

RECENT ADVANCES IN THE PHOTO-OXIDATION OF POLYMERS

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Abstract - Recent results, mainly selected from the authors work on polystyrene, clearly indicate that a sound understanding of the photo-oxidation of polymers cannot be gained without quantum yields determination. These show that transfer of energy has a major role in the initiation of the photo-oxidation because of the high local concentration of reactive groups in polymers. It is also possible to find correlations between the rate of ageing of industrial polymers and the extent of chemical transformation of the materials prior to the exposure to ultra-violet light.

INTRODUCTION

Ageing of polymers on exposure to sunlight in the presence of air has always been a concern of users and producers of polymeric materials. Since more than two decades many papers have been published on that topic but, despite of the interest of most of them as contributions to specific problems, very few help towards a general understanding of the photo-oxidation of polymers. The main reason for such a situation is that the published data are usually not directly comparable because neither the spectral distribution of the light sources nor the incident intensity on the samples is mentioned. Moreover, quite often only relative values of some properties have been measured as a function of exposure time.

In recent years, however, owing to the development of photochemistry, more quantitative studies have been undertaken including quantum yield determinations. These often lead to rejection of previously accepted ideas and promote new ways of viewing the problems. That aspect is illustrated with some examples in the first part of this paper. On the other hand, the photo-oxidation of polymers is a field where fundamental and applied research are so closely connected that progress in the understanding of the mechanism of the degradation contributes to the laying down of correlations between changes of mechanical properties and chemical transformations. This will be discussed in the second part of the paper.

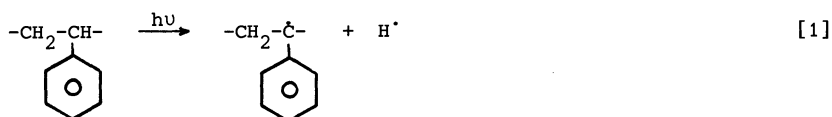
ELUCIDATION OF THE MECHANISM OF PHOTO-OXIDATION

The examples presented below are mainly selected from our work on polystyrene. This is justified because

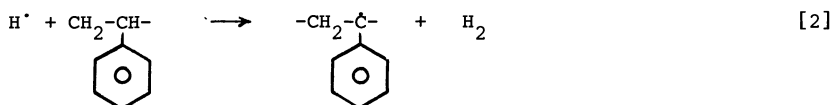
- polystyrene is, with polyethylene and polyvinylchloride, one of the most important industrial polymers.
- polystyrene is extremely susceptible to photo-oxidation. On exposure to sunlight it very quickly becomes brittle and a yellow color is observed.
- polystyrene exhibits two well distinct absorption ranges.

One, with a maximum around 260 nm, is typical of the phenylchromophore and thus related to the intrinsic structure of the polymer. The other, barely detectable in thin samples, extends into the solar ultra-violet range above 290 nm. It is due to the presence of impurities or anomalous structures. The photo-oxidation of "pure" polystyrene can thus be quantitatively studied at 254 nm and the results obtained facilitate the understanding of the ageing of commercial samples in conditions similar to the exposure to sunlight.

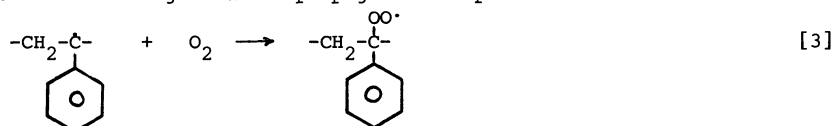
The quantum yield of oxygen absorption measured on irradiation of polystyrene at 254 nm (600 Torr oxygen) is $2.7 \cdot 10^{-2}$ (1). The ease of oxidation of polystyrene has often been ascribed to the presence of labile tertiary hydrogen atoms. The primary effect of light could then be :



We have indeed observed that hydrogen is evolved when polystyrene is irradiated under nitrogen at 254 nm, probably as a consequence of reaction [2]

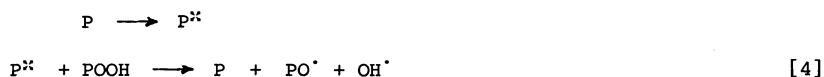


The quantum yield of hydrogen production is $4.6 \cdot 10^{-5}$ (2). On the other hand, crosslinks are formed by recombination of macroradicals produced close together in reactions [1] and [2]. The quantum yield of crosslinking has been measured by GPC to be about 10^{-5} (3) in agreement with the mechanism proposed. These values however clearly indicate that oxygen absorption cannot be initiated by reaction [1] followed by reaction [3] unless a chain reaction is assumed involving about 50 propagation steps.

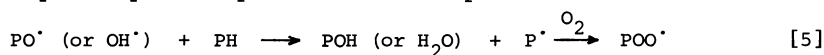


This is quite unlikely in a rigid matrix. This first example thus illustrates how quantum yields disprove a mechanism proposed on a qualitative basis. Another mechanism has to be searched to justify the results quantitatively.

An indication is found by observing that the intensity of the excimer fluorescence of polystyrene very quickly decreases on irradiation in the presence of air whereas no appreciable change is detected in vacuo (2). This has been ascribed to transfer of energy from the excited phenyl chromophores to hydroperoxide groups formed in the polymer :

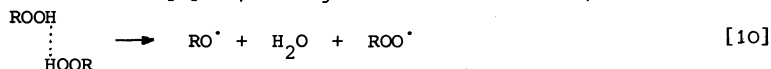


These are expected to decompose with a quantum yield close to 0.5, a value measured for cumyl hydroperoxide (a model compound for polystyrene hydroperoxides) in a polystyrene matrix (2). The radicals produced in reaction [4] will then bring about the absorption of oxygen with a quantum yield compatible with the experimental value :

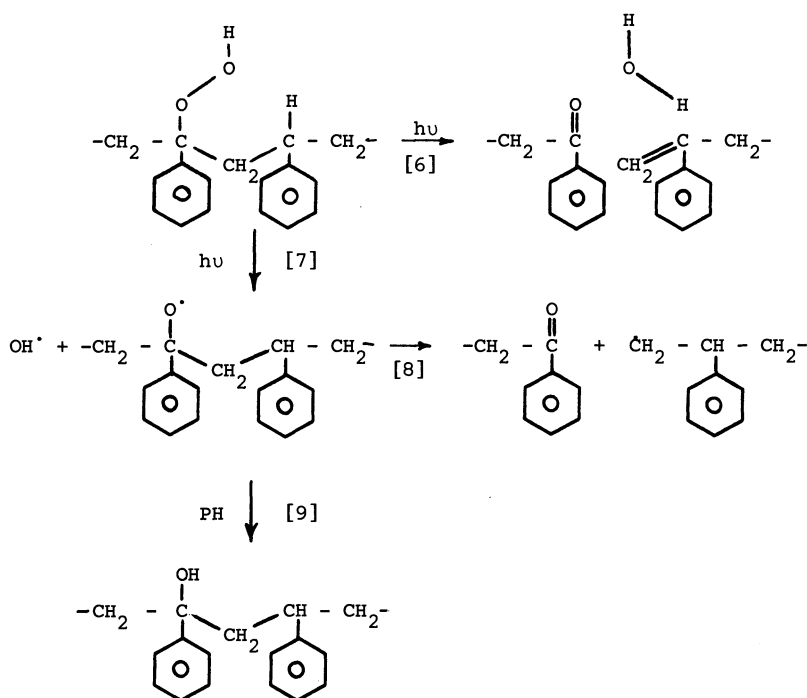


This mechanism is supported by the fact that added cumyl hydroperoxide accelerates the rate of photo-oxidation of polystyrene (2).

The absorption of oxygen is not by itself detrimental to the mechanical properties. These mainly depend on the molecular weight of the polymer. On irradiation of polystyrene at 254 nm (600 Torr oxygen) chain scissions are produced with a quantum yield of $5.5 \cdot 10^{-4}$ (4). This indicates that only a small fraction of the primary oxidation products ultimately results in breaking of C-C bonds. It is also found that acetophenone end groups are produced simultaneously since their quantum yield of formation is $6.4 \cdot 10^{-4}$ (1). The mechanism proposed is summarized on Scheme 1. A small fraction of the hydroperoxide groups decomposes as a consequence of energy transfer according to reaction [6]. Most follow reaction [7] or, at high local concentration, a bimolecular mechanism :

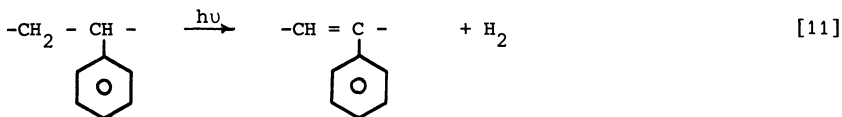


Reaction [6] is thermodynamically favored over reaction [8] by about 150 kJ/mole. Moreover, it not only produces an acetophenone end group, in agreement with quantum yields measurements, but also an unsaturated chain end, the importance of which will be realized later. Finally, it is found that the quantum yield of alcohol groups formation by reaction [9] is more than ten times higher than the quantum yield of acetophenone groups formation. It can thus be concluded that reaction [8] contributes for a negligible part to chain scission in the photo-oxidation of polystyrene at ordinary temperature. This conclusion is probably valid for other polymers also at variance with the often proposed but never demonstrated mechanism involving β -scission of an alkoxy radical.



Scheme 1. Decomposition of polystyrene hydroperoxides.

Now, another detrimental consequence of the photo-oxidation of polystyrene is the appearance of a yellow coloration. For a given dose this is much more intense when polystyrene is irradiated in oxygen than in vacuo (1). This unexpected result can be ascribed to the presence of a higher concentration of terminal unsaturations produced by reaction [6] in the former case than of random unsaturations in the latter. Indeed, in vacuo the quantum yield of reaction [11] is only a fraction of the quantum yield of hydrogen production and thus more than ten times smaller than that of reaction [6].

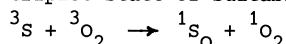


Both terminal and random unsaturations can act as energy acceptor, as well as monomeric styrene (5), and decompose by a molecular mechanism similar to [11] with production of dienes. In the same way, these are later transformed into higher polyenes by successive reactions. Evidence for the presence of up to five conjugated double bonds in photo-oxidized polystyrene has been obtained by absorption and emission spectroscopy (1). These examples once more point out the importance of quantum yields measurements for understanding the photo-oxidation of polymers. They also demonstrate the predominant role of energy transfer processes in the mechanism of the reaction.

The ageing of industrial polystyrene samples on exposure to sunlight is clearly due to the presence of impurities or anomalous structures since model compounds are perfectly transparent in the solar ultra-violet range. The presence of acetophenone groups, that can be produced by thermal oxidation (6), has indeed been demonstrated by phosphorescence measurements in most samples (7). To test the efficiency of such aromatic ketone groups, we have used acetophenone as an additive in polystyrene and measured the quantum yield of oxygen absorption on irradiation at 310 nm, i.e. in the solar U.V. range. At 600 Torr oxygen pressure, this was found to be $2.8 \cdot 10^{-2}$. The same experiment can be performed at 365 nm with polystyrene samples containing benzophenone. A value of $2.7 \cdot 10^{-2}$ is obtained. It is remarkable that both these values are identical to that obtained at 254 nm with pure polystyrene.

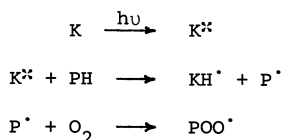
How can ketones initiate the photo-oxidation? Different mechanisms can be proposed.

The singlet oxygen mechanism. It is known that singlet oxygen can be produced by quenching of the excited triplet state of suitable sensitizers :

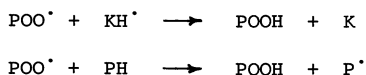


Singlet oxygen is a reactive form of the molecule that exhibits several specific reactions. However, the participation of singlet oxygen in the photo-oxidation of polystyrene in the solid state can be ruled out since the absorption of oxygen can be completely inhibited by the presence of naphthalene (8) (9). This of course results from the quenching of the excited triplet of the ketone by the aromatic hydrocarbon which, by the way, is promoted to its own excited triplet state also susceptible to sensitize the formation of singlet oxygen.

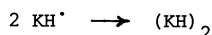
The hydrogen abstraction mechanism. Aromatic ketones in the excited triplet state can abstract hydrogen atoms from polystyrene to produce ketyl radicals KH^\cdot and macroradicals P^\cdot that immediately react with oxygen :



The so formed peroxy radicals cannot be detected at room temperature (9) because they readily abstract a hydrogen atom either from the polymer matrix or from the nearby ketyl radicals. In this latter case, the ketone is regenerated.

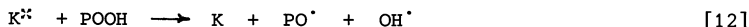


Evidence for such a mechanism is obtained from the presence of pinacol produced by recombination of ketyl radicals :



It is clear that hydrogen abstraction is the primary mechanism of initiation of the photo-oxidation of polymers containing aromatic ketone groups.

The energy transfer mechanism. Ketones excited in the triplet state can transfer their energy to hydroperoxides thereby causing the decomposition of the acceptor :



This can be demonstrated by the progressive decrease of the intensity of phosphorescence of ketones in rigid media with increasing hydroperoxide concentration (fig. 1).

It can be argued that the average concentration of hydroperoxide groups in partly oxidized polymers is usually of the order of 10^{-3} to 10^{-2} M (10) and in those conditions fig. 1 indicates that the efficiency of the transfer is very low. However, one should not forget that in the photo-oxidation initiated by ketones they are very close to the hydroperoxide groups produced and remain there because of the rigidity of the matrix. Therefore, the local concentration is much higher than the average concentration. It can be calculated easily that a distance of 0.8 nm between ketone and hydroperoxide is equivalent to an average concentration of 0.8M that makes the transfer of energy about 80 per cent efficient (fig. 1). Obviously, the energy transfer mechanism cannot be operative from the very beginning of the photo-oxidation process unless hydroperoxides are already present but it can be expected that it will become predominant as soon as the hydroperoxide concentration is high enough. From that moment, free radicals produced in reaction [12] will initiate the oxidation according to reaction [5] in exactly the same way as radicals produced in reaction [4] when polystyrene is irradiated at 254 nm and the quantum yield of oxygen absorption will be the same. Chain scissions also are produced by the same mechanism in both cases (reaction [6]) and discussion of Scheme 1 is still valid.

The successive roles of the hydrogen abstraction and energy transfer mechanisms can be visualized as the photo-oxidation of cumene containing benzophenone is studied (fig. 2).

The concentration of primary (cumyl hydroperoxide) and secondary oxidation products (dimethyl-benzylalcohol and acetophenone) increases linearly with irradiation time whereas the concentration of benzophenone initially decreases as a consequence of the hydrogen abstraction mechanism but remains practically unchanged as soon as the energy transfer mechanism becomes predominant. From those results, it can be concluded that absorption of energy by carbonyl groups followed by transfer to hydroperoxides is likely to be the

main mechanism of photo-oxidation of most industrial polymers exposed to sunlight.

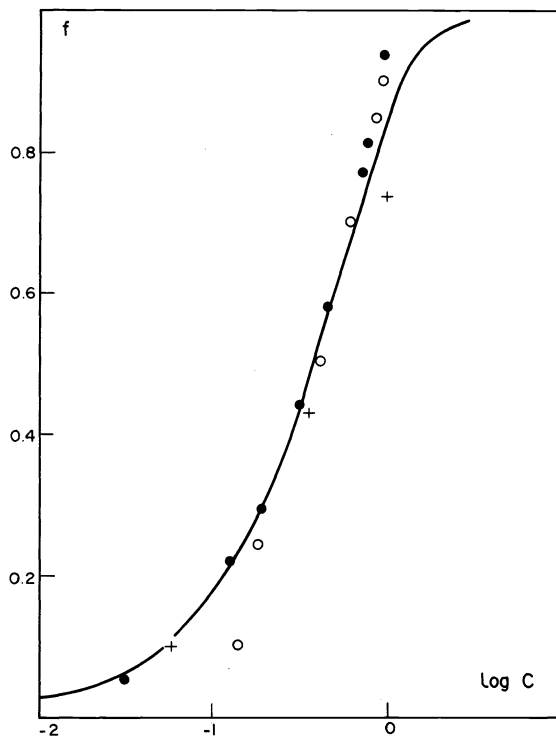


Fig. 1. Efficiency of energy transfer from aromatic ketones to cumene hydroperoxide at 77°K (phosphorescence measurements).

- valerophenone in methyltetrahydrofuran
- benzophenone in methyltetrahydrofuran
- + benzophenone in a polystyrene film.

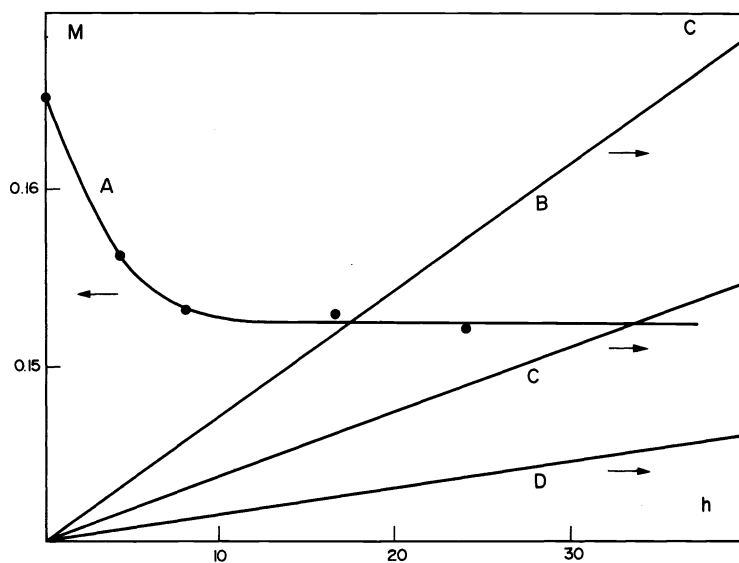


Fig. 2. Photooxidation of cumene containing benzophenone (irradiation at 365 nm). A : concentration of benzophenone in mole l^{-1}

B, C, D : concentration of cumyl hydroperoxide, dimethyl-benzyl-alcohol and acetophenone respectively, in arbitrary units (as measured by HPLC from the signal of the absorption detector set at 254 nm).

INFLUENCE OF THE PROCESSING CONDITIONS ON THE RATE OF AGEING OF POLYMERS

On exposure to sunlight polymers undergo a change of their physical and mechanical properties that is the consequence of photochemical reactions occurring in the sample. The most detrimental effect is usually a decrease of the ultimate tensile strength that makes the material brittle. This is related to scissions of the polymer chain and it is important to find a quantitative relationship between cause and effect. When polystyrene containing 3 per cent benzophenone is irradiated in air at 365 nm a fast decrease of the ultimate tensile strength is observed. The ultimate tensile strength decreases linearly with exposure time (8) and for a given irradiation period, the effect is proportional to the benzophenone concentration (11). It can be shown (fig. 3) that the ultimate tensile strength varies linearly with the reciprocal number average molecular weight of the photo-oxidized samples.

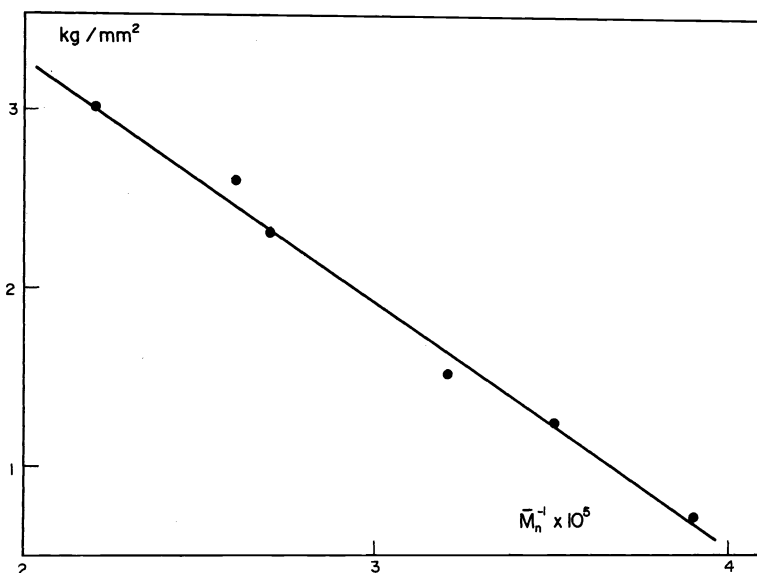


Fig. 3. Ultimate tensile strength of polystyrene samples containing 3 per cent by weight benzophenone irradiated at 365 nm in air for different periods of time as a function of their reciprocal number average molecular weight.

This relationship is in agreement with an empirical equation derived by Flory for a wide variety of samples (12). It makes possible the prediction of the rate of change of the ultimate tensile strength provided the quantum yield of chain scission has been previously determined.

In industrial practice, it is usually impossible to determine the quantum yield of a photochemical reaction because the concentration of light absorbing groups varies from one sample to another depending on the processing conditions. Nevertheless it can be expected that the rate of ageing will depend on the extent of thermal oxidation if the initiation of the photo-oxidation is due to carbonyl groups produced thereby. The influence of processing conditions on the rate of ageing has been investigated for a series of polystyrene samples obtained after different treatments of the same commercial sample characterized by $\bar{M}_w = 310,000$ and $\bar{M}_n = 45,500$. The polymer was processed in a Brabender Plastograph at 160°C for various periods under three sets of conditions: full chamber closed thus practically in the absence of air, half-full chamber giving the polymer a good contact with air, these last conditions but with 0.1 per cent of a phenolic anti-oxidant added to the polymer. The ultimate tensile strength of the samples has been measured after processing. The results are summarized in Table 1.

Table 1 shows that processing in all cases results in a decrease of the ultimate tensile strength but it is faster in the presence of air. The anti-oxidant, however, efficiently inhibits the degradation. Chemical measurements indicate that no oxidation occurs when processing is performed in the absence of air. The decrease of the ultimate tensile strength is thus the consequence of chain scissions produced by shearing forces. On the contrary, oxidation products (ketones and hydroperoxides) are formed in the presence of air and thermal oxidation undoubtedly contributes to chain scission in that case.

TABLE 1. Ultimate tensile strength (kg/mm^2) of polystyrene after processing at 160°C in different conditions (initial value $3.4 \text{ kg}/\text{mm}^2$)

Period (min.)	Absence of air	Presence of air	Presence of air +0.1 per cent anti-oxidant
10	3.1	3.1	-
20	2.9	2.3	3.3
60	2.4	too small to measure	3.1

Now, when all these samples are exposed to an ultra-violet light source exhibiting a maximum of intensity at 310 nm , they all undergo photo-oxidation and a further decrease of the ultimate tensile strength is observed. However, the rate of change (in per cent of the initial value) is the same for all three samples processed in the absence of air whereas fig. 4 clearly show that processing for a longer period in the presence of air results in a faster rate of degradation.

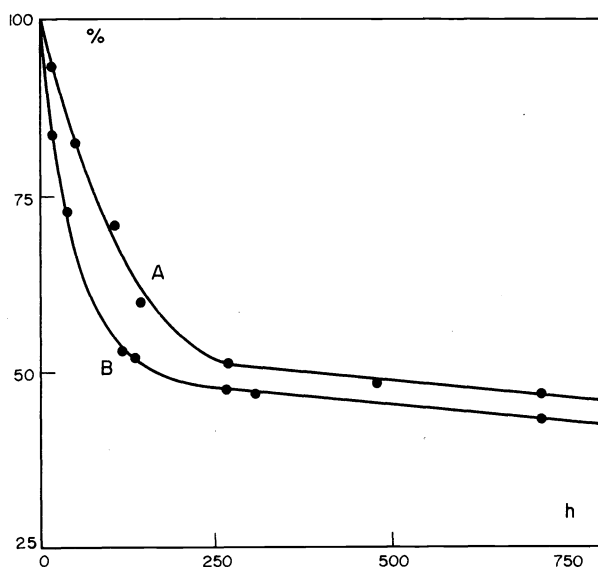


Fig. 4. Ultimate tensile strength of polystyrene irradiated in air at 310 nm . Polymer previously processed at 160°C in the presence of air for 10 min. (A) or for 20 min. (B).

This is easily explained because the concentration of oxidation product has not increased during processing in the absence of air. On the contrary, processing in the presence of air produces oxidation products responsible for the initiation of the photo-oxidation at a higher rate when their concentration is higher. As the photo-oxidation proceeds the polymer turns yellow and the optical density at 310 nm increases making the absorption of energy progressively more superficial. Finally a protective layer is formed at the surface of the sample: it is very brittle but prevents the light from penetrating the sample and thereby any further degradation (fig. 4). At that stage of degradation, however, the polymer is already useless. As the yellow superficial layer is removed carefully by polishing the surface the initial tensile strength is restored and photo-oxidation can be resumed.

In the presence of 0.1 per cent anti-oxidant, thermal oxidation is inhibited during processing and therefore the rate of decrease of the ultimate tensile strength is also lower during the subsequent exposure to ultra-violet light (fig. 5). The influence of the processing period is nevertheless clearly visible.

Table 1 and fig. 5 indicate that the presence of an anti-oxidant favours the keeping of the mechanical properties during both the processing and the exposure to ultra-violet light. This last effect can be due to an inhibition of the photo-oxidation or to a reduction of the oxidation during processing resulting thereby in a lower concentration of absorbing groups and in an indirect protective effect. We have found that this problem can be solved if one study the initial rate of ageing as measured from the rate of decrease of the ultimate

tensile strength as a function of the extent of degradation produced by the processing. This can be estimated from the molecular weight change but can also be related to the ultimate tensile strength after processing as discussed above (see for instance fig. 3). The results obtained are presented on fig. 6.

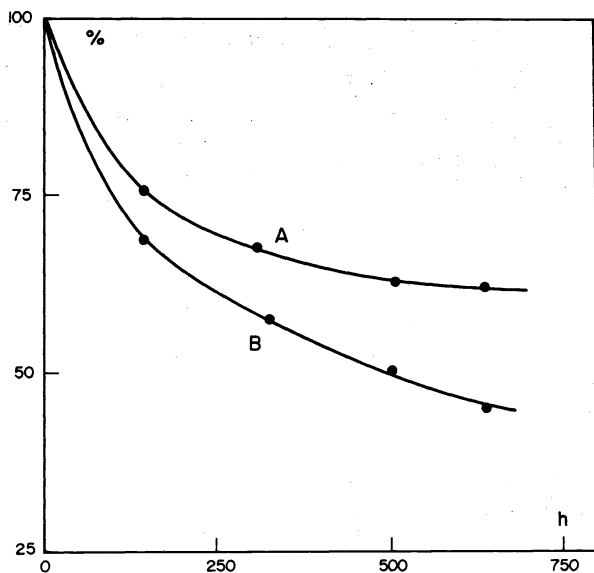


Fig. 5. Ultimate tensile strength of polystyrene irradiated in air at 310 nm. Polymer containing 0.1 per cent anti-oxidant and previously processed at 160°C in the presence of air for 20 min. (A) or for 60 min. (B).

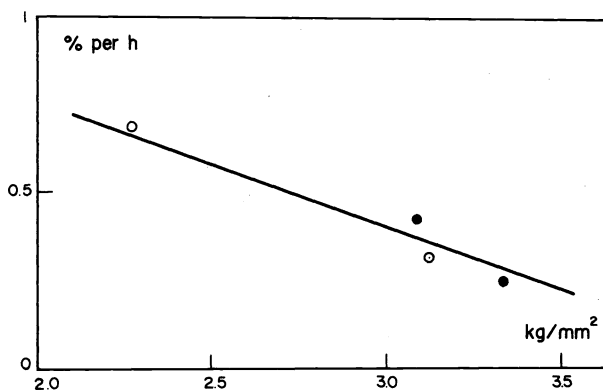


Fig. 6. Initial rate of change of the ultimate tensile strength resulting from irradiation at 310 nm as a function of the initial ultimate tensile strength. Samples have been previously processed at 160°C in different conditions.

- without anti-oxidant
- with 0.1 per cent anti-oxidant.

The experimental data corresponding to processing with or without anti-oxidant fit the same relationship. This indicates that the important factor on which the resistance to ageing depends is the extent of oxidation reached, independently of the processing conditions. It can be characterized by a certain amount of chain scission and an equivalent amount of absorbing groups. Both are related to the ultimate tensile strength of the sample after processing and prior to irradiation. Whether this has decreased to a certain value after 10 min. in the absence of anti-oxidant or after 60 min. in the presence of anti-oxidant does not matter. This clearly shows that the anti-oxidant has no specific

effect on the photo-oxidation. It exhibits only an indirect influence through the inhibition of the oxidation during processing.

CONCLUSION

The present paper does not provide a general explanation of the photo-oxidation of polymers. It aims at pointing along which lines progress in the field can be expected in coming years. This undoubtedly will require

- a more quantitative approach of the photochemical reactions involved in the ageing of polymers
- the awareness of the predominant role of energy transfer in the mechanism of the photo-oxidation
- attempts to find correlations between change of the mechanical properties and extent of chemical transformation of polymers.

REFERENCES

1. G. Geuskens, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and C. David, Europ. Polym. J., **14**, 291 (1978).
2. G. Geuskens, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and C. David, Europ. Polym. J., **14**, 299 (1978).
3. C. David and D. Baeyens-Volant, Europ. Polym. J., **14**, 29 (1978).
4. C. David, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and G. Geuskens, Europ. Polym. J., **14**, 501 (1978).
5. L.J. Basile, Trans. Farad. Soc., **60**, 1702 (1964).
6. H.C. Beachell and L.H. Smiley, J. Polymer Sci. A-1, **5**, 1635 (1967).
7. W. Klöppfer, Europ. Polym. J., **11**, 203 (1975).
8. G. Geuskens and C. David, Pure Appl. Chem., **49**, 479 (1977).
9. G. Geuskens and C. David, Pure Appl. Chem., **51**, 233 (1979).
10. M.V. Amin, G. Scott and L.M.K. Tillekeratne, Europ. Polym. J., **11**, 85 (1975).
11. G. Geuskens and C. David in Degradation and Stabilization of Polymers, p.113, edit. G. Geuskens, Applied Science London (1975).
12. P.J. Flory, J. Amer. Chem. Soc., **67**, 2049 (1945).