably be an error if there are gaseous reaction products. To overcome this it is necessary to analyse the gas composition and to deduce the amount of oxygen taken up [142]; identification of the products of reaction is an added bonus.

The depth of oxidation can sometimes be recognized by optical examination of a polished section [231]. A microspectrometric infrared depth-profiling method has been described by Jouan and co-workers [232, 233] in which measurement of the carbonyl index and hydroxyl concentration were made in regions approximately 15 μm thick in a section of a 200 μm film. The sections made by Jouan and co-workers were cut perpendicular to the exposed surface and the region for analysis was selected using an image-masking aperture. Jouan and co-workers showed that oxygen depletion restricted reaction in the interior of films as thin as 200 μm.

6.3. Bonding state

The bonding state of reacted molecules can be determined in part by infrared measurements: for example the resonance peak for ketone carbonyl groups is at 1712 cm^{-1}, whereas that for ester carbonyl is at 1740 cm^{-1}. An example of the use of Fourier self-deconvolution of the carbonyl absorption to separate the different contributions is given by Maddams and Parker [225]. More detailed information about the bonding state can be obtained from X-ray photoelectron spectroscopy (XPS), alternatively called electron spectroscopy for chemical application (ESCA) [224, 234–236]. This method provides information from a depth of only a few nanometres from the surface and is therefore especially suited to the investigation of the early stages of weathering degradation [237].

Munro [238] studied the uptake of oxygen during the photo-oxidation and γ-radiation-induced oxidation of low-density polyethylene using ESCA. He identified the functional groups responsible for binding the oxygen and showed that the rate of reaction decreased gradually in the top 15 nm from the surface. He claims that under conditions of photo-oxidation (but not γ-radiation) there is a variation in oxygen uptake within the first 4 nm and that this effect is not found with aromatic polymers. By using a sample consisting of sandwich layers he was able to make measurements at chosen depths using the same equipment, and found that at 20 μm from the surface the uptake of oxygen was half that at the surface. These studies were conducted as model experiments and the u.v. source used was a black lamp of unknown spectral output, probably not representative of solar radiation.

ESCA is a specialized research technique requiring expensive equipment, skilled operators and significant knowledge to enable interpretation of the data. It is unlikely that it could be developed or adapted into a method for routine monitoring of polymer degradation.

6.4. Molecular weight

The concentration of oxygen in a weathered polymer is an indication of the extent to which the reaction has proceeded, but the presence of oxygen does not lead directly to deterioration of the engineering properties. Deterioration is generally the result of chain scission that follows the oxidation of the polymer. Thus it is the change in molecular weight that is the important parameter and this can be measured by a range of techniques [224, 239].

The technique most favoured for making molecular weight measurements for weathering studies is gel permeation chromatography [224, 239]. This method provides the molecular weight distribution (Fig. 1), from which can be derived the number-average (M_n) or weight-average (M_w) molecular weights as convenient parameters to follow the progress of degradation. Other methods give averages directly but do not provide the distribution of molecular weight; study of the changes in the distribution of molecular weight can sometimes reveal information about the underlying reactions. As with many of the analytical methods, samples can be taken from chosen depths within a weathered polymer test-piece to determine the variation in degradation as a function of the distance from the surface (Fig. 2).

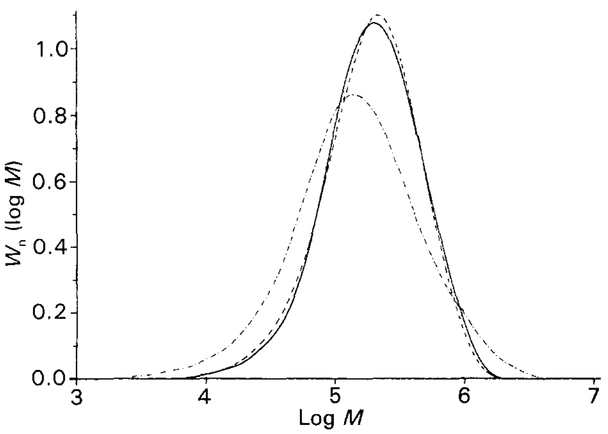


Figure 1 Molecular weight distribution for polystyrene (———) virgin sample, (b) (— —) from the surface of an injection-moulded bar, (—·—) from the exposed surface of a bar irradiated with u.v. for 6 weeks in the laboratory (from O'Donnell and White [240]).

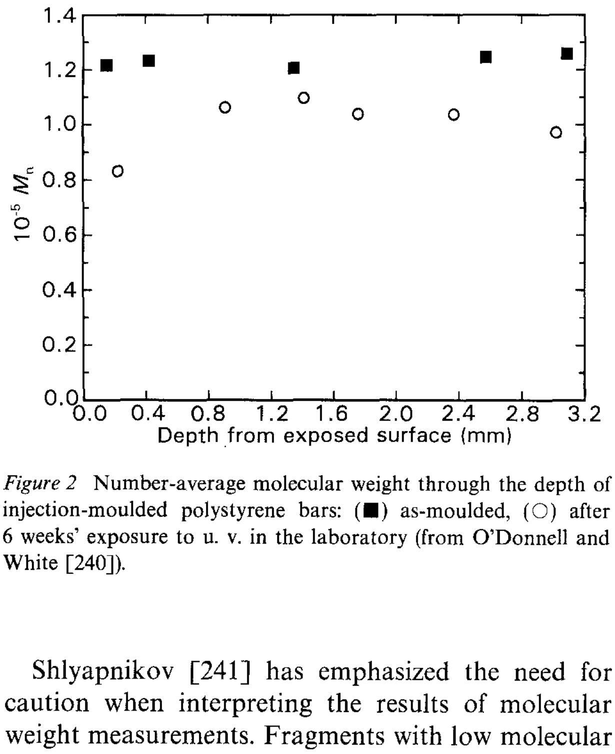


Figure 2 Number-average molecular weight through the depth of injection-moulded polystyrene bars: (■) as-moulded, (○) after 6 weeks' exposure to u. v. in the laboratory (from O'Donnell and White [240]).

Shlyapnikov [241] has emphasized the need for caution when interpreting the results of molecular weight measurements. Fragments with low molecular weight may not register in the molecular weight measurements, and if several scissions occur close together on a molecule the result may be indistinguishable from a single scission.

Although significant improvements in the instrumentation for gel permeation chromatography have taken place in recent years it is still not really a routine method except in the hands of experienced operators with a research background.

6.5. Free radicals

Free radicals are either formed or take part in many of the important reactions involved in polymer degradation and it would be of great assistance if their concentrations could be measured during weathering. Electron spin resonance [224, 242, 243] can be used to identify free radicals and measure their concentrations but is not sufficiently sensitive to study the low levels of concentration produced in natural weathering. It has been used in studies of degradation using high-energy irradiation (e.g. γ-radiation) [8, 224]. Another related application is in the study of molecular fracture, produced under conditions in which over-stressing of chemical bonds produces scission without the assistance of chemical reaction. Because of the short lifetime of radicals produced this way it is necessary to use special testing rigs accommodated within the spectrometer magnetic field [244]. Electron spin resonance is another specialized technique that is unlikely to lend itself to routine testing of degraded polymers.

6.6. Emission of volatiles

Volatile components in plastics may be lost during fabrication at elevated temperature and may even disappear slowly at service temperatures. Water is a common volatile and may be driven off at temperatures well below the moulding temperature; hygroscopic thermoplastics such as nylons and polycarbonates should be dried prior to moulding. In the field of degradation the volatiles of interest are low molecular weight stabilizers, plasticizers, and products of chemical degradation. The loss of stabilizer renders the polymer vulnerable to attack; the loss of plasticizer alters the mechanical properties and the polymer may no longer match the specifications required for a given application; the products of degradation may catalyse further reaction and their very presence indicates that degradation is occurring.

The method best suited to studying the volatilization of components from polymers is thermogravimetric analysis (TGA) [224]. The instrument measures the weight of a sample continuously while the volatiles are driven off either using isothermal conditions at elevated temperature or, more commonly, heating the sample so that the temperature rises at a constant rate. This type of temperature ramp is at the heart of many methods of thermal analysis. Care must be taken to ensure that none of the volatiles condense on the sensitive weight-measurement apparatus. In principle the volatiles could be collected for identification, for example, by mass spectrometry, but this is not done in the common commercially available TGA rigs. Instead the likely species are deduced from the temperatures at which steep changes in weight occur.

6.7. Glass transition temperature

The glass transition temperature T_g is determined mainly by the molecular structure of the repeat unit in a polymer. In the early stages of degradation the majority of the repeat units remain unchanged but there are important secondary factors that may alter T_g, including molecular size, the extent of cross-linking and the concentration of plasticizer. Chain scission creates more free chain ends and lowers T_g; increasing the cross-link density increases T_g; and a decrease in plasticizer concentration, through diffusion and/or volatilization, causes an increase in T_g. All of these effects change with distance from the surface and the most meaningful measurements are made using samples from narrow bands at chosen depths.

The most convenient method of measuring T_g is by differential scanning calorimetry (DSC) or the related differential thermal analysis (DTA) [224, 245]. In both methods the sample is heated at a chosen rate. In DTA the temperature rises at a constant rate except when a physical transition, such as a phase transition, is taking place, or when a chemical reaction is occurring. If the transition or reaction is exothermic (endothermic) the temperature rises (falls) above (below) the programme target temperature, which is set to increase at a constant rate, and the departure of the actual temperature from the target value is recorded continuously. In DSC the temperature of the sample is held at the target value at all times by altering the power input to compensate for exotherms and endotherms using a sensitive feedback system; the power input is recorded as a function of time (or, equivalently, temperature). The glass transition is shown by a change in slope of the thermogram and to define a particular temperature suitable for comparison between different samples showing minor variations, such as a polymer degraded to different extents, careful measurement procedures and analysis must be applied [224, 246, 247]. T_g fell about 20° after one year of outdoor exposure in Jeddah with both poly(vinyl chloride) and polystyrene [179, 180].

Another method of measuring T_g is dynamic mechanical thermal analysis, (DMTA) [30, 224, 248]. This technique involves deforming the sample cyclically and measuring the load and deformation continuously. This permits computation of the storage modulus, E', the loss modulus, E'', and the loss tangent, $\tan\delta$. The commercially available machines compute these quantities automatically and provide a temperature programmer that controls the temperature in the sample enclosure so that they can be plotted as a function of temperature. The peak of the $\tan\delta$ plot is taken to be at T_g. Samples should be extracted from the surface but the specimen preparation and mechanical limitations of the test set a lower thickness limit of about 0.2 mm, giving only limited scope for depth profiling.

6.8. Stiffness and hardness measurement

Stiffness changes often accompany degradation. Cross-linking will cause increased stiffness whereas scission might be expected to cause a reduction. In semi-crystalline polymers there is sometimes the possibility of chemi-crystallization (see section 2.3) which might increase stiffness at the surface of a degraded polymer. The storage modulus of thin samples extracted from weathered polymer parts can be made by DMTA but this method does not permit depth profiling with small measurement intervals, as noted in section 6.7.

An alternative method is to measure the bending stiffness of a bar-shaped sample (in three-point bending, for example) and then to machine away a thin layer and repeat the measurement. These steps are repeated until the bar is too thin for satisfactory bend testing. The Young's modulus distribution through the thickness of the bar can be deduced from the data [249]. The analysis is much simplified if it can be assumed that the modulus distribution is symmetrical about the mid-plane of the bar [250], but this is unlikely to be the case in a weathered bar unless it is continually rotated during exposure so that opposite faces are degraded equally.

Another way of assessing the mechanical properties of a surface is by using a hardness measurement. If information is to be confined to the surface then a microhardness measurement should be made; larger indenters and loads cause indentations that involve deformation to depths that may be beyond the region in which degradation is located. Microhardness measurements have been used in a number of polymer investigations, including studies of the properties of injection-moulded materials at different locations within the mouldings [251–255], ageing and T_g [256, 257], structure and morphology [258–263], blends [264], and correlation with mechanical properties [265–267]. The detection of different properties at different depths within injection mouldings [251–255] by this method indicates that it might be suitable for monitoring property changes at different depths due to degradation. There are few reports of applications of microhardness measurements in weathering studies, though González *et al.* [268] monitored u.v. degradation of PVC window frames using this method. The standard hardness measurement procedure in which an indenter is pressed into a surface under controlled loading conditions followed by measurement of the indentation that is left behind relates to the yield and plastic properties of the sample, but information can be obtained about the elastic properties if the load–displacement relationship is monitored during the indentation process. This procedure has been described by Gillen and Clough [269, 270] who modified a thermomechanical analyser to measure the tensile compliance of elastomers (with modulus values in the range 1–20 MN m^{-2}) with a spatial resolution of 0.05 mm.

A recent development in indentation testing is the "nanoindenter" which uses a very fine indenter and probes material properties at spatial resolution levels in the nanometre range. The apparatus consists of a very fine indenter drive and force-measuring system to monitor the resistance to the motion of the indenter, and is normally set to record the load–displacement relationship when the indenter is pressed into the sample under test using a preset loading or displacement programme. The machine is microprocessor-controlled and alternative modes of operation such as stress relaxation are easily set. The sample is mounted on a table that is provided with very fine x–y control and the nanoindenter can be set to make tests at chosen positions automatically, permitting hundreds of tests to be made unsupervised (e.g. overnight). The scale of the volume of material that is under test coincides with important morphological features within plastics materials, including the lamellar thickness in semi-crystalline polymers and the domain size in phase-separated block copolymers. For example, Williams *et al.* [271] have shown that the nanoindenter is capable of detecting differences in property in an epoxy resin as a function of the distance from a fibre in a composite. As yet there is very little information available on the application of this technique to polymer studies, but the specifications of the apparatus provide optimism that it will emerge as a valuable tool and that it should be capable of modulus depth profiling in degraded polymers.

6.9. Morphology and structure

The effects of molecular orientation and of crystallinity on degradation have been referred to above, mainly in sections 2.3 and 2.4. The rates of diffusion of reactants, including oxygen and stabilizing molecules, are lower in a highly oriented polymer than in the corresponding unoriented polymer, causing the oriented polymer to be more resistant to degradation. If a load is applied the stress is fairly evenly distributed over the bonds in an oriented polymer, so that the contribution to degradation from stress-aided chemical reactions is likely to be less than in disordered polymers in which a fraction of the bonds will be seriously overstressed. In semi-crystalline polymers degradation is concentrated in the amorphous regions. This is because defect sites on the molecule, where reaction is most likely to occur, are rejected from the growing crystals, and also because the diffusion of oxygen is generally much slower in the crystal phase. Thus it is often important to know the morphology of a polymer component in order to explain or to predict its degradation behaviour. Methods of studying the morphology, including measurement of orientation and crystallinity, are found in several reviews [224, 272, 273].

6.9.1. Molecular orientation

This can be measured using birefringence, though stress also produces changes in birefringence and it is sometimes difficult to separate the two contributions [48, 49, 274–277]. To measure the birefringence as a function of depth within a polymer article it is necessary to remove layers and either to measure the layer birefringence (if layers can be removed without modifying the structure) or to measure the relative retardation of the remainder at each removal and then deduce the through-thickness birefringence distribution [278–280]. This is a destructive method, though the material removed can be used for further analysis, such as infrared determination of the carbonyl index and/or molecular weight measurement by gel permeation chromatography. Another method for assessing orientation is the measurement of the dichroic ratio [224] in which the absorption of a beam of infrared irradiation polarized with the polarization axis parallel to the orientation axis is compared with that obtained when perpendicular to the orientation axis. This gives a measure of the average orientation of a particular bond or group on the molecule. The measurement is normally conducted on a thin film of material and requires the extraction of suitable samples by microtoming or machining.

6.9.2. Crystal orientation

The orientation of crystals can be determined using X-ray diffraction. Diffractometer scans taken with the sample mounted in different orientations can be used to obtain a useful guide to the state of orientation [281–284] but a more comprehensive assessment requires the determination of pole figures [252, 285, 286].

6.9.3. Crystallinity

This can be determined using

(i) wide-angle X-ray diffraction, by comparing the integrated intensities in the crystal peaks with the integrated intensity from the non-crystal regions [224];

(ii) DSC from the heat of fusion if a suitable standard sample is available so that a meaningful comparison can be made [245];

(iii) infrared absorption from a group that is specific either to the crystal phase or to the amorphous phase; and

(iv) density, where the individual densities of the crystalline and amorphous phases are known. (Care must be taken here over interpretation of density measurements in degraded samples because oxidation can change the density without a change in crystallinity [63, 121]).

Again, sample preparation is normally destructive for all of these techniques.

The arrangement of the crystals in a macroscopic sample can have an important influence on behaviour and can be determined by microscope observation. Spherulitic structure can normally be resolved by the light microscope but lamellar structure within the spherulite requires electron microscope techniques [224, 273, 287]. Apart from the difficulties associated with radiation sensitivity of polymers that limit their lifetime in an electron beam instrument, there are severe problems in specimen preparation for best results, including sectioning, and etching and/or staining to produce contrast between the crystal and amorphous regions [224, 273, 287]. Transmission electron microscopy has rarely been applied to the study of weathered polymers, though it can be used for special applications of relevance to the weathering behaviour of polymers, such as the determination of the size distribution of second-phase particles, including rubbery inclusions in toughened polymers and finely divided particulate filler [273].

6.10. Surface topography

The appearance of the surface of a polymer article usually changes during weathering. This of itself may be sufficient to render the article unserviceable in some applications, if, for example, a particular colour or level of reflectivity is required, and tests may be required that are targeted specifically to the observation of this property [288, 289]. More generally the change in surface appearance may indicate the extent of degradation and the imminence of mechanical failure.

Study of the surfaces of failed components can assist the determination of the mechanism of failure.

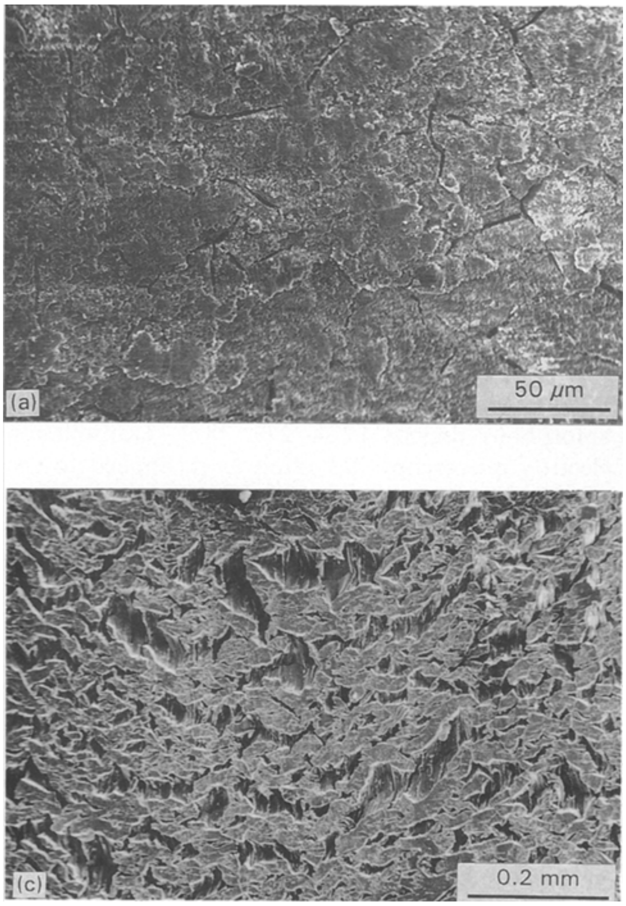
6.10.1. *Light microscopy*

This technique is simple to use and is usually non-destructive [224, 273, 290, 291]. The most common feature of interest on the surface of a weathered polymer is fine cracking. This is usually well within the resolution capability of a light microscope and the cracking is often located on relatively flat surfaces so that the depth-of-field limitation is not a serious handicap. Fracture surfaces show much greater variations in depth and light microscope images are almost always inferior to scanning electron microscope images.

6.10.2. *Scanning electron microscopy*

The electron microscope has superior resolution and depth of field compared to the light microscope. The specimen chamber is of limited size and it is often necessary to cut a sample from the object of interest. With polymeric samples it is normally necessary to provide a conductive coating to prevent charging of the sample with consequent destruction of the image [224, 273, 291, 292]. The need to coat the sample will almost always preclude its return to service even if it can be accommodated whole in the specimen chamber. With severely weathered samples even a conductive coating of generous thickness is insufficient to prevent charging, presumably because the damaged surface layer may be partly detached from the bulk of the sample [293]. Even if satisfactory images are obtained it is always necessary to be alert to the possibility of artefact production when imaging polymers in an electron beam instrument [224, 273, 291, 292].

For maximum information it is advisable to inspect the surface of the as-weathered sample and then, after the sample has been broken in a laboratory test, to study the same surface again as well as the fracture surface. This can help to deduce the mechanism of fracture [179, 180, 182, 294]. A selection of scanning electron micrographs of bars that were tensile-tested to failure after a prolonged period of u.v. exposure is given in Fig. 3. The following characteristic features are illustrated:



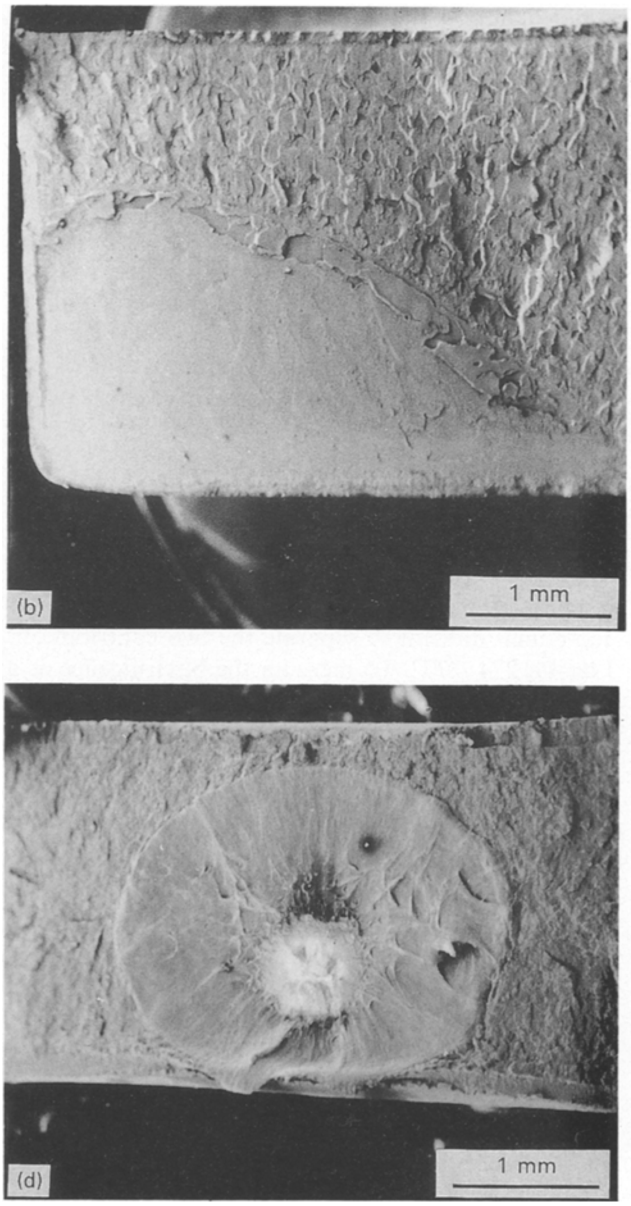


Figure 3. Scanning electron micrographs of samples exposed for 2 years outdoors in Jeddah then tensile-tested to failure: (a) end face of polystyrene bar section, (b) fracture surface of the specimen shown in (a) (the exposed face is at the bottom), (c) exposed surface of a nylon moulding, (d) fracture surface of a moulding made from polypropylene containing a light stabilizer (from studies by M. M. Qayyum and J. R. White).

(a) Fracture of a brittle layer formed on the surface of a brittle polymer. The final test-piece fracture does not necessarily nucleate here.

(b) Fracture nucleated in a corner on the surface facing the u.v. source.

(c) Fracture of brittle layer formed on the surface of a polymer that retained significant ductility in the interior: failure occurred by plastic fracture from a diamond-like cavity developed from one of the surface cracks [294].

(d) Fracture from an internal site: the sample was exposed outdoors in Jeddah for two years and had a highly degraded surface [182], yet fracture nucleated in the interior.

These observations are relevant to the discussion in section 2.5.

7. Mechanical testing of weathered polymers

It is most important to measure the deterioration of mechanical properties in any assessment of the resistance of materials to their working environment. Even if their primary function relies on some other property, such as transparency [295] or electrical resistivity, they are rendered useless if they fail mechanically. There are many tests available for the assessment of mechanical properties [296–298]. The procedures found in the relevant standards have been discussed in some detail in the book edited by Brown [296], which provides a good introduction to the use of Standards and includes reference to ASTM tests as well as BS and ISO standards. The book by Shah [298] has a similar mission but concentrates narrowly on ASTM tests. The procedures and limitations of the standard tests are generally presented satisfactorily and the comments made here are confined to the special problems posed by degraded samples, in particular those in which the most severe damage is near the surface.

7.1. Tensile tests

Tensile tests are very common for the assessment of all classes of materials. It is conventional practice to mould polymers into test bars with shapes defined by the various standards for tensile testing. Thermoplastics are injection-moulded and if the bar is made using a single-end-gated mould the properties will generally be favourable because of the enhancement provided by molecular orientation during mould filling. It is convenient to use similar bars for weathering studies but it is important to be aware of the possible advantages and disadvantages. The oriented skin at the surface of an injection moulding has quite different properties from the material in the interior. This is not confined to mechanical properties, and of relevance in a study of degradation is that oxygen diffusion may be different and the photo-oxidative reactivity may be different. The use of test specimens in injection-moulded form is therefore recommended if information is required to predict the behaviour of injection-moulded articles, a very common and important class of products. Extrusion, blow-moulding and thermoforming can all produce similar morphological variations within the wall thickness and corresponding property gradients, but may show fabrication-related degradation characteristics that differ in detail from those displayed by injection mouldings.

Another point that must be considered is the effect of thickness. A common thickness for injection-moulded test bars is 3 mm and the degradation of properties will vary strongly through a moulding of this thickness. This is because absorption of u.v. causes the intensity to fall as it penetrates from the exposed surface and because of the depth variations of oxygen and other reagents controlled by diffusion. Many plastics products have a wall thickness of about 3 mm and it is a sensible thickness to use in tests, but in some polymers the damage is confined primarily to a near-surface region and this leads to a mode of failure that may be quite different to that which would be obtained in a thin sheet of the same material. It is prudent to choose a test-piece thickness that matches the wall thickness of the product for which the information is required.

The most common tensile test is the monotonic loading test conducted under constant crosshead speed conditions. The importance of standardizing on crosshead speed and conducting tests within fairly narrow temperature limits is similar to that for undegraded viscoelastic material. The whole of the load–deformation characteristic should be recorded but the performance is usually judged with reference to the maximum (engineering) stress sustained during the test and the elongation to break. It is possible in principle to derive a (time-dependent) Young's modulus but this will have only limited accuracy unless an extensometer is used, and it will be an average value for the whole cross-section. The strength often changes very little even after prolonged exposure, whereas the elongation to break is usually a fairly sensitive indicator of degradation and often correlates quite closely with outdoor exposure (Figs 4 and 5). It is recommended that the fracture surface is retained for microscopical examination.

7.2. Impact testing

Impact tests fall into two categories. In the pendulum type of test, such as the Izod or the Charpy, a bar-shaped sample is broken by a swinging pendulum striker and the loss of energy of the pendulum is measured by the follow-through height and is used to characterize the toughness of the sample. In the "falling dart" test a striker with a round nose is allowed to fall a given height on to the sample in the form of a disc supported on a ring. The energy of the striker at impact is adjusted by changing the mass and/or the distance of fall until approximately 50% of the samples fail (see the relevant Standards for a full description of the procedures).

Fracture is normally initiated at a flaw, and because of the sensitive size-dependence of stress concentration the results of pendulum impact tests on as-fabricated polymers are very variable. As a

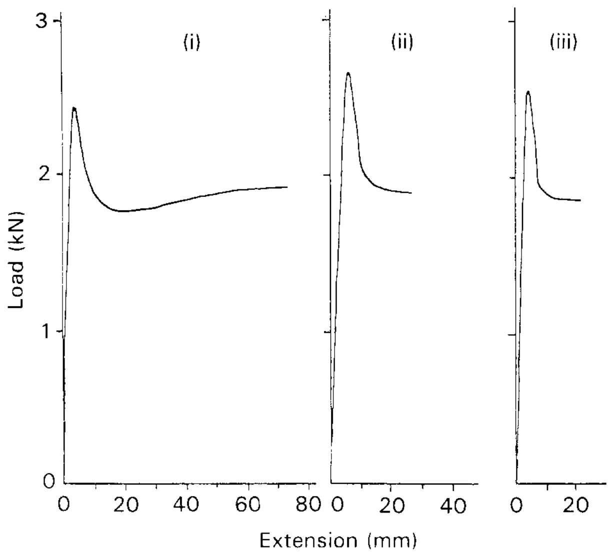


Figure 4. Load–deformation curves for uPVC injection-moulded tensile bars weathered outdoors in Jeddah [179]: (i) as-moulded, (ii) weathered for 8 weeks, (iii) weathered for 16 weeks.

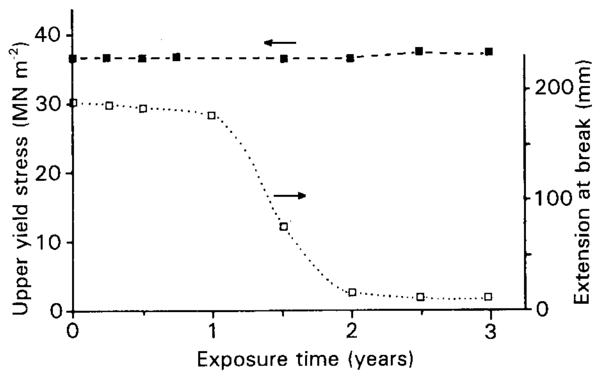


Figure 5. Upper yield stress and (□) extension to break versus exposure time for polypropylene tensile bars weathered outdoors in Jeddah [182].

consequence, pendulum impact tests on polymers are most frequently applied to notched samples, using a notch of standard dimensions [297–299]. Although this ensures that fracture will initiate at a chosen position and that the geometrical aspects of the test are standardized, it raises serious problems when dealing with moulded products and with weathered polymers in particular. Injection mouldings made from polymers contain a skin at the surface of the order of 0.2–0.4 mm thick that has very different properties to the interior (core). The action of cutting a notch exposes the core material, which can be expected to have quite different fracture properties to the skin. In addition, the skin is normally in a region of moderately high compressive residual stress, which discourages crack propagation, whereas the root of the machined notch will be located in a region of weaker stress, possibly tensile [48, 49]. Thus the use of this procedure for a moulded polymer must be viewed with much caution. In the case of a polymer that has suffered surface degradation the position is even worse. Firstly the notch would penetrate the most degraded material, so that the crack would start in material quite different from that in which a crack is likely to nucleate in service conditions. Secondly it is commonly observed that weathered polymers form surface cracks that appear to nucleate failure, and this aspect of the deterioration would not be taken account of in a notched test.

The information obtained from impact testing is necessarily limited though some optimism exists that modern instrumented impact testing may lead to improved understanding and hence reliability [299].

7.3. Other mechanical tests

Dynamic mechanical thermal analysis can be used to test quite small test pieces, for example 10 mm × 2 mm × 0.2 mm, and samples can be extracted from chosen locations within a weathered article to study variations in degradation with depth [30, 224]. This technique is used to measure the storage modulus, the loss modulus and the loss tangent, but these parameters may not be as sensitive to degradation as the extension to break [71].

Some *ad hoc* tests have been introduced specifically for testing weathered samples. Cooney [300] describes a method in which exposed samples are bent around a mandrel. He used nine mandrels with different diameters and recorded the fraction of samples that failed at the mandrel size at which breakages first appeared.

8. Modelling degradation: lifetime prediction

8.1 The purpose and limitations of modelling

The ultimate aim of a testing programme should be to provide a prediction of the performance of the material under service conditions. It is desirable to develop models that allow short-term laboratory data to be used to give an accurate forecast of the lifetime of a component to assist the choice of material and to permit economic planned replacement. From the review of degradation and stabilization presented in sections 2 and 3 it is evident that it is unlikely that a simple universal formula to do this for all polymers will ever be found. This is because of the many chemical and physical processes that are involved in degradation and of their interactions. This was realised as early as 1967 when Kamal and Saxton [301] stated that:

> Data [from outdoor and indoor exposure] have failed to contribute significantly to the analysis or prediction of outdoor weathering under generalized conditions...

To model the degradation of a polymer accurately the minimum data that are required are the rate constants for all of the reactions involved in the degradation process, including those involving the products of the reactions, and the diffusion constants of all of the reagents, including oxygen, low molecular weight stabilizers, and products of the reactions. The model would have to keep account of the concentrations of all of the reagents both with respect to time and to position within the component, and would have to allow for the change in u.v. level as a function of distance from the exposed surface. A list of some of the relevant kinetic parameters for the degradation of polypropylene has been presented by Slobodetskaya [70]; although it is fairly extensive it does not contain all of the data specified above. The model would have to allow for diurnal and seasonal variations in temperature and u.v. intensities, and for the effect of applied and/or residual stresses. This is clearly a formidable task even for a simple polymer protected by a simple, well-understood stabilizing system and operating in a pollution-free atmosphere, though modelling of systems with similar complexity is now well established in many other fields of technology. Considerable effort has been put into this problem in the former USSR and has been reviewed by Deyun *et al.* [302]. The empirical approach described by Deyun *et al.* does not appear to be suitable for wide application. An attempt by Danforth [303] with more limited scope proved unsuccessful, confirming that a more comprehensive treatment, taking account of all of the variables listed above, is needed.

The reasons why the objective still seems so remote are easy to understand. Firstly it is necessary to identify the various reaction pathways, then to measure the rate constants. This may not be easy when products of reactions play a significant part. Determination of diffusion coefficients may be equally difficult for transient products of reaction, especially when it is recognised that the polymer matrix may have morphological variations through the depth as a consequence of the fabrication process and that they may cause the diffusion behaviour to vary correspondingly; further changes in diffusion rates may occur as a consequence of the degradation of the polymer [304]. It would probably be feasible to undertake a detailed, computer-based study of this kind but the motivation to do so is not great because the results would be unlikely to have any relevance to any other polymer–stabilizer system, in particular the multi-component products that dominate the commercial world.

Although a complete model of the kind discussed above is likely to remain elusive, there are circumstances when degradation appears to follow a predictable course, usually when it is dominated by a single process. The remaining sections on modelling are devoted to reviewing studies in which this has been exploited, often narrowly in a particular material and product application.

8.2. Oxygen-diffusion-limited degradation

DeBruijn [61] has related the depth-dependent variation in degradation in polyethylene to oxygen concentration and developed an expression for the degradation depth in terms of the oxygen diffusion parameters and the u.v. intensity. This subject has recently been reviewed in this journal by Audouin *et al.* [305] and will not be pursued further here. The review by Audouin *et al.* also considers the fracture mechanics of polymers with an embrittled surface layer [305].

8.3. Time–temperature–dose-rate superposition

The concept of time–temperature superposition is well established in polymer science and technology. The rate of chemical reaction depends on temperature according to the Arrhenius expression, while physical processes such as mechanical relaxation follow a fairly similar trend for which slightly more complicated mathematical time–temperature relationships, such as the WLF equation, have been developed theoretically or empirically [306–308]. In polymer degradation studies it is necessary to consider in addition the effect of the radiation intensity when a radiolytic process is involved. It is likely that dose rate, and not just total accumulated dose, will be important either because of the sequential nature of the some reactions or when diffusion rates partly control the degradation processes. This has been noted by Bityurin *et al.* [217], who observed that the size of the photodegraded layer near the surface of PVC samples increased with dose rate for a particular value of total accumulated dose. This may have a second-order effect because the photo-degraded layer is believed to provide some protection against further photo-oxidation [309, 310]. The layer is brittle and is unlikely to be permanently effective if the sample is strained. More details of the degraded layer are given by Aleksandrov *et al.* [133] (see section 3.2).

Gillen and Clough [311, 312] have made a fairly successful attempt to conduct a time–temperature–dose-rate superposition for insulation materials for use in nuclear plant where γ-radiation is the hazard. They used a Co^{60} source for their laboratory irradiation experiments and included a PVC insulation material and a low-density polyethylene. They based their theoretical framework on the Arrhenius expression and characterized degradation by the ratio of the elongation obtained in a tensile test with the degraded sample to that obtained with an unaged sample. Plots of this quantity versus time for different exposure temperatures, T, were displaced along the time axis and they found that good superposition could be achieved by applying shifts equal to

$$a_{\mathrm{T}} = \exp\left(\frac{E_{\mathrm{a}}(T_{\mathrm{ref}}^{-1} - T^{-1})}{R}\right)$$

where T_{ref} is the reference temperature (chosen to match the service conditions for predictive studies), E_{a} is the activation energy for the process and R is the gas constant. To include the effect of dose rate, Gillen and Clough rationalized their data by comparing values of the dose required to produce a condition that they termed "equivalent damage" and which they took to be indicated by the elongation falling to 50% of the value for unaged samples. Dose rates r_1 and r_2 required to give equivalent damage at temperatures T_1 and T_2, respectively, are given by

$$\frac{r_1}{r_2} = \exp\left(\frac{T_2^{-1} - T_1^{-1}}{R}\right)$$

This was found to work for some materials, but the authors point out that it is very material-specific and that they would not be prepared to predict the behaviour of another grade of polyethylene from the results obtained with the grade studied by them. Essentially the same equation was used by Goldfein [313], but he did not pursue weathering-related degradation in much depth.

Karpukhin [82] found that the rate of oxidation of polyethylene was given by

$$\frac{\mathrm{d}c}{\mathrm{d}t} = aI + bI^{1/2}$$

where c is the carbonyl concentration and I the irradiation intensity. He claimed that the rate of oxidation depended only slightly on oxygen pressure, contrary to the reports discussed in section 5.2.4. He found that the highest levels of oxidation were near the inner surface of cable insulation, where the temperature was highest and the oxygen level lowest.

Minsker *et al.* [314] suggest that the time to reach a given level of degradation in PVC is

$$\tau = \tau_0 \mathrm{e}^{U/T} W^{-\alpha} H^{-1}$$

where U is proportional to the activation energy, W is the relative humidity and H is the u.v. dose for wavelengths below 400 nm.

8.4. Predicting stress-aided degradation

The most common approach to modelling the effect of stress is that introduced by Zhurkov. Damage is attributed to thermally activated events that can be assisted by the application of stress. This can be conveniently introduced into an Arrhenius-type expression by subtracting from the energy barrier term, ΔG, a quantity that is proportional to the stress, σ. Thus the rate of degradation can be expressed as

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

where A and B are constants; A is a frequency factor and B has the dimensions of volume. This formula is clearly derived from a consideration of the molecular processes involved and does not take account of the conventional continuum fracture mechanics. It is likely to be most successful when molecular fracture is the major fundamental degradation mechanism. As such it would seem most appropriate to apply it to weathering and this has been done in several studies, mainly by groups working in the former Soviet Union. It also has been shown to fit the rate of degradation of polycarbonate caused by electron beam irradiation [315]. Natov and co-workers [316, 317] claimed that the application of strain caused changes in the chemical reactions that complicated the time-temperature dependence. Nevertheless they showed that stress accelerated degradation in both polyethylene and polypropylene, and plotted the logarithm of lifetime versus stress to produce a series of S-shaped curves, one for each temperature studied [316, 317].

Minsker *et al.* [314] include much discussion of the application of this approach in their substantial book on the degradation and stabilization of vinyl chloride-based polymers. They give an example of the use of an expression derived from the Arrhenius formula for the lifetime of samples and use data obtained in tests at 293 K and 323 K to predict behaviour at a reference temperature of 393 K. Despite their enthusiasm for this approach, they emphasize that it can only be used with confidence when degradation is dominated by a single process.

8.5 The use of chemical degradation characteristics to predict long-term behaviour

It is often relatively easy to monitor a chemical characteristic such as the carbonyl index, and it would be most useful if this could be related to the engineering properties. This would be a most convenient aid to testing procedures. An even more valuable prospect would be the possibility of using a chemical parameter, measured on a component that had been in service for an unknown time and under unknown conditions, to predict the remaining lifetime under the conditions it is to be exposed to. This is the approach investigated by Hamid and Prichard [318] who use Fourier transform infrared spectroscopy (FTIR) to determine the carbonyl concentration in linear low-density polyethylene. They also use DSC measurements to indicate changes in crystallinity. Despite the title of their paper, their work is not strictly "modelling" in the sense used here in that their strategy is to attempt to identify the important weathering agents and then to describe the experimental data with a semi-empirical formula. Hamid and co-workers present details of some of their experimental studies and procedures in other publications [319–321].

9. Discussion and conclusions

There exists a reasonable level of understanding of the chemical mechanism of outdoor degradation of polymers. As a consequence, very effective stabilizing systems have been developed. It is impossible to prevent degradation altogether, but lifetime improvements of the order of 100-fold can be achieved. The chemical pathways in polymer degradation and stabilization are often complex and it is not yet established which reaction(s) are most important in many particular polymer–stabilizer systems, and further improvements in stabilization may be possible as deeper understanding is developed.

Many plastics are used as part of multiple-component consumer goods such as cars and electrical appliances. The article will normally have an "expected lifetime" and plastic components that do not fail as the result of wear (for which different design specifications must be chosen) should have a lifetime in excess of this. If the lifetime of the plastics component is less than this then the consumer is faced with the cost of replacement and the problem of disposal. If the lifetime of the plastic component is significantly higher than that of the article of which it forms a part then the material may be over-designed, for example it may contain more u.v. stabilizer than is necessary and may be unnecessarily costly as a consequence.

Reliable predictions of lifetime cannot be made at present even if experimental data from accelerated artificial weathering tests are available. The reasons for the unreliability of existing methods for lifetime prediction have been discussed in section 8. The ideal method would involve a series of different artificial weathering exposures followed by either a chemical or mechanical test, the results of which could be extrapolated to give a prediction of lifetime under service conditions. The problem with accelerated testing is that different chemical processes are accelerated disproportionately, and this may lead to failure by a completely different mechanism to that suffered in service. Identification of chain scission occurring in both natural and artificial weathering is not a sufficient basis for meaningful comparison between accelerated weathering and service conditions. The connection must be made with the macroscopic mechanism of failure. Emphasis should be placed on attempting to deduce the mechanism of failure when samples are tested to fracture after artificial weathering, and comparison with field experience should be made whenever possible. If different mechanisms of failure are observed with laboratory and service samples, respectively, then predictions of service behaviour based on the results of laboratory tests are unlikely to be reliable.

Accelerated weathering tests can often rank the weatherability of different polymers in reasonable agreement with outdoor behaviour, but even this may not always happen. Stress accelerates photo-oxidation and should be taken into account when modelling degradation. The application of stress should be incorporated into test procedures.

There are two distinct requirements for monitoring chemical changes. One is for a method that can detect the early stages of chemical degradation, and the other is for a method that can measure the extent of the damage when it is at a more advanced stage. The latter would be of greatest value if it could be applied to articles already in service and used to predict the remaining lifetime. Correlation of the change in an easily measured chemical characteristic with the degradation of key properties (such as strength and toughness) must be established. Infrared spectroscopy is probably capable of providing the required chemical information but sampling is destructive. There are many surface-analytical techniques that are of great value as research tools but which will never find widespread application in surface degradation assessment because of their cost or the difficulty in using them and interpreting the results. For surface degradation assessment the most valuable tool would be one permitting infrared analysis in a reflection mode on a surface without extraction from the article or any other special preparation, and preferably with a depth-profiling capability. Photo-acoustic spectroscopy might be developed to fulfil this function.

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