Macromol. Symp. **2005**, *225*, 129-146

Basic Aspects of Polymer Degradation

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Summary: Knowledge on the mechanisms by which polymers degrade on exposure to natural or artificial ageing has considerably increased during the past few years. One reason for this is the development of novel experimental procedures and analytical techniques. The analyses of the chemical changes permit determining the main degradation routes applicable to the degradation of the properties of materials and ensures the relevance of the laboratory experiments.

Keywords: ageing; infrared spectroscopy; mechanisms; photodegradation; polymers

Introduction

One major problem associated with the applications of polymers is their instability to weathering.[1-9] Various reactions are responsible for this instability, including rearrangements of the chemical structure, formation of oxidation products, crosslinking and chain scission.

Understanding the mechanisms by which these reactions occur has been the subject of intensive research for the past thirty years. In addition to the academic interest, developing and adapting new stabilizers on a rational basis and predicting the lifetime service of polymers are most valuable for the practical applications of polymeric materials.

In most cases, the effects of weathering on polymers are studied under artificial accelerated conditions. Many different methods exist, from the simple evaluation of the color changes, to the determination of the technological properties of the material.[10] The translation of the results obtained under these conditions of testing to natural weathering conditions is not easy.[11-13] Most industrial activity concerning the long term durability of polymers is still based on determining and characterizing changes in the in-use properties of the

DOI: 10.1002/masy.200550711

materials. Prediction of long-term durability on the basis of these empirical methods, developed in the 1950s have many shortcomings. These also arise from the definition of the ageing parameters, and from the test methods used to experimentally determine the consequences of the weathering.

Because no experimental simplification can be made, the development of new complementary concepts is required. In the 1970s, novel experimental procedures and analytical techniques were proposed in order to study the complex phenomena involved in the degradation of polymers under natural or artificial conditions of weathering. The basic concept that was proposed was the following : since most of the degradation of the physical and mechanical properties of polymers results from chemical changes in the polymer, the reliability of the observed phenomena has to be controlled at the molecular level through the recognition of the chemical reactions involving the macromolecules.[14-15]

Basically, the chemical changes resulting from the weathering of a polymer can be described by a simplified scheme which involves several reactions sequences, including:

- the formation of the intermediate photoproducts,
- their conversion pathways,
- the routes leading to the formation of the final photoproducts that accumulate in the matrix.

The experimental conditions of the laboratory experiments have to be selected to observe the same "mechanisms" in accelerated conditions and in weathering.

In the case of photodegradation, several rules have to be strictly followed in order to ensure the relevance of the observed phenomena:

- Polychromatic light must be used and any wavelength shorter than 295 ± 5 nm, and must be strictly filtered. Medium pressure mercury arcs, avoided as light sources in simulation units because they emit discrete narrow lines, can be used;[16]
- Any control of oxidation by diffusion of oxygen into the polymer must be recognized. To avoid oxygen starvation effects, irradiation of very thin films (a few tens of microns) may be required;

- A correct balance between photo- and thermo-ageing has to be respected. For this reason, acceleration must result from an increase of both the light intensity and the temperature;
- The migration of additives must not interfere with the photochemical consumption of these additives.

It is therefore possible to derive from the time scale of the laboratory experiments a true time scale for the chemical changes throughout environmental weathering. Since the changes in physical properties of a material under outdoors conditions are controlled primarily by chemical changes in the polymeric matrix, it becomes possible to predict the fate of a macroscopic system.

Analysis of the Chemical Changes

The chemical changes that take place in a polymeric matrix under weathering conditions can be easily characterized by infrared spectroscopy.[17-20]

Changes in the IR Spectra

The chemical changes resulting from ageing involve the formation of various functional groups, at rates that are strongly dependant on the chemical structure of the polymer. The formation of these groups leads generally to dramatic changes in the infrared spectrum of the polymer. For example, Figure 1 shows the infrared spectrum, in transmission mode, of a polypropylene film at different irradiation times. The sample was irradiated in a medium accelerated artificial weathering device in the presence of air.

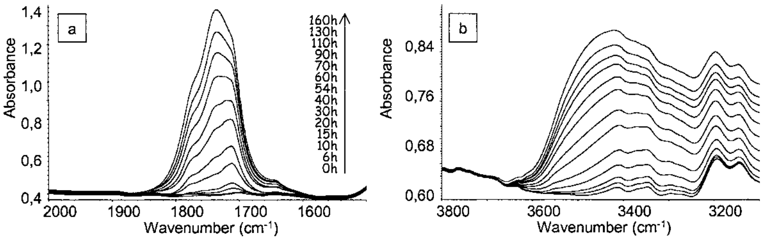


Figure 1. Changes in the infrared spectrum of a polypropylene sample (thickness 100 μm) irradiated in a medium accelerated artificial weathering unit SEPAP 12-24.

The main changes occur in the domains of the carbonylated and hydroxylated compounds: (2000-1500 cm^{-1} (Fig. 1a) and 3800-3100 cm^{-1} (Fig. 1b) respectively). The carbonyl band shows three absorption maxima, at 1713 cm^{-1}, 1735 cm^{-1} and 1780 cm^{-1}. The formation of hydroxylated photoproducts corresponds to the increase of a broad band with a maximum near 3400 cm^{-1}, due to hydrogen-bonded hydroxylated functions.

Plotting the variations of absorbance at 1713 cm^{-1} or 3400 cm^{-1} as a function of the irradiation time permits characterizing the oxidation kinetics of the polymer. Figure 2 shows the curves that are obtained in the case of the polypropylene sample.

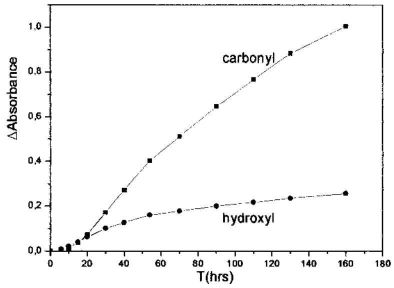


Figure 2. Kinetic curves of oxidation of a polypropylene sample (determined from the spectra in Fig. 1).

The kinetic curves present two different phases. In the first phase, the formation of no carbonyl product can be detected by infrared spectroscopic analysis of the photooxidized sample. This phase, which corresponds to the induction period of the oxidation, results, in part, from the consumption of the residual processing antioxidants used to transform the polymer. In the second phase, the oxidation starts and the absorbance increases at a constant rate.

Characterization of the Oxidation Photoproducts

The assignment of the various absorption infrared bands to well identified products is rather difficult.

Several authors attempted to determine the different carbonyl-containing functional groups[21-23] by various means, including mathematical methods using extinction coefficient evaluated for the various groups, or neutralization of acid groups followed by IR measurement of the ketones. Combined methods (chemical and spectrophotometric) were also developed for the determination of some carbonyl groups in the presence of others.

The resolution of infrared spectrometry can be extended by employing derivatization reactions. These methods involve treating the oxidized polymer samples with reactive gas that can specifically convert the oxidation products that have been formed. The result expected from derivatization reactions is a simplification of the infrared spectra, resulting from the disappearance of specific bands and the appearance of the absorption bands of the derivated products.

The derivatization method for the identification of oxidation products was at first applied to polyolefins by Carlsson *et al.*[24] The gases used and the groups quantified included diazomethane to convert acids and peracids to their respective methylesters, sulfur tetrafluoride (SF_4) to convert acids to acyl fluorides, nitric oxide to convert alcohols and hydroperoxides to nitrites and nitrates, respectively, and phosgene to convert alcohol and hydroperoxides to chloroformates.

SF_4 derivatization is very informative because there is an important shift between the carbonyl band (C=O stretching vibration) of the acyl fluoride and that of the corresponding acid. The carboxyl group of an acid is converted to a trifluoromethyl group. The reaction proceeds in two steps, formation of the acyl fluoride and replacement of the carbonyl oxygen:

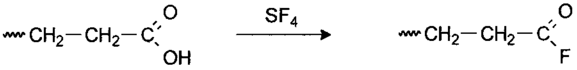
$$\mathrm{R\ COOH + SF_4 \rightarrow R\ COF + HF + SOF_2}$$

$$\mathrm{R\ COF + SF_4 \rightarrow R\ CF3 + SOF_2}$$

The first step occurs readily at or below room temperature, whereas the second step requires elevated temperatures. Acid anhydrides and carboxylic acids can also react with SF_4 but more rigorous conditions are required. In polymers, no reaction of ketones was detected under moderate conditions.

One of the advantages of SF_4 derivatization is that, depending on the structure of the acyl fluoride, noticeable shifts can be observed. The reactions of SF_4 with various carboxylic acids introduced into several polymeric matrix were studied.[25] Several factors of influence were observed: nature of the acid (aromatic or aliphatic), degree of substitution of the carbon atom in the α-position relative to the carboxylic group, and nature of the polymer matrix. It was determined that the frequency of the C=O absorption band of the acyl fluoride band was in the range of 1815 to 1853 cm^{-1}, depending on the structure of the acid.

In the case of oxidized polyethylene, SF_4 treatment leads to the generation of a C=O absorption at 1848 cm^{-1}.[26] This band was attributed to chain-end acyl fluorides formed by the reaction:



SF_4 treatment carried out on a photooxidized sample of polypropylene induces the formation of an absorption band with a maximum at 1841 cm^{-1}, and a decrease of the absorbance at 1713 cm^{-1}.[26] A comparison to the model compounds[25] permits the maximum at 1841 cm^{-1} to be attributed to a methyl α-substituted acyl fluoride formed following the reaction:

Derivatization reactions, based on the treatment of oxidized polymers by ammonia, are similar to the treatments by SF_4 described above. When carboxylic acids are treated with ammonia, or amines, salts are obtained:[26]

$$R\,COOH + NH_3 \rightarrow R\,COO^- NH_4^+$$

In the salt of a carboxylic acid, the C=O and C-O bonds of the acid are replaced by two $\mathrm{C} \overset{\cdots}{\text{—}} \mathrm{O}$ bonds. The antisymmetric CO_2 stretch band is usually seen at 1650-1540 cm^{-1}.[20]

Acylation of amines by an ester gives amides, following the reaction:

$$R\,COOR' + NH_3 \rightarrow R\,CONH_2 + R'OH$$

The C=O stretch band of unsubstituted amines absorbs at about 1680-1640 cm^{-1}.

The potential of the derivatization by nitric oxide to identify the hydroxylated products formed by the oxidation of polyolefins has been studied in detail by Carlsson *et al.*[27] Results of the derivatization reaction of oxidized polyolefins with NO are particularly informative. The infrared spectra of the nitrates produced from the reaction of NO hydroperoxides show different absorption bands, which can be used to discriminate between primary, secondary and tertiary hydroperoxides. Clear differences are also observed between the spectra of tertiary, secondary and primary nitrites formed from the corresponding alcohols. Derivatization by nitric oxide reaction has been applied successfully to the identification of the oxidation products obtained by γ-oxidation of ethylene/vinyl alcohol copolymers.[28]

Hydroperoxides are readily decomposed by reduction with sulfur dioxide. The decomposition of hydroperoxides in oxidized polymers leads to a decrease in the intensity absorbance of the OH absorption. Assuming an extinction coefficient of about 75 $M^{-1}.cm^{-1}$ for associated hydroperoxides (as determined for concentrated solutions of tert-butyl hydroperoxide), the treatment by sulfur dioxide coupled to infrared analysis permits measuring the concentration of hydroperoxides in oxidized polymers. This method has been applied with success to various polymers, such as poly(ether-urethane)s[29] and poly(ether-ester)s.[30]

The iodometric method[31,32] includes the reduction of hydroperoxides by sodium iodide in acidic media according to the reaction :

$$R_3COOH + 3I^- + 2H^+ \rightleftharpoons R_3COH + H_2O + I_3^-$$

The concentration of I_3^- ions formed by this reaction can be measured by their UV absorption at 350 nm, with an extinction coefficient of 25000 $M^{-1}.cm^{-1}$.

Characterization of the Volatile Products

The photo-oxidative degradation of polymers leads to the formation of low molecular weight photoproducts, including water, carbon monoxide and carbon dioxide. Most of these photoproducts can migrate out of the polymeric sample. The analysis of the solid sample has then to be completed by an analysis of the gas phase in order to take into account all of the photoproducts formed.

The formation of low molecular weight photoproducts is more likely to occur in the case of polymers that have short branched reactive groups. Significant concentrations of volatile photoproducts can then be formed, hence the identification of these products is needed to understand the mechanisms by which these polymers degrade.[33]

In the case of polymers that are mostly linear, a precise identification of volatile products is not strictly required, since these products usually represent only a small fraction of the oxidation products. However, identifying the volatile products can assist in establishing the oxidation mechanism.

Various methods exist for characterizing the low molecular weight products formed along with the oxidation of solid polymers. Extraction of the products trapped in the solid matrix can be realized with an appropriate solvent and the extract analyzed by a chromatographic method. Extraction can be obtained by trapping the volatile products and analyzing them by infrared IR spectrometry, by means of a gas-cell, or by gas-chromatography. More recently, a method based on mass-spectrometry analysis of the volatiles evolved during irradiation was developed.[34]

Collection of the volatiles evolved during irradiation of polypropylene shows that the major photo-oxidation products having low molecular weights are carbon monoxide and acetone.[34] Several other products are detected at lower concentrations. These products include methane, carbon dioxide, water, methanol, acetic acid and formic acid.

Characterization of Heterogeneous Oxidation

The most widespread cause of heterogeneous degradation at the macroscopic level results from oxygen diffusion-limited effects.[35, 39] These effects are likely to be observed under conditions of accelerated ageing. If the rate of oxygen consumption exceeds the rate of oxygen permeation then oxidation occurs in the surface layers whereas the core remains practically unoxidized.

The importance of these effects depends on several parameters:

- intrinsic parameters: sample thickness; oxygen consumption rate, which depends on the reactivity of the polymer; nature of the additives; oxygen permeability of the material;
- external parameters: light intensity and sample temperature: oxygen pressure during the weathering.[40]

A combination of these parameters leads to the definition of an optimal thickness, which is required to ensure that no limitation of the oxidation rate by oxygen diffusion occurs.

Increasing the light intensity and the temperature to produce an accelerated degradation may lead to a heterogeneous oxidation if oxygen is consumed more rapidly than it can be resupplied by diffusion processes. Oxygen starvation can be avoided by reducing the thickness of the samples.

The migration of additives is also an important factor which has to be considered. If the additives can migrate, their rate of diffusion must be fast enough in order to compensate for their consumption in the reactive layers. If this is not the case, their concentration in the front layers can be replenished by submitting the samples to intermediate periods of obscurity.

Infrared spectroscopy offers the great advantage of permitting monitoring the effects of heterogeneous oxidation. Two very simple methods are generally used:

- the intensity of an oxidation band can be measured as a function of the thickness of the film.[40] If oxidation is heterogeneous, a deviation from the linearity is observed above a definite thickness;

- the second method is based on successive analysis of slices, microtomed parallel to the irradiated edges.[41] Profiles of oxidation can be directly rebuilt by plotting the oxidation of the different slices vs. the depth at which the measurement is made.

Another approach that permits monitoring the infrared spectra at the surface of the sample is attenuated total reflection (ATR) spectroscopy. This technique is easily applied to both thick and thin films. By varying the reflecting crystal and the angle of incidence, one may measure the depth dependence of oxidation in the range of 0.1 μm to a few micrometers.[42]

Experimental techniques that are better adapted to the analysis of aged polymeric materials have been recently developed. These techniques are capable of profiling spatial variations in the concentration of oxidation photoproducts across the small distances of interest (10-20 μm):

The first method is based on the use of micro-FTIR spectroscopy and entails analyzing a microtomed shaving of the photo-oxidized sample obtained in a plane perpendicular to the axis of irradiation.[43,44] The IR spectra of narrow areas (around 10 μm in width) are successively monitored by moving the sample along the axis of irradiation and the profile of concentration of the photo-oxidation products is then plotted by analyzing the different spectra obtained. The experimental procedure followed to monitor the depth dependence of the oxidation entails first slicing an oxidized polymer sample with a microtome in a plane perpendicular to the irradiation axis (in the case of thin polymer films, the sample is first embedded in an inclusion resin). A thickness of about 50 microns is chosen. The slices that are obtained are then placed under the objective of an IR microscope and analyzed by transmission of the light through a small area delimitated by an image-masking aperture. The sample is moved along an axis that corresponds to the irradiation axis by successive steps and the IR spectra of each zone are successively recorded (Fig. 3).

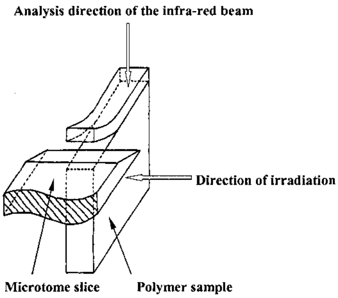


Figure 3. Schematic representation of the analysis method for preparation of thin microtome cross-sections.

Variations in the absorbance of the analyzed zone can be plotted as a function of the distance from the edge of the sample. As an example of this procedure, Figure 4 shows the oxidation profile of an epoxy resin (PKHJ) photo-oxidized by exposure in a medium accelerated artificial weathering device.

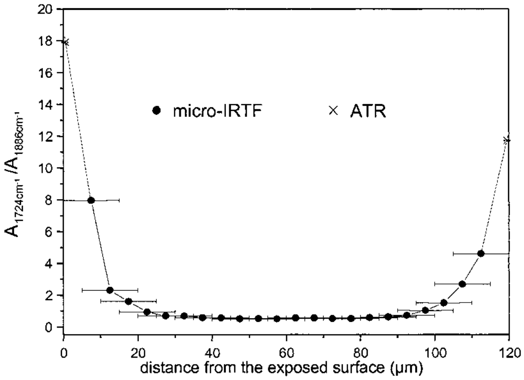


Figure 4. Oxidation profile for an epoxy resin film (thickness 200 microns) exposed for 100 hours in a SEPAP 12-24 unit (sample temperature 60°C).

The main limitation in terms of spatial resolution is imposed by the diffraction of the IR light through the small aperture. High performances microscopes that are equipped with a double masking aperture permit the physical limit of the diffraction (approximately 10 microns) to be approached.

The second method is based on analysis by photoacoustic-FTIR spectroscopy (PAS-FTIR) and permits analyzing the surface of the material without any preparation of the sample.[45] The thickness that is analyzed depends on the optical and thermal properties of the sample and on the frequency at which the IR light is modulated. The analyzed layer can range from a few microns to several tens of micrometers. The photoacoustic effect is produced when an intensity-modulated light impinges on a sample.[46-50] The sample under study is placed in a sealed PAS cell which also contains an inert gas and a sensitive microphone. The infrared spectrum is obtained by measuring the heat generated from the sample due to absorption processes. The heat is transferred by thermal diffusion to the surroundings gas which causes a small boundary layer of gas to expand and contract, resulting in a pressure wave within the cell. This pressure wave is detected by the microphone and the electric signal is Fourier transformed and recorded in the form of an infrared spectrum.

Theoretical predictions for thermally thick and optically transparent samples show that the magnitude of the photoacoustic signal generated from the surface of the samples depends on the modulation frequency and varies as $\omega^{-3/2}$. According to the theory, the thermal diffusion length μ is related to the modulation frequency ω through the equation:

$$\mu = (k/\rho\ C\ \omega)^{1/2}$$

where k is the thermal conductivity, ρ is the density, C is the specific heat, ω is the modulation frequency ($\omega = 2\pi V\bar{\nu}$), with V the mirror velocity (cm.s^{-1}), and $\bar{\nu}$ the wavenumber (cm^{-1}).

Heterogeneous oxidation resulting from oxygen diffusion limited effects are observed in the case of polymers having a weak permeability to oxygen[51] (PVC, PVDC, ...) or in the case of those polymers which are very sensitive to photochemical degradation. Pronounced oxidation profiles are also monitored when the oxidation is limited by the penetration of light in the polymer. Such effects have been reported in the case of several aromatic polymers (PEN[52], PS[53]).

Photo-Oxidation Mechanisms: the Example of Polypropylene

The wavelengths of the radiation from the sun which reach the surface of the earth extend from the infrared into the ultraviolet, with a cut-off around 300 nm, depending on the atmospheric conditions. If one considers the chemical structure of a number of aliphatic saturated polymers, no absorption of sunlight spectrum is expected. The presence of chromophoric groups is required to absorb the incident radiation.

In the case of aromatic polymers, such as polycarbonate or poly(butylenes terephthalate), the initiation is attributable to their strong inherent UV absorption above 300 nm. In the case of aliphatic polymers, however, the true nature of the chromophores responsible for photo-initiation of the degradation is generally not unambiguously established, and probably never will be. The chemical nature and the relative importance of these chromophores depends essentially on the thermal history of the polymer: conditions of polymerization, processing and storage.

The potential chromophores involved in the initiation of the photo-oxidation of polypropylene have been discussed by Carlsson and Wiles.[54,55] The authors have concluded that, of the many chromophoric impurities, hydroperoxides were the most susceptible to satisfy the kinetic parameters of photo-oxidation during the early stages. The introduction of these species during the polymerization or the processing of the polymer and their further decomposition can be described by the well established Bolland-Gee auto-oxidation mechanism, as shown in the following scheme:

Scheme 1: *Auto-oxidation mechanism showing formation and decomposition of hydroperoxides during the processing*

$$\text{Polymer} \xrightarrow{\Delta} P\bullet$$

Propagation:

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet}$$

$$PO_2^{\bullet} + PH \rightarrow POOH + P^{\bullet}$$

Termination:

$2\ PO_2^\bullet \rightarrow$ Inert products

$PO_2^\bullet + P^\bullet \rightarrow POOP$

$P^\bullet + P^\bullet \rightarrow P\text{-}P$

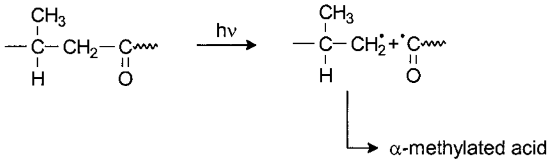
Branching:

$POOH \xrightarrow{\Delta} PO^\bullet + PO^\bullet$

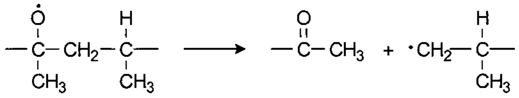
Hydroperoxides absorb weakly up to 360 nm ($\varepsilon^{360\ nm} = 1\ M^{-1}.cm^{-1}$). The light quanta produced by solar irradiation are energetically sufficient to cleave PO-OH bonds, which have a dissociation energy around 45 $kcal.mol^{-1}$. The photolysis of hydroperoxides produces very reactive radicals that can propagate the oxidation.

Most of the products generated by photo-oxidation of polypropylene have been identified and quantified.[26,56-58] These identifications permit the proposal of a simplified mechanism that accounts for the main routes of the photo-initiated oxidation of polypropylene.

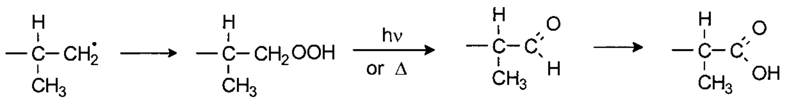
Considering that most of the primary oxidation products (hydroperoxides) in polypropylene are tertiary, with secondary representing around 10%, the probability of a direct oxidation of methylene or methyl groups to form α-methylated acids $\sim CH(CH_3)\text{—}COOH$ appears rather low. Carboxylic structures can be formed from the acyl groups resulting from Norrish I processes of the intermediate ketone groups that are obtained by oxidation of the tertiary carbon atom:



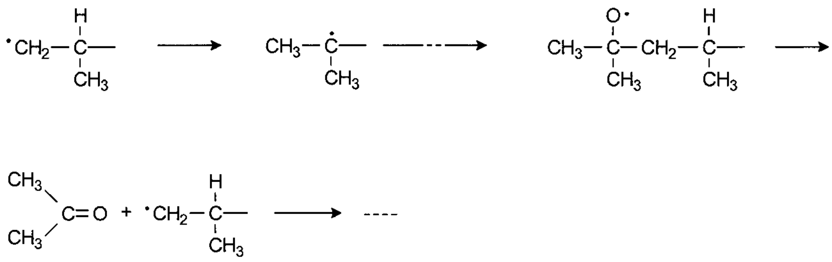
However, if one considers the kinetic curves corresponding to the formation of ketones and acids in photo-oxidized polypropylene, it appears that an additional route for acid formation has to be proposed. Acyl groups are indeed obtained along with the ketones by β-scission of alkoxy radicals formed by oxidation of the tertiary carbon:

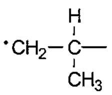


The primary radical so formed can be oxidized into a primary hydroperoxide, then into an aldehyde and finally into an α-methylated carboxylic acid:

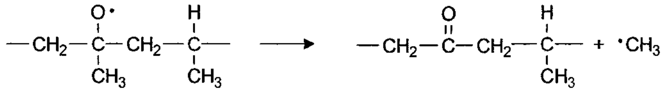


Oxidation of the primary radical competes with an isomerization that gives a more stable tertiary radical. Oxidation of the tertiary radical leads to the formation of acetone, whose formation is clearly shown by analysis of the volatile products:[34]



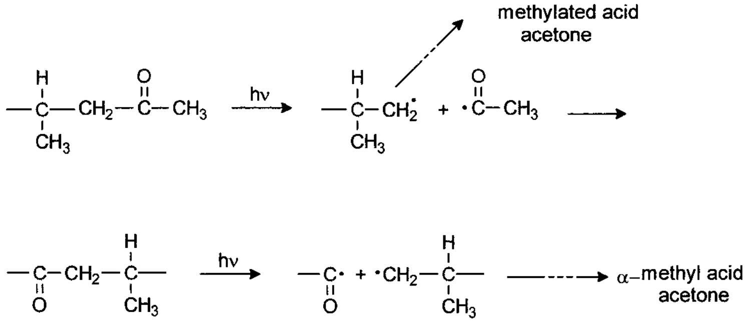
This reaction regenerates the primary radical  $^{\bullet}CH_2-\overset{H}{\underset{CH_3}{C}}-$ than can then be involved in a further reaction, producing acetone and acids.

The β-scission of the alkoxy radical may also involve the homolysis of the side bond, giving a methyl radical and a chain-end ketone:



Oxidation of the methyl radical would account for the formation of methanol, detected by analysis of the gas and liquid phases.[34]

As mentioned above, the primary radical responsible for the formation of acids and acetone could be formed in a Norrish type I photolysis of the chain-end ketones or the macroketones:



In addition to the fact that this behavior is not supported by the kinetic date, these routes should not be considered as important since the stoichiometries in photo-oxidation and thermo-oxidation are very similar. The photolysis of the chain-end ketones is, however, the source of production of acetic acid.

Conclusions

The extensive research carried out in the past 30 years in the field of polymer degradation has considerably increased the knowledge on the mechanisms by which polymers degrade upon exposure to natural or artificial ageing. Analysis of the chemical changes permits recognizing the main degradation routes involved in the loss of properties of the material and ensures the relevance of the laboratory experiments. On the basis of these analyses, it appears possible in most cases to extrapolate the data from the laboratory to the environment.

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