

PREDICTION OF POLYMER DURABILITY: *NATURAL VS. ACCELERATED AGEING*

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jméno

ABSTRACT

Three different weathering approaches, which allow examining or eventually simulating natural aging, were compared. Natural exposure was found the most authentic, but the most time demanding. Accelerated indoor aging was found the less time demanding, but with incorrectly chosen experimental conditions it can generate unrealistic results. Accelerated outdoor exposure was found as a compromise solution between two extremes mentioned above. Participation of all weathering approaches in process leading to prediction of material durability was discussed.

ANOTACE

Byly porovnány tři odlišné přístupy, které umožňují zkoumat, popřípadě simulovat, přirozené stárnutí polymerních materiálů. Přirozená expozice materiálu byla shledána nejrealističtější, časově však nejnáročnější. Zrychlené laboratorní stárnutí materiálu je nejméně časově náročné, při nesprávně nastavených podmínkách však může vést k nerealistickým výsledkům. Zrychlené stárnutí materiálu v přírodě je kompromisním řešením mezi těmito dvěma extrémy. Všechny tři zmíněné procesy vedoucí k předpovědi životnosti materiálu byly diskutovány.

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INTRODUCTION

For centuries, the durability of products has been controlled by the properties of naturally occurring materials. The human skills to process them, experience gained over long periods of observation, and local availability were the major factors in the selection of a material. Rapid development of polymer synthesis in this century produced a great variety of new materials which were attractive for producers of finished goods. These materials offered repeatable quality, ease of processing, and cost effectiveness.

But it was soon discovered that the new materials were substantially different and, although they had excellent initial properties, they usually suffered from limited durability. This has triggered an interest in the prediction of a materials lifetime [1]. It should be noted that acquisition of information from weathering research has great use for polymer industry and business. Needs of this industry are an engine, which moves forward research of polymer weathering.

Another factor, which has caused progress of weathering problems research, was influence of synthetic materials on the environment during and after their lifetime. Products from polymer materials are wanted to be durable over their useful life but they should be returned to nature when they are no longer needed and their disposal should not cause pollution.

This Bachelor thesis is divided into three chapters. First chapter is devoted to brief summary of theoretical background of weathering. There are explained an important topics as degradation factors, test methods and methods of weathered specimen evaluation.

Second chapter deal with fundamental comparison of three weathering or aging approaches - natural exposure, accelerated outdoor exposure and artificial accelerated indoor testing. Time demand and authenticity of a weathering experiment are the most important factors for comparing approaches mentioned above. Tractability of an experiment and its technical requirements are additional but also important factors suitable for making comparison. Second chapter should be used as a source of very basic information, which can help to choose the most convenient weathering approach.

Third chapter tries to found the most suitable procedure for making prediction of polymer material. This procedure is described from a general point of view and should be applicable for majority of weathering intentions.

1 THEORETICAL BACKROUND OF WEATHERING

1.1 WEATHERABILITY

There is no good definition of “weatherability”. But structure of this word shows us its right meaning. Weatherability can be separated into two nouns - “weather” and “ability”. Definitions of these two nouns are commonly accessible and even their joining can be successfully explained. For example “durability” refer to ability of an object to stay unchanged under the influence of time or other various forces or stresses. In that way “weatherability” can be understood as ability of an object or a material to resist the influence of weather.

In plastics technology weatherability refers to the ability of the plastics material to withstand treatment under complex and variable conditions similar or identical to prevailing in nature [3]. In these conditions every material returns - corrodes, oxidizes, chinks, permeates, delaminates, depolymerises etc. to its elemental forms. This natural tendency is called weathering or generally degradation [6].

Man attempts to prevent deterioration of physical properties due to the weathering by examining the nature of physics and chemistry at the interface of pigments, fillers and polymers and then creating the anti-corrosion, anti-oxidant additives or coating technology to extend the useful life of plastics.

1.2 DEGRADATION FACTORS

Degradation of plastics is caused by many factors, which can be sorted into three main classes. It can be recognized physical, chemical and biological factors. Every class of degradation factors include a lot of phenomenons or stresses, which can influence polymer material. Nearly always, in nature always, is polymer exposed to a combination of several stresses, often from various classes.

1.2.1 Physical factors

Physical factors are mainly represented by influence of solar radiation or generally irradiance, temperature and mechanical stress.

1.2.1.1 *Solar radiation*

In the earth’s conditions is solar radiation a part of the Sun emitted radiation, which

manage to pass through the earth's atmosphere.

Electromagnetic waves carry a discrete amount of energy depending on their frequency, as stated by Planck's Law:

$$E = h\nu \quad (1)$$

where E.....energy of radiation
 νfrequency of radiation
h..... Planck's constant [1].

It is evident that radiation with higher frequency, ergo with lower wavelength, carries a greater amount of energy. At the earth's surface lies the most energetic solar radiation in region of ultraviolet (UV) wavelength in electromagnetic spectrum.

Ultraviolet wavelengths from sunlight are an important component in outdoor degradation. The energy from sunlight is mainly visible light and infrared; ultraviolet makes up less than 5% of sunlight. However, the photo degradation of exterior plastic materials is caused mainly by UV light. The solar ultraviolet radiation spectrum is divided into three ranges (see Table 1.1).

Table 1.1: Wavelength regions of ultraviolet radiation and their characteristic [6].

Wavelength region	Wavelength, nm	Characteristic
UV-A	400 to 315	Always present in sunlight; 400 nm upper limit for UV-A is the boundary between light and ultraviolet light; energy at the 315 nm boundary begins to cause adverse effects and pigmentation in human skin and some polymers.
UV-B	315 to 290	Includes the shortest wavelengths found at the earth's surface; responsible for severe polymer damage; absorbed by window glass; ultraviolet light absorption varies with solar altitude.
UV-C	290 to 100	The UV-C nm boundary is a sharp cut-off of solar radiation at the earth's surface due to complete absorption by ozone; found only in outer space.

There is a simplified description of principles of photodegradation caused by UV light. At first electrons in molecule of polymer absorb the radiation energy. Depending on the energy absorbed by the molecule, the electrons are promoted from ground state to higher energy state levels [1]. The absorbed energy is then dissipated either in radiative processes as fluorescence and phosphorescence or in non-radiative processes. In them is absorbed energy converted. This process, in dependence on the balance of energy available in a particular molecule and the chemical structure of the excited molecule, can lead to cleavage into free radicals, abstraction of hydrogen atom, photosensitization, decomposition with formation of two or more molecules, photodimerization or crosslinking, intramolecular rearrangement, photoisomerization. Which reaction type predominates partly depends on the environment [1]. These primary photochemical reactions are mostly followed by secondary reactions. A mostly reaction with oxygen or ozone and photooxidation is realized.

Exposure of many plastics to ultraviolet radiation causes a loss in their mechanical properties and/or a change in their appearance. The mechanical property most severely affected is usually the ductility of the material. Deterioration in appearance leads to color shift and/or loss of gloss.

1.2.1.2 Temperature

It is obvious that increasing temperature increases rate of any chemical reaction. Real temperatures, frequently higher than ambient by as much as 30°C, are sufficiently high to have a considerable effect on the degradation rate of many materials [1].

For aging of polymers is important the surface temperature, because degradation processes occurs mainly at the surface or near the surface. The surface temperature of materials is greatly affected by the absorption of radial energy (Fig. 1.1). Material type and color determine surface temperature [1]. In outdoor exposure temperature depends on time of the day and color. It is known from practice that black specimen may reach 90°C, which is about 30°C higher than for a white specimen under the same conditions. The rule of a thumb in chemistry assumes that the reaction rate doubles with every 10°C increase of temperature. Therefore, black sample, according to this rule, should be degrading 8 times faster than the white sample [4].

The rate of heat penetration depends on the thermal diffusivity of the material, on its heat capacity, and on its thermal conductivity. All three factors together determine surface temperature. Absorption of solar radiation depends on the surface finish. A polished surface reflects more radiation than unpolished surface. Lighter colored materials reflect more than darker. Wind speed has considerable effect on surface temperature increasing the rate of heat exchange [1].

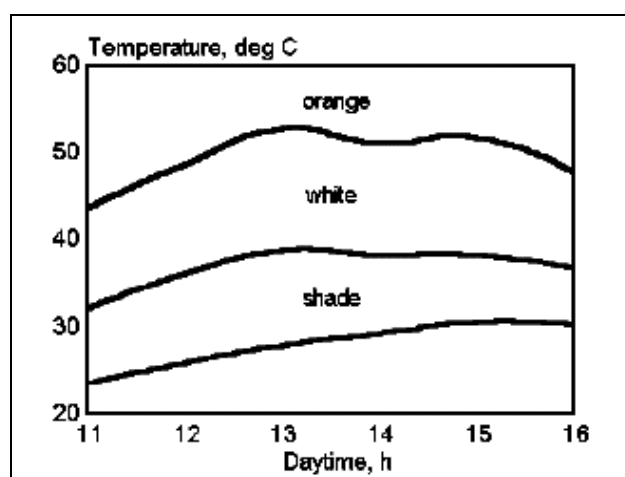


Figure 1.1 Air temperature behind awning material on sunny days. [7]

1.2.1.3 Mechanical stress

Stress is an essential parameter of weathering considering that thermal and moisture movements in materials are found in practical applications and are known to affect the rates

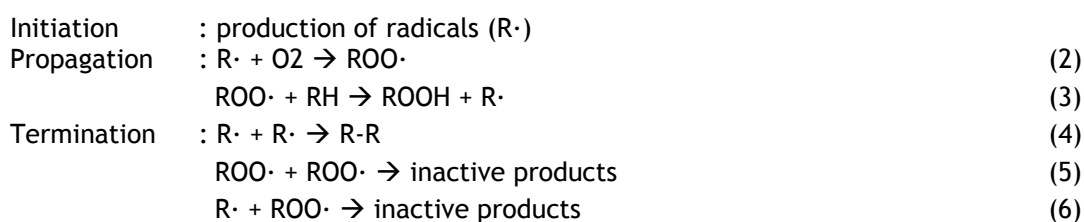
of degradation. Two aspects of stress interference can be considered: effect of external forces and residual stress retained in materials after processing. The existing sample holders allow inducing static stress to material exposed to radiation and other environmental conditions. The scientific literature makes suggestions to test specimens at 30 to 60% of elongation at break. At the same time, it should be considered that stress is an additional parameter of weathering therefore its introduction changes both rate and mechanisms of degradation [4].

1.2.2 Chemical factors

Polymer material can be brought in contact with thousand of chemical compounds during its application. It should not be forgotten that polymer material itself is not pure polymer, but it contains amount of low molecular weight additives. This situation can lead into huge number of chemical interactions of various types and mechanisms. But in weathering reactions with molecular oxygen (and other atmospheric gases or pollutants) and water are of general importance, because these substances are ubiquitous and their interaction with polymer is realized nearly always.

1.2.2.1 Oxidation

The oxidation, also called hydroperoxidation, is a radical chain process. The primary reactions steps of are detailed here:



RH is the parent compound; the hydrogen atom specified normally being the most reactive atom in the molecule. $R\cdot$ is the radical formed by removal of this hydrogen atom, $ROO\cdot$ is the hydroperoxy radical formed by the addition of oxygen to it, and ROOH is the corresponding hydroperoxide [5].

Initiation energy is usually supplied by solar radiation in natural exposure or irradiance in laboratory. Initiation could be catalysed by admixtures, filth or residues of substances which were used in production.

It is the reactivity of the hydrogen atoms, and hence the tendency for hydroperoxidation to proceed, which determines the susceptibility of any particular polymer to oxidation. Small concentrations of these hydroperoxides in themselves, however, do not affect very greatly the physical properties of the polymers. It is the subsequent reactions, as decomposition or crosslinking, of these very unstable groups which cause discoloration, embrittlement, cracking and other faults [5].

1.2.2.2 Wetness

A high incidence of wetness has important implications on the durability of a part.

In the first case, some polymers are straight affected by moisture. Polymers such as polycarbonate, polyester, polyamide and many others hydrolyze in the presence of water. The hydrolysis is time-related and water concentration-related phenomenon therefore the increase in water supply to the sample changes mechanism of degradation [4].

In the second case, water is not destructive in itself, but that water causes damage by bringing oxygen into intimate contact with the material and promoting oxidation. Generally, the potential for degeneration from dew exceeds that associated with rain. The fact that materials are exposed primarily to dew and not rain affects the type of degradation that will occur. Dew is saturated with oxygen and lies on materials for ours at a time allowing the water to penetrate deep within the material to cause internal oxidation [6].

The severity of wetness attack increases dramatically with increasing temperature.

1.2.3 Biological factors

Generally, natural and synthetic polymers can be attacked by living organisms either chemically or mechanically.

The mechanical mode of biodegradation of polymers pertains to the attack by animals, e.g. rodents and insects. In number of cases the reasons for attacking the natural polymers include nutritional needs. On the other hand, synthetic polymers are not attacked for reasons of nutrition. Polymer material is attacked because its physical properties are compatible with the natural needs of animal. A typical example is the need of rodents for biting.

The chemical mode pertains to the decomposition of polymers [2]. Three classes of microorganisms are responsible for the biodegradation of organic matter: fungi, bacteria, and actinomycetes. Microorganisms biodegrade organic materials by the use of their enzymatic apparatus. Enzymes are complex proteins (molecular weight 10,000 to 1,000,000) which are able to catalyze specific reaction (each enzyme catalyzes one specific chemical reaction). Enzymes can function only under certain (defined) conditions which include the concentration of substrates and products (typically low), temperature, and pH.

About 2000 enzymes are known which can be assigned to one of these categories:

- hydrolase - hydrolysis (esters, amides, acetals, etc.)
- esterase or amidase - esterification or amidation
- isomerase or transferase - transferring atoms within one molecule
- reductase or oxidase - electron transfer reaction
- hydrogenase or dehydrogenase - proton addition or removal
- Ligase - condensation reactions with formation of C-C, C-S, C-O, or C-N bond.

As can be expected, natural products are most prone to biological degradation [1]. But synthetic polymers are, in principle, susceptible to microbiological attack too. However, apart from a few exceptional cases, there are no microorganisms prepared to readily attack synthetic plastics, although many are capable of adapting. But it is not yet clear whether the ability to adapt refers really to all synthetic polymers.

There are many important factors which affect biodegradation rate of synthetic polymers:

- structural similarity - certain functional groups found in natural polymers, such as amide, ester, ether, etc., are more likely to be degraded by the existing microorganisms
- molecular weight - increasing molecular weight decreases biodegradation rate. In most cases microorganisms do not degrade synthetic polymers which have a molecular weight higher than 20,000
- crosslinking - reduces crystallinity but at the same time increases packing density which inhibits penetration of enzymes
- chain flexibility - increases probability of biodegradation by facilitating formation of complexes of enzyme-substrate which require a certain configuration
- functional groups - hydrophilic groups increase the probability of enzymatic reactions because they either increase polymer solubility or at least attract water (water is needed in most biodegradation reactions)
- crystallinity - amorphous regions are preferentially degraded, crystalline material can only be degraded on a lamellar surface. Enzymes cannot easily penetrate inside densely packed crystallites
- conditions - temperature, humidity, pH, oxygen, light. Specific conditions are preferred by various microorganisms
- structure porosity - increased surface area increases the probability of contact and concentration of enzyme-substrate complexes which are rate-controlling
- time - reaction time increases conversion, microorganism adaptation increases the probability of reaction
- concentration of substrate and product - enzymes work best in dilute solutions.

It should be noted that even if a polymer by itself does not support the growth of microorganisms, the material always has some imperfections and/or surface degradation which can accumulate nutrients which can support biological life. For a product to perform, it is important that the material does not lose its mechanical properties but in most cases the loss of its original aesthetic value [1].

1.3 TEST METHODS

There are three major approaches in weathering tests - natural exposure, accelerated outdoor exposure and artificial accelerated indoor testing.

1.3.1 Natural exposure

Real-time weathering data from natural environment exposure programs remains the standard to which all other weathering data is compared. Two of the most commonly used harsh aging sites are Arizona and Florida. Arizona is important of its annual radiation and ambient temperature. Southern Florida is unique because of its high radiation combined with high rainfall and humidity. These two areas have become U.S. and international reference climates for gauging the durability of materials since they represent the worst case for applications in the Northern Hemisphere.

With all outdoor tests it is important to be aware of bias introduced by the choice of location. Details about a few representative test sights are listed in Table 1.2.

Table 1.2: Climatological data from various locations [4].

Location	Lat./Lon.	Average rain mm	Average humidity % RH	Annual solar energy total/total UV, MJ/m ²
Phoenix, AZ	33°54'N/112°8'W	254	32	8000/330
Florida, MI	25°52'N/80°27'W	2010	79	6500/280
Sanary, France	43°8'N/5°49'E	1200	64	5500/285
Choshi, Japan	35°43'N/140°45'E	1825	78	4000/220
Lochem, Netherlands	52°30'N/6°30'E	715	83	3700/190

In addition to the hot, dry and hot, wet extremes, other frequently used climate zones for weathering are 1) seashore (salt air), 2) industrial, 3) temperate and 4) freeze-thaw. Often, the controlling specification or test method defines the exposure conditions.

At the figure 1.2 is shown weathering station in Florida.



Figure 1.2 Aerial photograph of AWSG's South Florida Test Service, Miami, Florida Weathering Station [4].

In outdoor tests the usual standard procedure calls for specimen exposure on racks facing due south at an angle of 45°. These are conditions that offer a maximum direct sunlight exposure and intensity. This tilt is also preferable to 0° as it allows for some drainage and wash off during rains.

1.3.1.1 Conventional aging

This test method is real time exposure at a 45° tilt form the horizontal. Direct exposures

are intended for materials which will be used outdoors and subjected to all elements of weather. Exposure times are generally 6, 12, 24 and 48 months. Location is an important factor in the harshness of this test. The assumption being that test results from a hostile environment will prevail in more moderate conditions [6].

1.3.1.2 Conventional aging with spray

This test method is real time exposure at a 45° tilt from the horizontal with a water spray used to induce moisture weathering conditions. Also the introduction of moisture plays an important role in improving both relevancy and reproducibility of the weathering tests results. The application of wetness has two reasons. First, the introduction of water in an otherwise arid climate induces and accelerates some degradation modes that do not occur rapidly, if at all without moisture. Second, a thermal shock causes a reduction in specimen surface temperatures, as much as 14°C. This results in physical stresses which accelerate the degradation process.

Spray nozzles are mounted above the face of rack at points distributed to insure uniform wetting of the entire exposed area. Direct exposures are intended for materials which will be used outdoors and subjected to all elements of weather. Exposure times are generally 6, 12, 24 and 48 months. Location is an important factor in the harshness of this test [6].

1.3.2 Accelerated outdoor exposure

Outdoor accelerated weathering is a relatively recent technique. It relies heavily on technology to follow the track of the sun and to keep a constant temperature on the sample.

1.3.2.1 Equatorial Mount with Mirrors for Acceleration (EMMA)

This is an accelerated outdoor weathering test which uses natural sunlight and special reflecting mirrors to concentrate the sunlight to the intensity of about eight suns. The test apparatus is a follow the sun track with mirrors positioned as tangents to an imaginary parabolic trough. The axis is oriented in a north-south direction, with the north elevation having the capability for periodic altitude adjustment. A blower, which directs air over and under the samples, is used to cool the specimens. This limits the increase in surface temperature that is reached by identically mounted samples exposed to direct sunlight at the same times and locations without concentration. Exposure periods of 6 and 12 months have been correlated to about 2,5 and 5 years of actual aging in a Florida environment, respectively [6]. A schematic representation of the EMMA device is shown at Figure 1.3.

1.3.2.2 Equatorial Mount with Mirrors for Acceleration plus Water (EMMAQUA)

This is an accelerated outdoor weathering test which uses natural sunlight and special reflecting mirrors to concentrate the sunlight to the intensity of about eight suns. In addition to intensifying the power of the sun, water spray is used induce moisture weathering conditions. The apparatus for this method is the same as was described above in EMMA method introduction.

Exposure to EMMAQUA is considered to be the harshest. Applications generally tested with EMMAQUA include adhesives, agricultural films, automotive exteriors, building materials, elastomers, glass, packaging, paints and coatings, plastics, roofing and sealants.

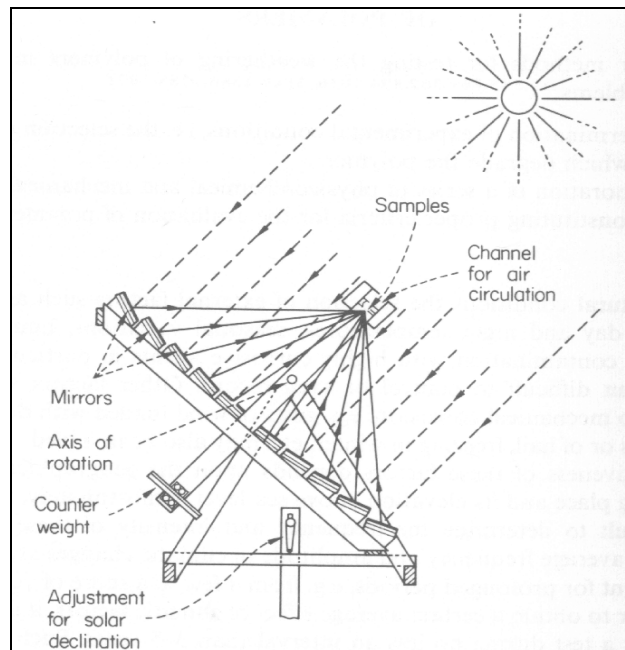


Figure 1.3 Schematic representation of the EMMA device [3]

1.3.3 Artificial accelerated indoor testing

Indoor testing is realized in special laboratory devices. These devices would match up to conditions shown in Table 1.3, if they can be used for testing giving high correlation with natural conditions.

Table 1.3: The list of important considerations for the selection of laboratory equipment which performs testing under conditions that may give a high correlation with natural exposures [4]

in addition to full spectrum of visible and IR, the UV radiation wavelength is limited to	295 to 380 nm
irradiance can be selected and controlled within the range	0.35 to 0.8 W/m ² at 340 nm
sample temperature (not air temperature) can be selected and controlled by black panel and ambient air control within the range	25 to 110°C
the sample temperature depends on color	temperature of samples varies
the real temperature of a specimen can be measured	
water quality can be controlled for water solids	<1 ppm
the rain duration can be selected and applied in selected intervals	0 to 50% of experiment time
the relative humidity can be selected and controlled	30-100%

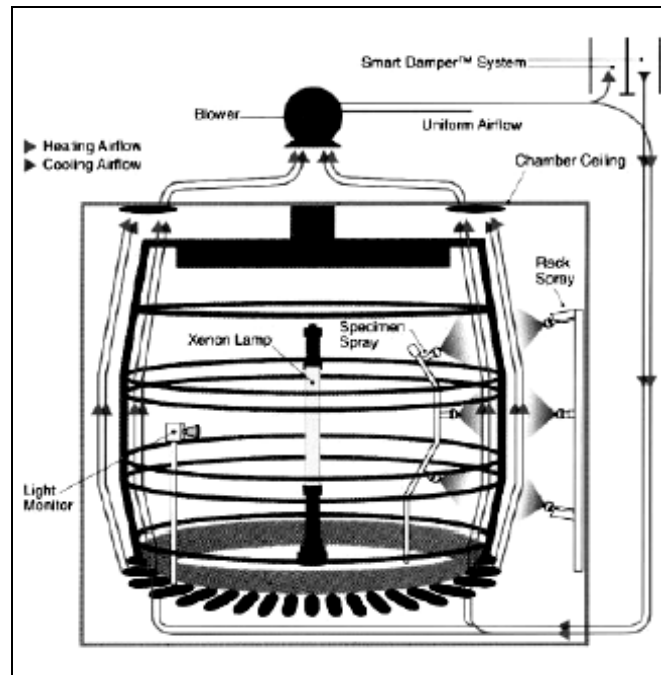


Figure 1.4 Schematic diagram of Weather-Ometer. [8]

Figure 1.4 shows schematic diagram of typical laboratory weathering device called Weather-Ometer. This device is equipped with a xenon lamp. The instrument provides full control of UV radiation, air temperature control, rain and rainwater control. All essential parameters can be selected by manual controls or from the computerized interfaces. Input and output data can be acquired to the remote computer and automatically controlled. These instruments are equipped with diagnostic functions which help users in troubleshooting and returning equipment to normal operation mode [4].

In indoor testing there are three eventualities that are predominately used to supply source of radiation - carbon arc, xenon arc or using Fluorescent UV lamps.

1.3.3.1 Carbon arc

Carbon arc lamps are historically the oldest source of artificial radiation. The enclosed carbon arc was introduced in 1918 and it is still specified for some test methods. In 1934, the Sunshine carbon arc, which was an improvement over the enclosed carbon arc, was introduced.

Much of the wavelengths produced by the Sunshine carbon arc are not found in daylight radiation at the Earth's surface. The radiation spectra of these carbon arcs are very different from daylight spectra. Enclosed carbon arc has two strong peaks at 358 and 386 nm which are respectively 4 and 20 times stronger than daylight at the same wavelengths. In other ranges of UV, radiation is substantially lower than in daylight. Sunshine carbon arc offers a substantial improvement over enclosed carbon arc but it has a stronger radiation below 300 nm than daylight. This radiation can cause an unrealistic degradation of materials [1].

1.3.3.2 *Xenon arc*

Xenon arc was adapted for accelerated weathering in 1954 in Germany. The xenon arc lamp emerged as the source most closely resembling UV radiation in the daylight spectrum.

Two facts are pertinent: its light does not contain radiation below daylight cut-off; its radiation intensity is similar to that of daylight radiation. It is possible to increase the radiation output by selecting the appropriate filters and by increasing the energy supplied to the burner. In 1979, the light monitor control system was introduced to monitor and adjust the radiative energy output delivered to the sample. This system further improved the reliability of the source by providing a constant repeatable output. The lamp cooling system is another important refinement. The burner has temperature of about 1000°C. It is enclosed in a double wall quartz cylinder. Water or air flow between the walls to reduce temperature. Water has an advantage as a cooling medium because it also eliminates part of infrared radiation above 1200 nm. There is no doubt that xenon arc is the artificial radiation source closest to natural daylight (see Appendices)[1].

1.3.3.3 *Fluorescent UV lamps*

Several fluorescent UV lamps are used by industry. FS-40 was the first lamp introduced in the 1970's. UVB-313, introduced in 1984, is essentially a second generation of FS-40. UVA-340 was introduced in 1987 in order to achieve better correlation with natural weathering.

There is no question that the radiation output of FS-40 and UVB-340 is not comparable with natural conditions. Studies using these lamps were severely criticized and there is basically no rationale behind using such a source. In spite of this, some industries, attracted by the possibility of obtaining fast results (using less expensive equipment), spent a considerable amount of resources on such testing. UVA-340 simulates daylight radiation well in a certain range but does not produce the acceleration caused by higher temperatures. Some wavelengths in the UV range, which are known to degrade materials, are missing or have negligible intensity [1].

1.4 METHODS OF WEATHERED SPECIMEN EVALUATION

More than fifty techniques are employed to analyze weathered specimens [1]. It is obvious that purpose and scope of this bachelor thesis allows doing only very brief and general summary of evaluation problems and methods.

At first it would be declared that infrared spectrophotometry is a dominating method of sample testing during exposure and other methods including UV spectrophotometry, electron spin resonance, nuclear magnetic resonance, and gel permeation chromatography are much more frequently used now than before [1]. But established and traditional visual methods and analysis of mechanical properties cannot be omitted. Molecular weight analysis is added.

1.4.1 **Visual methods**

This group of methods can be used to examine gloss retention, color changes and to watch surface morphology of evaluated specimen.

1.4.1.1 Gloss retention

The weathering mostly affects the material surface, which causes a loss of initial gloss. Therefore, it makes good sense to analyze surface changes, especially since the measurement is simple, and the equipment cheap, relatively accurate, and available. Several standard techniques exist, for example ISO 2813.

Gloss measurement was successfully used in paints to determine: binder durability; effect of pigment concentration; effect of proportion between the pigment and the extender; effect of pigment type and grade; on the stability of weathered coatings [1].

1.4.1.2 Color changes

The change of material color relates to changes in the chemical composition of the material and in many cases it decreases the material value. Weathering progress is indicated by color changes in colored products such as artists' pigments, museum textiles, dyed and undyed fabrics, paints and coatings, polymeric materials, building materials, etc. Results from studies of color measurement are typically interpreted in three ways: fading units, color change, and yellowness index [1].

1.4.1.3 Surface morphology

There have been numerous studies of surface morphology. Scanning electron microscopy (SEM) is the major technique used. Morphological studies concentrate either on the exposed surface or on the interface between the coating and substrate or between the fibre and the binder. SEM alone cannot detect chemical changes; it allows one to consider the chemical mechanisms as well because it gives such a precise picture of damage (Fig. 1.5) that many conclusions can be intuitively reached [1].

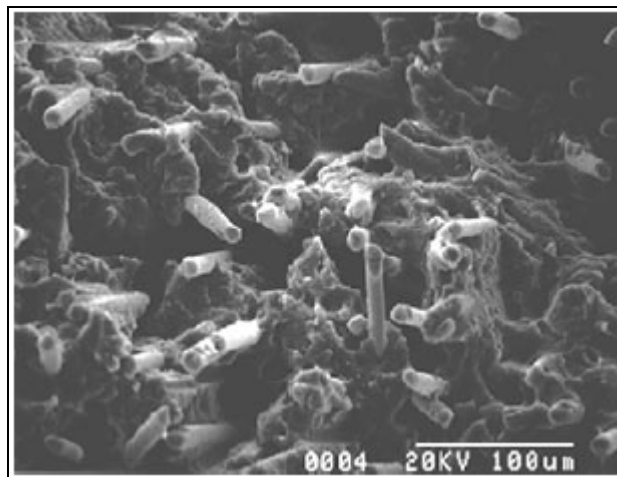


Figure 1.5 The SEM image of the fracture surface of glass fiber-reinforced polyphenylenesulfide after exposure to 90°C air for 6500 hrs [4]

1.4.2 Mechanical properties

Most materials tested for weathering performance must retain their mechanical properties during their expected service-life duration. A specific mechanical property becomes the reference to which most studies relate [1].

In this thesis tensile strength, elongation and flexural strength measurements are mentioned.

1.4.2.1 Tensile strength

Tensile strength retention during weathering was studied for most commonly used materials. It is always an individual characteristic of a material. Tensile strength may either increase or decrease during weathering. Usually, its changes are quite sensitive to the changes in the molecular weight of the polymer. In most cases, tensile strength decreases during exposure. However, in some cases, an initial increase of it is followed by quite rapid deterioration [1].

Tensile strength measurements are more precise when measured on durable specimens and less precise when applied to more severely degraded specimens. However, the precision of the method also depends on the method of specimen preparation and on the morphology of degraded specimen [1].

1.4.2.2 Elongation

Photodegradation of a material produces a greater effect on its ability to stretch than on its tensile strength. There is no correlation between tensile strength and elongation retention. Elongation depends more on changes occurring in the amorphous phase; tensile strength depends more on what happens in crystalline regions. Elongation measurements are much less precise than tensile strength measurements. Elongation retention correlates very well with chemical change during photooxidation [1].

1.4.2.3 Flexural strength

Flexural strength retention is important for many products, especially structural composites used for demanding applications. Flexural strength retention follows the pattern of tensile strength retention. Changes of flexural strength are clearly related to material surface deterioration. The cracks in the degraded surface layers act as the notch for fractures and dominate as the failure mode [1].

1.4.3 Spectroscopic methods

The main difference between visual and spectroscopic methods is that the visual methods help to define what changes occur but they do not offer an explanation for the chemical mechanism of these changes. Spectroscopic methods can provide this information [1].

The important spectroscopic methods are infrared spectrophotometry (IRS), UV

spectrophotometry, nuclear magnetic resonance (NMR), electron spin resonance (ESR) and methods using X-rays.

1.4.3.1 Infrared spectroscopy

IRS is the leading method used to analyze the changes in weathered specimens.

There is a brief description of principle of IRS. IRS relies on the resonance principle requires that the frequency of infrared radiation passing through a molecular substance be equal to or in resonance with a frequency of two bonded atoms vibrating. As one of the prerequisites for an infrared absorption to occur, the frequency of radiation must equal a frequency of vibration. In addition, the molecular dipole moment must undergo a change as the molecular vibration takes place. If both of these conditions are met, then the molecule will absorb energy from the Infrared beam passing through it [9]. This absorption of energy can be recorded in output infrared spectrum. This spectrum is then analyzed, usually backward Fourier transformation is used, and the final output is reached (see Figure 1.6).

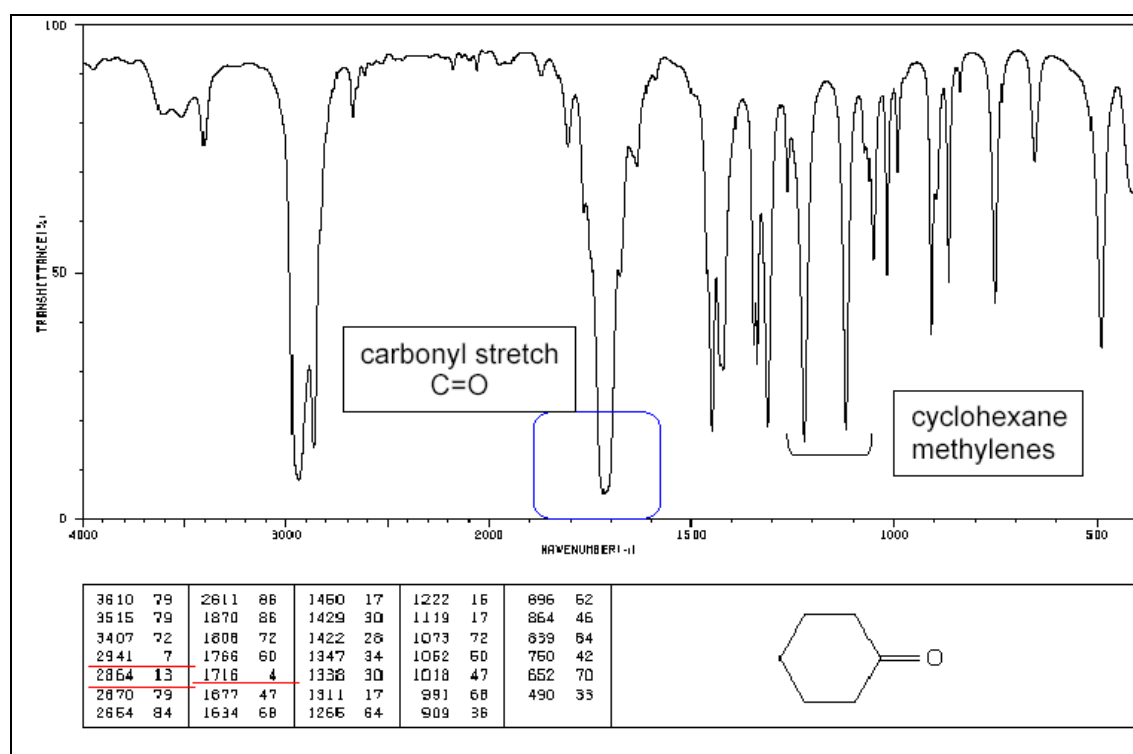


Figure 1.6 IR spectrophotometry output of cyclohexanone [10]

Every chemical substance or even a functional group of atoms has own characteristic IR spectra considered analogous to a fingerprint of an individual.

IR spectrophotometry has a broad range of usefulness in studying weathering characteristics of materials. The most useful area of application is in monitoring the photooxidative changes that occur during exposure [1].

The majority of the work in IR is conducted with bulk samples exposed to a variable length of irradiation. A typical approach consists of monitoring one or more absorption bands

in relation to a band which does not change during the irradiation process. Usually, the C-H band is taken as reference [1].

1.4.3.2 UV spectrophotometry

The progress of weathering introduces new chromophores in the polymer chain which frequently absorb in the UV region. UV spectrophotometry is very sensitive to these changes and may help to resolve a broad range of technical difficulties related to the monitoring of kinetical changes. UV spectrophotometry is best applied in predicting how materials absorb UV radiation and in determining or monitoring the kinetics of degradation, but it is also useful in studying of the mechanisms of reactions [1].

1.4.3.3 Nuclear magnetic resonance

NMR is one of the few techniques available for studying crosslinked systems and systems loaded with inorganic materials or other additives all of which may interfere with other spectroscopic measurements. NMR is also a very important method in verifying and confirming results obtained by other methods [1].

1.4.3.4 Elektron spin resonance

Since photodegradative processes proceed according to radical mechanisms, ESR is one of the methods of choice in the studies of photodegradation because it is capable of detecting radicals. The full potential of this method has not been realized until recently. During the last five years, the extent of application of ESR has improved and now it is probably the second most frequently used instrumental method in weathering studies next to IR.

ESR allows identification of the radical type. This is critical to the understanding of the mechanism of degradation. The study of such radicals is difficult because their lifetime is short. In order to improve the analytical capabilities of ESR, the measurements are made at temperatures close to liquid nitrogen, which stabilizes the radicals. Radical decay begins around -75°C ; below -75°C they are stable. Temperature dependency complicates measurement and generates discussions between scientists when they detect different radicals and suggest different mechanisms of degradation.

Using hindered amine nitroxide, which is able to produce a durable nitroxide radical, can minimize this problem. Nitroxide scavenges the radicals produced by the photodegradation, converting short-lived species to stable radicals. This approach makes possible the quantitative evaluation of radical formation rate [1].

1.4.3.5 X-ray scattering methods

Wide angle X-ray scattering and small angle X-ray scattering are two methods that are used occasionally to study changes in the crystalline structure of materials during weathering. These methods show that the degradation increases molecular mobility, facilitating the crystallization of molecules in the amorphous phase. This is important because it shows that material frequently changes during weathering into a more crystalline

material, which may result in higher UV resistance. It also shows that, if all effort is directed to monitoring chemical changes occurring during photodegradation, the results for various degradation stages are not comparable because the material is actually a continuously changing structure. Polymers are usually semi-crystalline materials and the crystalline structure is responsible for many of their properties. X-ray analysis provides us with very important information on the proportion of crystalline and amorphous phases, the distribution of crystallites, and it can distinguish between a variety of amorphous states [1].

1.4.4 Molecular weight analysis

Molecular weight is one of the parameters most affected by weathering. However, when molecular weight is used as an indicator of degradation, both crosslinking and chain scission occur simultaneously, and the interpretation of results is complicated.

Molecular weight distribution is most often determined by gel permeation chromatography (GPC). It is sometimes estimated by measuring polymer solution viscosity using capillary viscometers. When GPC is used, samples of materials are dissolved in a good solvent, filtered to remove insoluble particles, and the solution analyzed by GPC. Changes in molecular weight can be observed from the surface area under the GPC peak and from the change in elution volume as degradation progresses. A calibration curve is obtained, using polystyrene, polyethylene, and n-paraffins as standards but frequently, an absolute viscosity detector (universal calibration procedure) is used. Mark-Houwink constants of standards are used to calibrate a method for each polymer used.

Molecular weight measurements, although influenced by complexity of degradation mechanisms, are an important indicator of degradative changes and molecular weight analysis is certainly the most popular method of degradation monitoring. It cannot be used in the case of crosslinked polymers; crosslinking reactions during degradation may induce considerable error [1].

2 NATURAL VERSUS ACCELERATED AGING

As mentioned above in Chapter 1 there are three approaches which can be used to get relevant prediction of polymer durability. In this chapter will be compared natural exposure, accelerated outdoor exposure and artificial accelerated indoor testing. As the most reliable factors of following comparison are taken time demand and authenticity of each aging approach. As additional but also significant factors are chosen tractability and technical requirements.

2.1 TIME DEMAND AND AUTHENTICITY

These two factors are very closely connected. There is a strong need to get authentic weathering data in the shortest possible time for making predictions of polymer durability. Balancing between required authenticity and time demand is the most significant circumstance, which determines choice of aging approach.

The importance of time demand is proved by an exigency, which caused development of accelerated aging methods. On the other hand, fact that natural exposure was not marginalized and weathering studies based on natural exposure are realized in recent time proves the importance of authenticity.

2.1.1 Natural exposure

This approach is the most time demanding. As shown on Figure 2.1 natural exposure can take years before the data for predicting polymer durability are gained.

In closer look at process of natural exposure become obvious that in night time is polymer material degraded slower than in daytime. In night no photooxidation is realized and lower temperature slows all chemical degradative reactions. Even cloudy and/or cool days retard the degradation process. These retardations are natural, but they are the reason which increases exposure time dramatically and causes substantial time loss. This time loss prolongs period between beginning of aging exposure and gaining an useful output.

The main advantage of natural exposure consists in the highest reached authenticity, which allows to determinate the mechanism of degradation process. Certainly, it does not exist more realistic and authentic way to examine weatherability of plastic. However predictions of polymer durability based on natural exposure are limited. Lifetime of concrete material application in concrete locality can differ because of broad variations in climatic condition between localities around the Earth. For example testing materials in a tropical climate of Florida does not expose them to the proper natural conditions if the material will be used in Alaska.

Even in the same locality can weather differ year by year, which can distort data gained

from natural exposure and call for several year's exposure to minimize influence of these differences.

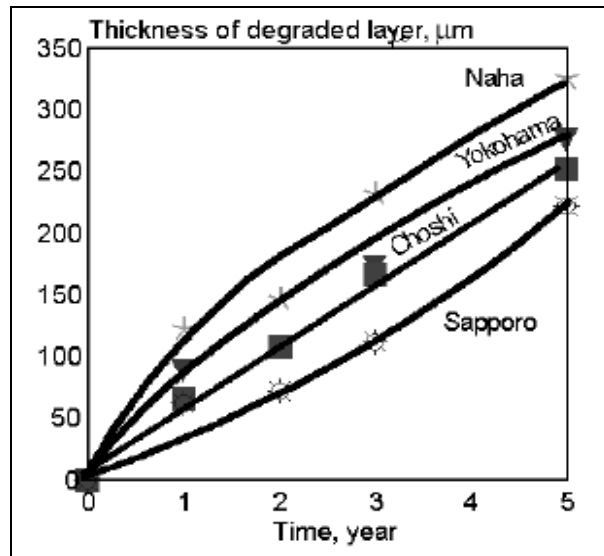


Figure 2.1 PVC: Thickness of degradation layer vs. exposure time of natural aging [11].

2.1.2 Accelerated outdoor exposure

This approach reduces the usual exposure times from years to months. Usual exposure time takes 6 or 12 months [6]. Time loss, as described above, influences also accelerated outdoor exposure times.

Reduction of exposure time naturally reduces the authenticity of accelerated outdoor exposure. Decreased authenticity is connected with unnatural specimen temperatures during exposure. The rate of photochemical reaction depends not only on the energy of radiation but also on the temperature, and on other parameters; therefore, the higher the temperature of specimen, the higher the degradation rate.

Figure 2.2 shows typical temperatures during exposure on EMMAQUA tester with cooling and after stopping of cooling. At temperatures between 60-90°C, which are usual for EMMAQUA testing, some different degradation reactions can occur. This circumstance calls for cautious interpretation of accelerated outdoor tests data.

2.1.3 Artificial accelerated indoor testing

There is a strong need to reduce exposure times of degradation examinations. For example some products available in the market today, are expected to last a minimum of 20 years and nobody is willing to wait for another quarter of a century to approve an updated versions of the product [1].

Accelerated laboratory testing is the less time demanding approach. Figure 2.3 shows that a typical exposure time of laboratory test takes less than 2000 hours, that is about 83 days.

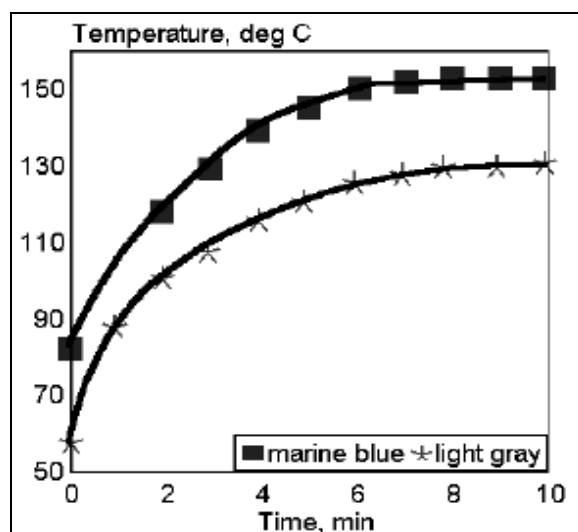


Figure 2.2 Temperature rise after stopping of cooling blower on EMMAQUA tester for samples of different colors [12].

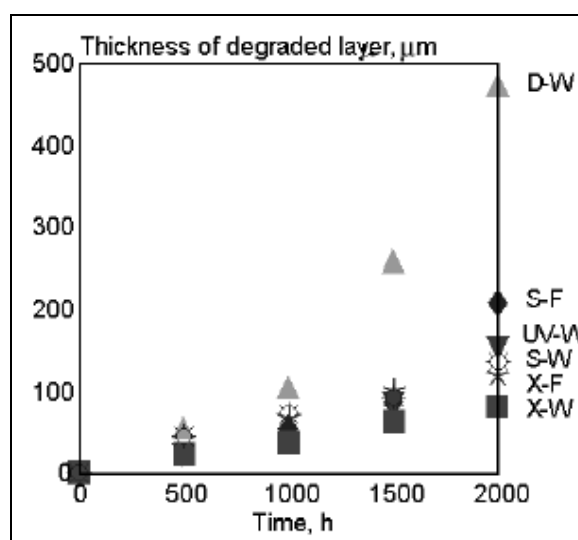


Figure 2.3 PVC: Thickness of degradation layer vs. exposure time. (SW-Sunshine weatherometer, XW-xenon weatherometer, UVW-UV-carbon weatherometer, DW-dewcycle weatherometer, SF-Sunshine fadeometer, XF-xenon fadeometer) [11].

The massive exposure time reduction demands different ways to get sufficient level of correlation with natural exposure. It is not reasonable to expect that accelerated weathering conditions will simulate natural weathering conditions. The accelerated weathering conditions should be selected to give the highest possible accelerating factor. However, the conditions selected must produce degradation mechanisms which are as similar as possible to the way in which the material would degrade in natural conditions. The method of evaluating degradation in these conditions must also be chosen carefully to ensure identification of the same factors that are changed in natural exposure [1].

The limited factor for reaching good authenticity of accelerated laboratory test is similarity of irradiation source to daylight. As can be seen in Appendices not even quality

aspect represented by presence of radiation with concrete wavelength but also quantity aspect represented by irradiance value is essential to get high similarity with daylight. Temperature and moisture can be well selected and controlled, so they do not complicate achievement of test conditions, which produce “natural” degradation mechanisms.

2.2 TRACTABILITY

This attribute has a close relation to setting and measuring experimental conditions as important factors which limit reliability of weathering test. Every aging approach has its specific sort of complications, which can devalue researcher’s work.

2.2.1 Natural exposure and accelerated outdoor exposure

In natural exposure experimental conditions are very variable and it is relatively difficult and time demanding to measure them. For example seasonal and latitudinal variations, sun elevation, pollutant composition, cloudiness, scattering by particles, etc. cause the composition of solar radiation reaching the Earth surface to vary [1].

It is unthinkable to expose material in natural conditions without knowing the precise long-term meteorological data of an experimental locality. Mainly properties of solar radiation, average temperature and relative humidity are important. Table 2.1 shows a collection of meteorological data from South Florida.

Table 2.1: Conditions of exposure in South Florida Test Service in Wittmann, Arizona average data for the four years - 1989, 1992, 1993, and 1994) [Data from South Florida Test Service, Wittmann, USA] [1]

Month	Radiation energy MJ/m ² at 45°			Radiation energy MJ/m ² at 5°			Temperature °C			RH %	Wet time h
	Total	UV	%UV	Total	UV	%UV	ambient	under glass	black panel		
JAN	573.20	20.60	3.59	415.72	18.21	4.38	11	15	21	49	84.10
FEB	547.48	20.69	3.78	466.24	20.43	4.38	13	17	22	50	56.15
MAR	660.43	29.39	4.45	657.08	29.11	4.43	17	21	26	52	62.48
APR	706.75	32.86	4.65	801.58	36.76	4.58	22	26	29	34	8.23
MAY	679.79	33.64	4.95	896.67	41.32	4.61	26	29	31	32	16.63
JUN	643.84	34.54	5.36	910.22	42.08	4.62	31	34	36	25	0
JUL	649.87	33.00	5.08	863.10	39.89	4.62	33	35	39	33	13.48
AUG	680.91	35.16	5.16	727.16	39.75	5.47	32	34	38	42	26.10
SEP	728.43	32.20	4.42	686.71	33.82	4.92	30	32	37	29	5.7
OCT	678.79	27.58	4.06	581.80	27.15	4.66	22	25	29	34	11.2
NOV	641.96	20.46	3.19	467.20	18.59	3.98	14	17	22	36	11.1
DEC	573.42	17.29	3.02	391.52	15.05	3.84	11	14	18	47	66.9
Total	7764.8	337.44		7865	362.16						361.97
Ave.	647.07	28.12	4.35	655.42	30.18	4.60	22	25	29	39	30.16

It is obvious that existence or accessibility of these specific data can be another limiting

factor of exposure under natural conditions. It is imperative to have accurate information on these conditions (UV irradiance, temperature, relative humidity, concentration of pollutants, etc.). Some of these data can be obtained from the local weather monitoring station (statistical data are usually expensive) but UV irradiance is less frequently available and must be measured by the experimentator. These requirements are usually taken into account in studies conducted by stations providing a natural exposure service for customers [1].

2.2.2 Artificial accelerated outdoor testing

In modern laboratory weathering devices can be set experimental conditions at very exactly values and can be well controlled during testing. But there is hidden danger in this possibility. Some values of experimental conditions can cause that unrealistic mechanisms of degradation occur. The border between the most effective accelerating of degradation process and undesirable unreal mode of degradation can be very thin. And can be exceeded without proper experience with degradation problems and behaviour of degraded materials.

2.3 TECHNICAL REQUIREMENTS

The accessibleness of experimental devices and technical and economical requirements connected with purchase and pursuit these devices also influences the choice between mentioned aging approaches.

2.3.1 Natural exposure

Natural exposure is realized with simple apparatus. For specimens are mainly exposure racks used, see Figure 2.4. Financial and technical requirements for natural exposure apparatus are usually the lowest than for accelerated outdoor and indoor testing.

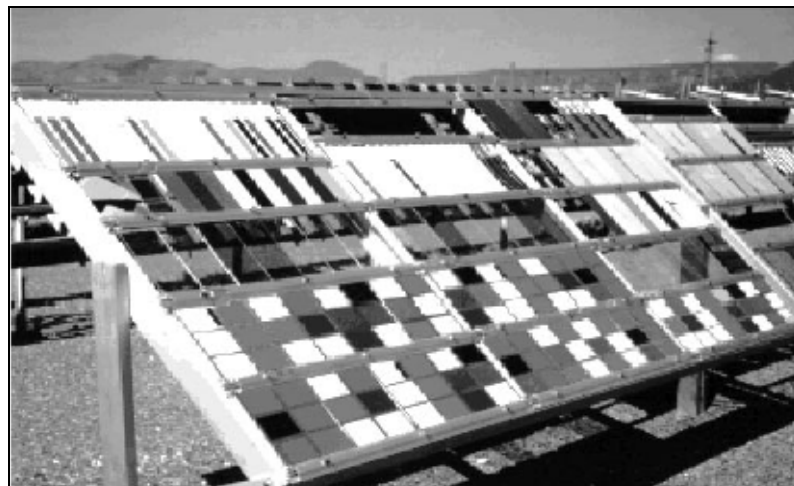


Figure 2.4: Exposure rack [4]

2.3.2 Accelerated outdoor exposure

For EMMA and EMMAQUA tests the Fresnel-reflector test machine, which is a follow-the-sun rack, has a ten-mirror collector array to concentrate sunlight onto an exposure area mainly used, see Figure 2.5.

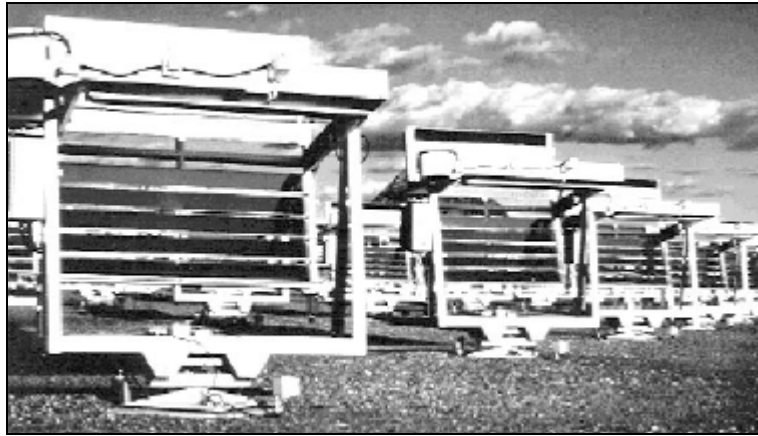


Figure 2.5: Fresnel-reflector test machine [4].

The sophistication and cost of Fresnel-reflector machine is higher than the primitive rack apparatus for non-accelerated exposure under natural conditions.

2.3.3 Artificial accelerated outdoor testing

Laboratory devices for accelerated aging tests are very sophisticated and thus very expensive. For example costs of devices, which are shown at Figure 2.6, are 8.000-11.000€ for Suntest CPS, 50.000-80.000€ for Xenotest Alpha and 40.000-100.000€ for Ci3000+ Xenon Weather-Ometer® [korespond.].



Figure 2.6: Three laboratory devices. From left: Suntest CPS, Xenotest Alpha and Ci3000+ Xenon Weather-Ometer® [13].

Higher service costs and operating costs of these devices can be expected. For example one xenon lamp with average lifetime about 1.500 hours costs 700€ [14]. Comparing to other two aging approaches the financial expenses are enormous. From these reasons commercial companies offers implementation of weathering tests on their own devices as a less expensive alternative.

3 RECOMMENDED PROCEDURE

Making prediction of durability for concrete material should consist of three steps. At first the predominant mechanism(s) of degradation (PMD) under natural conditions has to be determined. Then degradation has to be simulated with preservation of PMD in accelerating outdoor or laboratory devices. At last the most efficient way of acceleration should be found. Even this way has to preserve a leading participation of PMD in degradation process.

3.1 DETERMINATION OF PMD

Concrete polymer material is mostly a complex system, which consists of macromolecular portion as a polymer matrix and broad scale of low molecular additives as fillers, antioxidants, stabilizers, fire retardants etc. In application of material many interactions between those substances themselves and between those substances and substances from environment can arise. This complexity of material promotes situation, which allows many mechanisms of degradation to occur and compete. Figure 3.1 shows some primary photochemical reactions and Figure 3.2 demonstrates reactions with singlet oxygen. Some of these reactions are useful in explaining the peculiarities of various degradation mechanisms.

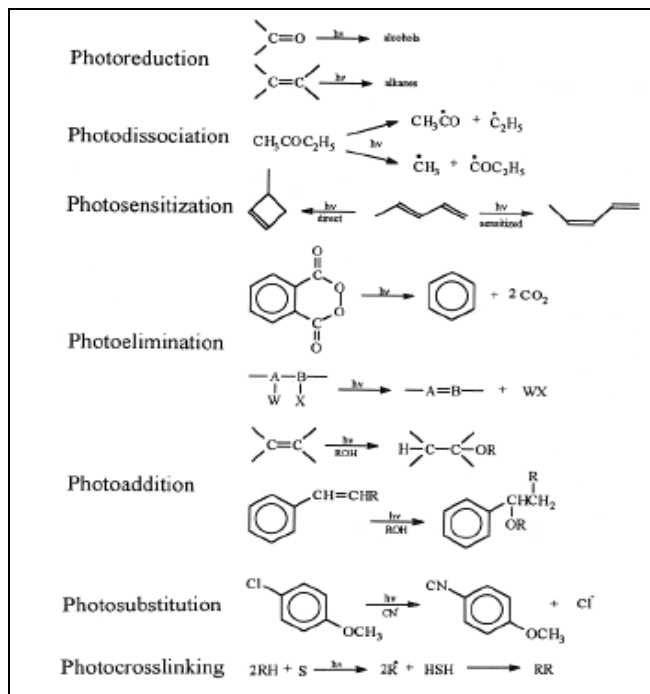


Figure 3.1: Primary photochemical reactions [1]

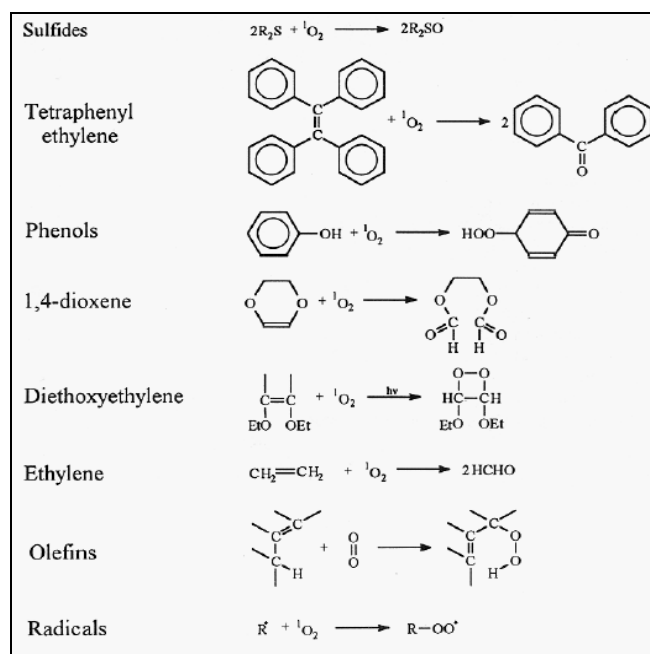


Figure 3.2: Reactions characterizing singlet oxygen reactivity [1]

In concrete natural conditions some of degradation mechanisms will prove insignificant and some of them will prove predominant and important. Categorization of all possible degradation mechanisms and determination of the predominant ones is the key challenge and very important first step for prediction of material durability.

It is obvious that natural exposure has an irreplaceable role in realization of this first step. No other weathering approach can provide conclusive output for classification of degradation mechanisms in conditions of future material application.

3.2 SIMULATION

When PMD is determined, the simulation of degradation process becomes important. Simulation is necessary condition for future acceleration attempts. Relocation of weathering experiment to non-natural conditions with well-preserved role of PMD can include various problems.

Accelerated outdoor and indoor tests methods are used to realize this step.

3.3 ACCELERATION

Accelerated testing with valid results is the most effective mode for examining degradation process. Its preserved authenticity and the lowest time demand are very suitable for predicting durability of concrete material and/or group of related materials.

Artificial accelerated indoor testing is mainly used in this step. It allows reaching the highest acceleration for examined material. But it should be mentioned that it is a complimentary technique, the nature of which largely depends on how intelligently it is used. All important weathering factors must be adequately simulated by the accelerated test. The accelerated test must be designed to simulate as closely as possible the worst-case

in service conditions. The guiding principle should be: "simulate, then accelerate as much as is possible" [13].

CONCLUSION

There are three major approaches, which could help to make prediction of polymer durability - natural exposure, accelerated outdoor exposure and artificial accelerated indoor testing. Each approach has its own advantages and disadvantages.

There are two fundamental issues, which must be considered in sequence when selecting a convenient weathering or aging approach. These are time demand and authenticity. These two terms are connected. The general statement is that the approach, which is most time demanding, is simultaneously the most authentic. The decisive factor is time, which can be given to realization of weathering experiment with preservation of authenticity and veracity of realized experiment results.

All aging approaches were devised under the rule of the general statement and the decisive factor, which are adduced in previous paragraph. Natural exposure is the most time demanding, but it offers the greatest amount of authenticity, which is needed to determinate natural mechanisms of degradation. Artificial accelerated indoor testing is in contrast with natural exposure, it offers the lowest time demand, but its decreased authenticity can cause unrealistic results of aging experiment in some cases. Accelerated outdoor exposure is a compromise solution.

Application of each aging approach is limited by specific circumstances. Natural exposure is limited by accessibleness of meteorological data, especially the data, which refer to attributes of solar radiation. Natural conditions of each concrete locality are variable. This fact forces to make long-term meteorological studies, which give average values of natural conditions. Artificial accelerated indoor testing is limited by high financial requirements and high costs of laboratory devices. Full-equipped laboratory is very expensive and many institutions cannot afford it. Accelerated outdoor exposure is limited by both circumstances mentioned above.

Predicting material durability is very complicated and demanding process. Each aging approach can participate on it and each aging approach has its irreplaceable use in this process. Natural exposure is irreplaceable in determining the predominant mechanism of degradation and the other two approaches are alternatives, which allow realization of accelerated degradation.

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REVIEW OF SYMBOLS

EMMA	Equatorial Mount with Mirrors for Acceleration
EMMAQUA	Equatorial Mount with Mirrors for Acceleration plus Water
ESR	electron spin resonance
IRS	infrared spectrophotometry
NMR	nuclear magnetic resonance
PMD	predominant mechanism of degradation
UV	ultraviolet

REVIEW OF FIGURES

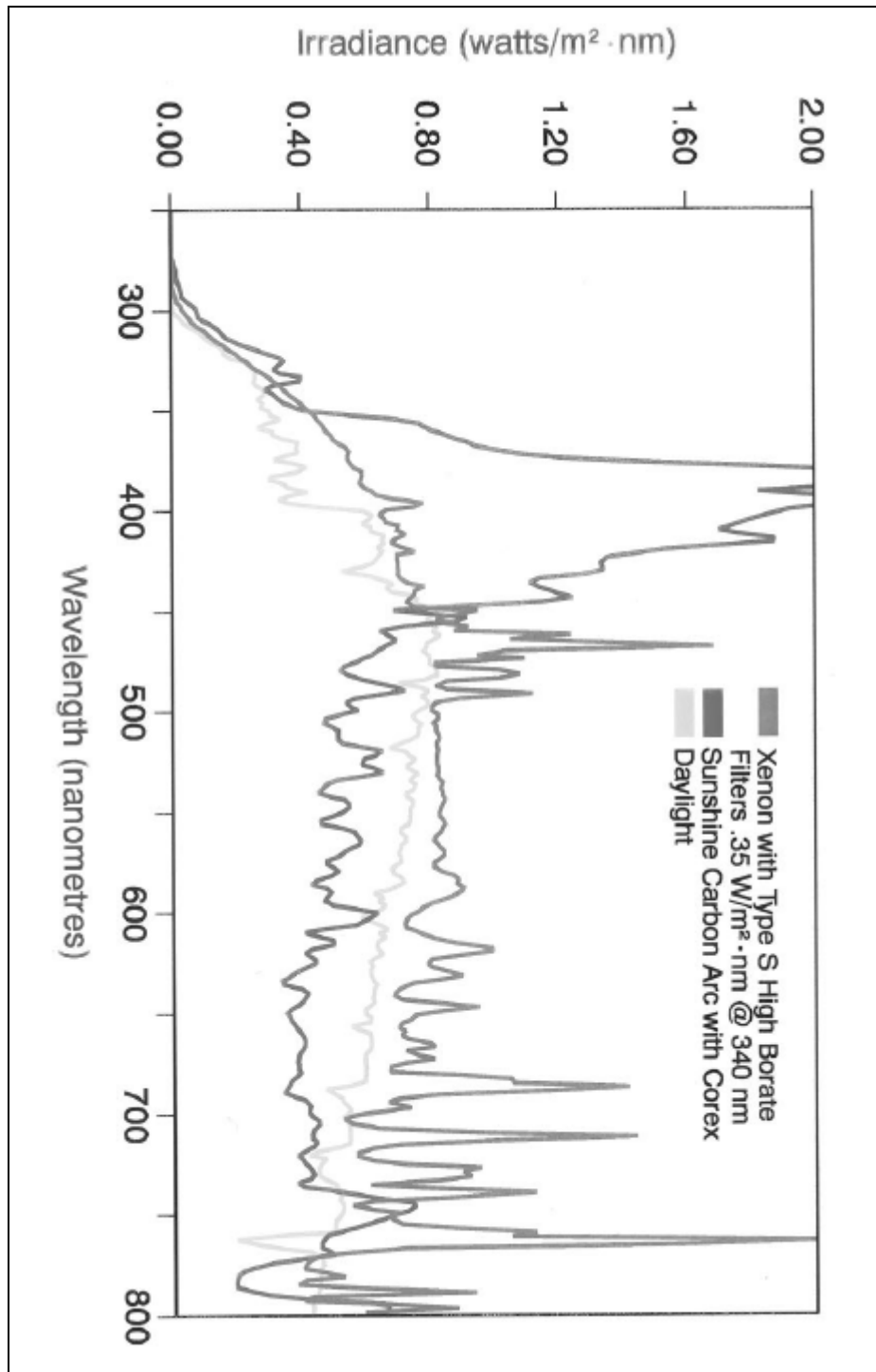
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APPENDICES

Appendix 1: Xenon arc vs. Sunshine carbon arc vs. Miami average 45° daylight [1].



Appendix 2: Xenon arc vs. enclosed carbon arc vs. Miami average 45°S daylight [1].

