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**Plastics — Methodology for assessing  
polymer photoageing by FTIR and  
UV/visible spectroscopy**

*Plastiques — Méthodologie d'évaluation du photovieillissement des  
polymères par spectroscopie IRTF et UV/visible*

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## Foreword

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Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10640 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 6, *Ageing, chemical and environmental resistance*.

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## Introduction

One of the main interests in the use of artificial accelerated weathering tests is to provide an estimate of the lifetime of polymeric materials exposed in outdoor conditions. This is a very difficult task, and ISO 4892-1<sup>[1]</sup> describes some of the reasons why it is difficult and why the use of simple “acceleration factors” relating time in an accelerated test versus time in an outdoor exposure is not recommended without special care.

One way to evaluate whether an artificial accelerated test can predict the relative performance of materials used in outdoor applications is to compare the chemical changes caused by the artificial accelerated test with the chemical changes that occur in outdoor exposure.

Changes in visual appearance (gloss, discoloration, yellowing, bleaching, micro-cracks, etc.) and deterioration in physical (or functional) properties are consequences of chemical changes, even if there is not always a direct relationship between the chemical changes and the mechanical changes. The use of Fourier transform infrared (FTIR) spectroscopy to follow the chemical changes can facilitate the research of correlations between different ageing tests (natural or any kinds of accelerated devices).

This International Standard describes the methodology and a procedure for using FTIR spectroscopy and UV/visible spectroscopy.

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# Plastics — Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy

## 1 Scope

This International Standard provides a methodology to assess the ageing of polymeric systems during exposure to laboratory accelerated weathering as well as in outdoor exposures.

NOTE This methodology applies mainly to photoageing, but it can also be applied to thermal ageing.

This methodology identifies analyses that follow the chemical changes which control the deterioration of physical properties of materials during photoageing. The main procedure is based on infrared (IR) spectroscopy analysis and is described in this International Standard. In addition, UV spectroscopy is used for monitoring the behaviour of some additives and to identify the origin of discoloration in polymeric materials (degradation of pigments and colorants, or polymer yellowing).

Examples of applications of this methodology are given in Annex A as guidance for the interpretation of the results.

## 2 Terms and definitions and abbreviated terms

### 2.1 Terms and definitions

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For the purposes of this document, the following terms and definitions apply.

#### 2.1.1

##### **photoageing**

entirety of the irreversible chemical and physical processes occurring in a material over the course of time that are initiated by radiation and that can be affected by heat, oxygen and moisture

#### 2.1.2

##### **artificial accelerated weathering**

exposure of a material in a laboratory weathering device to conditions which can be cyclic and intensified over those encountered in outdoor or in-service exposure

NOTE 1 This involves a laboratory radiation source, heat and moisture (in the form of relative humidity and/or water spray, condensation or immersion) in an attempt to produce more rapidly the same changes that occur in long-term outdoor exposure.

NOTE 2 The device can include means for controlling and/or monitoring the light source and other weathering variables. It can also include exposure to special conditions, such as acid spray to simulate the effect of industrial gases.

#### 2.1.3

##### **natural outdoor weathering**

exposure of a material to global solar radiation under outdoor climatic conditions

#### 2.1.4

##### **absorption spectrum**

fraction of the incident electromagnetic radiation absorbed by a material or a molecular entity over a range of frequencies

#### 2.1.5

##### **transmission spectrum**

fraction of the incident electromagnetic radiation that is not absorbed but passes through a material or a molecular entity over a range of frequencies

#### 2.1.6

##### **reflection spectrum**

##### **reflectance spectrum**

fraction of the incident electromagnetic radiation reflected or scattered by a material or a molecular entity over a range of frequencies

NOTE The re-emitted radiation can be composed of two kinds of radiation referred to as specular reflection (when the angle of reflection is equal to the angle of incidence) and diffuse reflection (at all other angles).

## 2.2 Abbreviated terms

ABS acrylonitrile-butadiene-styrene

ATR attenuated total (internal) reflection

EVAC ethylene-(vinyl acetate) plastic

FTIR Fourier transform infrared

PA polyamide

PAS photoacoustic spectroscopy

PBT poly(butylene terephthalate)

PC polycarbonate

PE polyethylene

PEBA polyether block amide

PEEK polyetheretherketone

PE-LD polyethylene, low density

PET poly(ethylene terephthalate)

PMMA poly(methyl methacrylate)

POM poly(oxymethylene); polyacetal; polyformaldehyde

PP polypropylene

PPE poly(phenylene ether)

PS polystyrene

PUR polyurethane

PVC-P plasticized poly(vinyl chloride)

PVC-U unplasticized poly(vinyl chloride)

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SAN	styrene-acrylonitrile plastic
TPU	thermoplastic polyurethane
UP	unsaturated polyester resin
UV/VIS	ultraviolet/visible

### 3 Principle

When a polymeric material is exposed to UV radiation and other moderate environmental stresses, the change in most physical properties is attributable to chemical ageing, and the extent of the chemical changes can be related to the duration of the exposure under natural outdoor weathering or artificial weathering exposure.

Chemical changes control the degradation of mechanical properties and contribute to changes in the visual appearance of polymer materials during photoageing. These chemical changes are analysed primarily by IR spectroscopy, with additional analyses using UV/visible spectroscopy during the photoageing of polymers. The analysis at this earliest stage of degradation allows the identification of the critical oxidation products, allows the stoichiometry of reactions to be checked and, in some cases, indicates weak points in the polymer material (e.g. a weakness in the specific structure of the polymer, such as a double bond, an ether group or a urethane group, unstable colorant, lack of UV stabilizers, or migration of low-molecular-mass components of formulations to the surface and their accumulation there).

The relevance of artificial ageing can be determined by comparing the chemical changes that occur in the accelerated test to those that occur in natural weathering. It should be pointed out that, in some cases, oxidation products can be partially eliminated by hydrolysis or erosion caused by water under humid climates (e.g. southern Florida) or by wind under very dry climates (e.g. Arizona). Kinetic analysis is recommended to determine the rate of degradation under different conditions of ageing in order to rank different formulations or to determine the range of acceleration possible for an artificial ageing test compared to a given natural outdoor weathering exposure (without distortion of the photodegradation mechanism of the polymer). In addition, these analyses can be used as a tool for developing improvements in polymers and polymeric products.

## 4 Methodology

### 4.1 General

Since the mechanism of degradation of polymers is a function of the polymer composition, it might be necessary to identify the chemical composition of the exposed plastics to allow comparison of results from laboratory experiments with those from actual use conditions. This will help in the design of better accelerated tests in those cases when existing accelerated tests have not given useful results for comparison with actual use conditions.

The specific chemical changes which control a given physical deterioration should be identified. For example, mechanical failures are generally controlled by the extent of oxidation, which makes their prediction possible.

In many cases, the extent of oxidation and the extent of changes in mechanical properties are often closely linked via main-chain scissions. A specific correlation study could be carried out for a given material in order to predict mechanical-property changes from the measurement of the concentration of oxidation products.

Except in the case of yellowing due to direct phototransformation, e.g. in the case of aromatic polymers, the change in visual appearance is generally controlled by several chemical processes (loss of gloss, discoloration, bleaching, micro-cracks, etc.). Therefore, an accelerated photoageing test is only predictive if one single process prevails over the others.

## 4.2 Guidance on the assessment of chemical changes

### 4.2.1 General

Different chemical changes take place that depend on the mechanisms of the degradation. These changes vary in importance and include matrix oxidation, chain scission and/or crosslinking, yellowing, bleaching, formation of fluorescent products, modification of stabilizer molecules, hydrolysis and photolysis.

Analysis of the chemical changes in polymeric materials submitted to exposure is performed by applying the following two rules:

- a) only changes in the solid state are relevant, so the analysis shall be carried out on solid-state materials, of particular importance when examining the stability of intermediate products.
- b) chemical changes shall only be considered at very low levels of change since the physical (mechanical or appearance) deterioration occurs at a very early stage in the chemical process, except when the “ultimate” fate of polymeric materials is being examined for environmental-protection purposes (e.g. the oxodegradation or oxobiodegradation of polyolefin films).

Although the main chemical changes take place in the polymer matrix, the fate of additives and colorants shall also be considered.

NOTE These rules are general ones and apply to any polymeric material exposed to light, heat, O<sub>2</sub>, H<sub>2</sub>O and other potentially degrading exposure stresses.

### 4.2.2 Identification of the main degradation route

An important route of degradation for many polymers is a photooxidation mechanism, the products of which are formed at concentrations high enough (depending on the extinction coefficient) to be observed by vibrational spectroscopy. Changes in visual appearance caused by photoageing are the result of chemical changes that occur by several different routes. Acceleration of these chemical changes cannot occur without distortion of the results, except in special cases.

The extent of the chemical changes is better determined from the degree of accumulation in the matrix of “critical” photoproducts that, when properly chosen, will measure the main degradation pathway of the matrix. Although a chemical change such as oxidation might involve many elementary photochemical and thermal processes, it is possible to describe such chemical changes in a simplified manner through the accumulation of the critical photoproducts, chosen based on the best understanding of the ageing mechanism.<sup>[2]</sup>

A critical photoproduct is defined as follows:

- It shall allow the main degradation pathway of the matrix to be determined.
- Ideally, it shall be a stable final product which accumulates in the matrix (but not a low-molecular-mass product or a yellowing product). It shall be chemically and photochemically inert in the matrix, shall not diffuse out, and shall accumulate linearly with time until the relevant functional property of the polymer has been completely lost.

The degradation of the polymeric matrix may also be followed by monitoring the decrease in the relevant functional groups.

FTIR spectroscopy is used to identify critical photoproducts<sup>[3]</sup> with complementary information obtained using UV/visible spectroscopy, such as:

- the monitoring of the screening effect of organic UV-absorbers and pigments;
- the determination of changes in UV-stabilizers and absorbers and colorants;
- the determination of the origin of the sample's discoloration (degradation of colorants or degradation of the polymer material).

A list of critical photoproducts associated with the degradation of polymeric materials, and their identification, is given in Table 1.

Since the spectroscopic techniques used are mostly non-destructive (or need only small quantities of aged test specimens), it is recommended that an analysis of the kinetics of the oxidation be carried out in order to determine the rate of photooxidation and whether there is a pseudo-induction period. A procedure to measure the development of relevant functional groups that is based on FTIR spectroscopy is described in Clause 6.

The critical photoproducts of degradation must be known in order to determine the photodegradation mechanism. Many different photoproducts can be identified by coupling infrared analysis and specific chemical derivatization (e.g. conversion of carboxylic acid groups to acid fluoride groups using  $\text{SF}_4$  gas). Additional correlation between oxidation and in-use properties can also be carried out. Table 1 shows the critical photoproducts, how they are identified, and the properties that are affected by photooxidation for a number of different polymers.<sup>[4][5]</sup>

**Table 1 — Critical photoproducts and modified properties**

Polymer	Critical photoproducts	Identification of critical photoproducts	Effect/properties modified	References
PVC-P, PVC-U	$\beta$ -chlorocarboxylic acid group	IR at 1 718 $\text{cm}^{-1}$	Chalking	[6], [7]
	Acid chloride	IR at 1 785 $\text{cm}^{-1}$	Discoloration Mechanical resistance	
Extruded PE film	Carboxylic acid	IR at 1 714 $\text{cm}^{-1}$	Tensile strength Elongation	[8], [9], [10]
	Vinyl unsaturation	IR at 909 $\text{cm}^{-1}$	Tensile strength Elongation	
EVAC film	Carboxylic acid	IR at 1 705 $\text{cm}^{-1}$	Tensile strength Elongation	[11], [12]
Moulded PP	Carboxylic acid	IR at 1 714 $\text{cm}^{-1}$	Micro-cracks Bleaching Chalking	[13], [14]
Moulded, filled PA, PA6 and PA66	Carboxylic acid	IR at 1 715 $\text{cm}^{-1}$	Appearance	[15]
	Imide group	IR at 1 735 $\text{cm}^{-1}$ and 1 690 $\text{cm}^{-1}$	Mechanical resistance	
PET, PBT, moulded, filled PET and PBT	Carboxylic acid	IR at 1 717 $\text{cm}^{-1}$ and 1 776 $\text{cm}^{-1}$	Mechanical resistance	[16], [17], [18]
	Benzoic acid	IR at 1 696 $\text{cm}^{-1}$ and 1 733 $\text{cm}^{-1}$		
	Acid hydroxyl groups	IR at 3 260 $\text{cm}^{-1}$		
PMMA and acrylics	Carboxylic acid	IR at 1 705 $\text{cm}^{-1}$	Increased haze	[19]
	Hydroxyl groups	IR at 3 250 $\text{cm}^{-1}$		

Table 1 (continued)

Polymer	Critical photoproducts	Identification of critical photoproduct	Effect/properties modified	References
PC	Carboxylic acid	IR at 1 713 cm <sup>-1</sup>	Mechanical properties	[20], [21]
	Photo-Fries rearrangement products: — phenylsalicylate — dihydroxybenzo-phenone — biphenyl species	IR at 1 689 cm <sup>-1</sup> ; UV at 320 nm IR at 1 629 cm <sup>-1</sup> ; UV at 355 nm IR at 3 607 cm <sup>-1</sup> , 3 547 cm <sup>-1</sup> and 3 470 cm <sup>-1</sup> ; Vis at 450 nm	Yellowing	
PUR, TPU	Carboxylic acid	IR at 1 705 cm <sup>-1</sup>	Whitening	[22], [23]
	Urethane group degradation products	IR at ~1 530 cm <sup>-1</sup> (band decreasing in size)	Yellowing Cracks (aggravated by hydrolysis)	
Moulded ABS, PS, SAN	Butadiene degradation products (in ABS)	IR at 912 cm <sup>-1</sup> (band decreasing in size)	Mechanical resistance	[19], [24]
	Carboxylic acid	IR at 1 717 cm <sup>-1</sup>	Appearance	
UP	Aromatic carboxylic acid	IR at 1 700 cm <sup>-1</sup>	Yellowing Mechanical properties	[25], [26]
	Carbonyl group	IR at 1 780 cm <sup>-1</sup>		
	Hydroxyl groups, mainly from carboxylic acid	IR at 3 300 cm <sup>-1</sup>		
	Conjugated aromatic species	UV at 350 nm; Vis at >400 nm		
POM	Formate/ester	IR at 1 714 cm <sup>-1</sup>	Brittleness	[27]
	Alcohol from chain scission	IR at 3 475 cm <sup>-1</sup>	Mechanical properties	
PPE	Saturated carboxylic acid	IR at 1 714 cm <sup>-1</sup>	Bleaching Mechanical properties	[28], [29]
	Quinone methide	IR at 1 657 cm <sup>-1</sup>		
	Ether group degradation products	IR at 2 736 cm <sup>-1</sup> (band decreasing in size)		
		IR at 1 021 cm <sup>-1</sup> (band decreasing in size)		
	Quinone methide	UV at 330 nm	Yellowing	
PEEK	Aromatic carboxylic acid	IR at 1 725 cm <sup>-1</sup>	Yellowing	[30]
	Hydroxyl groups	IR at 3 370 cm <sup>-1</sup>		
		Vis at 400 nm to 600 nm		
PEBA	Ether group degradation products	IR at 2 791 cm <sup>-1</sup>	Cracks Mechanical properties	[2], [31]
		IR at 1 111 cm <sup>-1</sup> (band decreasing in size)		
	Carboxylic ester	IR at 1 725 cm <sup>-1</sup>		
		IR at 1 180 cm <sup>-1</sup>		