

UV stability of PE foils

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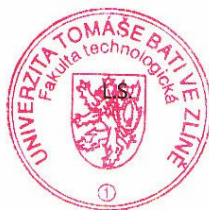
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ABSTRAKT

Cílem diplomové práce je návrh a provedení stabilitních studií polymerních fólií využívaných v zemědělství. Pro vlastní testování byly vybrány polyetylenové fólie, které jsou v podmínkách reálného využití extrémně zatíženy povětrnostními podmínkami, zejména působení přímého slunečního světla (UV záření) a vysoké vlhkosti vzduchu, ale i přímým působením chemických prostředků.

Podmínky prováděných laboratorních experimentů, postaveny především na metodě urychleného stárnutí s využitím tzv. veterometru, mají za úkol pomocí střídání cyklů zatěžujících materiál UV zářením, změnami teplotních a vlhkostních podmínek, zajistit co nejdokladnější simulaci přirozeného stárnutí polymerních materiálů. Tyto experimenty jsou dále doplněny studiem vlivu chemické zátěže aproximující reálné podmínky při vlastní aplikaci fólie.

Pro studium vlivu experimentálních podmínek na materiálové vlastnosti byly vybrány analytické metody využívající infračervené spektroskopie, širokouhlé rentgenové difrakce, diferenciální skenovací kalorimetrie a sledování mechanických vlastností.

Klíčová slova: PE, UV stabilita, urychlené stárnutí, FT-IR, DSC, WAXS, mechanické vlastnosti

ABSTRACT

Accelerated physical aging of polymeric materials plays unsubstitutable role in simulation of lifetime prediction of polymeric products. Classic accelerated ageing test using weatherometers does not include influence of chemical treatment that can have significant effect on degradation process.

This work is focused on study of influence of selected nutrient, agents used for fertilization in agriculture, on photodegradation of polyethylene mulch foil. Tested samples were treated using nutrient baths, UV radiation and their combination.

The influences of chemical and physical treatments were evaluated using infrared spectrometry, thermal analysis, X-ray diffraction, spectrophotometry and mechanical testing.

Keywords: PE, stability, ageing, FT-IR, DSC, WAXS, mechanical properties

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I declare I worked on this Master thesis by myself and I have mentioned all the used literature.

In Zlín 11.8.2011

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INTRODUCTION

Polymeric materials have become widely used for many different applications ranging from food packaging, medical devices, and construction materials to many other consumer products.

Most of common polymers are commercially useless separately for their low stability during processing and low resistance to weather conditions. In general, the degradation of polymeric materials is caused by exposure to various factors such as heat, UV light, aggressive chemicals, irradiation, mechanical stress and microbes, moreover it is promoted by several other factors, as oxygen concentration, humidity and strain. The mechanism of polymer degradation is complicated and involves chemical changes in materials, resulting in such flaws as brittleness, cracking, and fading [1]. These changes are possible to slow-down by using stabilizers that undergo chemical changes instead of polymeric chains. Therefore without additives, mainly stabilizers, polymers cannot be directly utilized due to fast ageing caused by chain scission (degradation).

Anyway the function of additives is limited and because of that polymeric products have limited lifetime in dependence of environment where they are used. The choice of polymer composition thus is given by the requirements for the application [2]. Estimation of this lifetime is usually based on tests simulated real function of article. But products designed for longtime usage, mainly for outdoor application, makes problem for testing. Natural weathering tests are commonly used to evaluate the weather resisting property of materials, but they are time consuming and their reproducibility is not good. In the laboratory, artificial weathering test is often adopted to simulate natural weathering test. In artificial weathering devices, UV lamps are commonly used as light sources to simulate ultraviolet radiation of sunshine and water is periodically sprayed to material surface to simulate raining [3].

Artificial weathering enhances possibility to test many polymeric products for outdoor usage which are exposed to weather conditions during all of their lifetime such as for example mulching foils, stretch foils, plastic tarps used in agriculture.

I. THEORY

1 POLYETHYLENE FOILS IN AGRICULTURE

In agriculture polymers are used for many applications from packaging, water distribution pipes, plastic tarps to mulch foils. In the case of mulching, polymeric foils have lower permeability for water than nature mulching materials especially in drought periods and in environment with higher temperatures and lack of rainfalls or water. Polymeric mulch foils give e.g. certain possibility of protection from weed, animals or can help as a thermal insulation in environments with large temperature differences between day and night. In the case of black foils, the warming of substrate is possible due to light absorption and on the other hand reflective mulches offer the advantage of not overheating the soil.

For this application polyethylene is preferred due to its availability and relative easy processing.

1.1 Polyethylen

Polyethylene is the oldest and simplest in structure of the crystalline polyolefins. Polyethylene was first produced in a branched form LDPE in the 1930s, LDPE contained varying amounts of long chain branches and had a crystalline melting temperature of about 110 °C. Linear polyethylenes HDPE were produced in the early 1950s. These had a higher crystalline melting temperature of about 135 °C [4].

Nowadays there are several kinds of polyethylene (LDPE, LLDPE, HDPE, UHMWPE and other), which are synthesized with different molecular weights and chain architectures.

LDPE and LLDPE refer to low density polyethylene and linear low density polyethylene, respectively. These polyethylenes generally have branched and linear chain architectures, respectively, each with a molecular weight of typically less than 50,000 g/mol.

High density polyethylene (HDPE) is a linear polymer with a molecular weight of up to 200,000 g/mol. UHMWPE, in comparison, has an average molecular weight of 6 million g/mol [5].

Nevertheless in agriculture two kinds of polyethylene are used: LDPE and HDPE. LDPE is preferred due to his lower modulus. HDPE has higher stiffness which cause lower flexibility to rough surface and this could be problem for mulching by combination of foil (bottom layer) and nature mulching material (upper layer).

1.2 LDPE

LDPE typically has long side-chain branching off the main molecular chain and therefore is a more amorphous polymer. LDPE is defined by a density range of 0.910–0.940 g/cm³. This range depends on branch points at material. As the number of branch points in PE chains increases, PE density decreases. The amount of unsaturations in PE also increases with the decrease in the density. For the example, an average number of methyl branches per 1000 carbons on LDPE increased from 21 at 0,922 g/cm³ to 43 at 0,916 g/cm³. An average number of vinylidene unsaturations/branches per 1000 Da (molecular weight) segments of LDPE increased from 16 at 0,922 g/cm³ to 35 at 0,912 g/cm³. As a result of branching, LDPE shows lower shrinkage compared to a more crystalline HDPE, in which many of the polymer molecules are packed closely together.

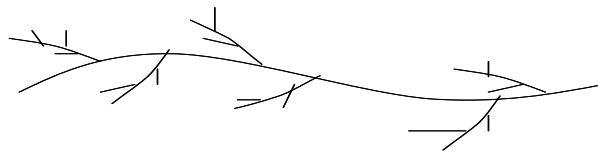


Figure 1: LDPE chain

1.3 HDPE

HDPE is defined by a density of greater or equal to 0.941 g/cm³. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. Due to its higher crystallinity compared to LDPE, HDPE is stronger and stiffer than LDPE, but is more prone to warpage. It shows a higher shrinkage, due to formation of crystalline, packed areas upon transition from melted state to solid one. Its tensile strength is two or three times higher than LDPE [6].

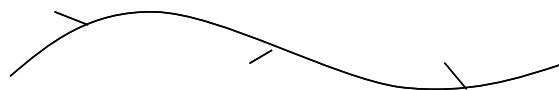


Figure 2: HDPE chain

2 POLYETHYLENE DEGRADATION

Thermo-oxidative processes which occur during polymerization, storage, and processing result in the formation of a crystalline structure which contributes to further diversity. Several kinds of PE are highly diverse because of chain irregularities (branches), unsaturations, molecular weight variations, and components added during the polymerization reaction to influence basic mechanical properties and durability. General properties depend on a mix of factors which are not easily quantified. Because of this diversity, it is difficult to apply one general principle of degradation to the entire group. For example sensitivity of PE to oxidation increases at its density decrease. LDPE is more prone to oxidation compared to HDPE. On the contrary, LDPE is oxidized rather uniformly compared to HDPE.

2.1 Mechanism of polyethylene degradation

Both HDPE and LDPE contain unsaturations (see Fig. 3). The presence of these unsaturations (vinylidene groups) leads to formation of allylic hydroperoxides during the thermo-oxidative processes, and this becomes the major mechanism of initiation (see Fig. 4).



Figure 3: PE unsaturations

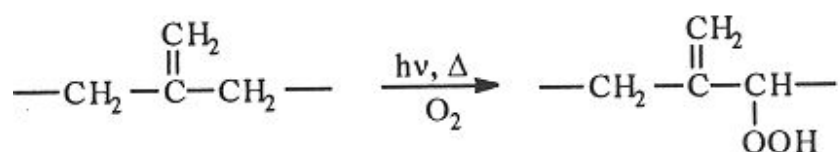


Figure 4: formation of allylic hydroperoxides

One primary initiation step may produce three free radicals, then secondary processes also give rise to compounds containing hydroxyl, carbonyl, and vinyl groups which also absorb radiation and undergo further degradative processes. The structure of polyethylene determines the probability of further conversion.

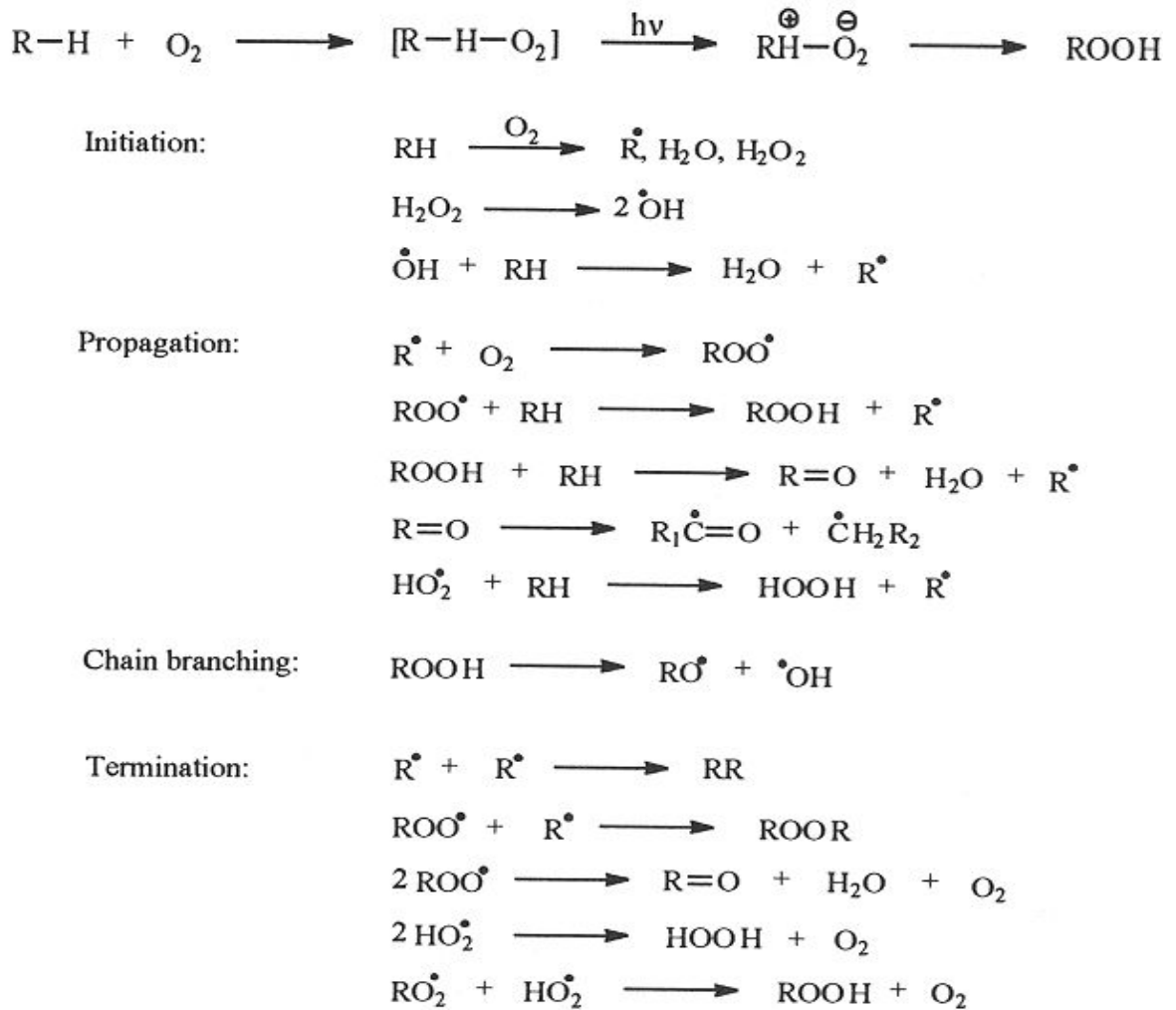


Figure 5: Photooxidation of polyethylene proceeds by a free radical chain mechanism

Three major functional groups are accumulated during PE degradation: ketones, carboxylic acids, and vinyl groups. Ketones absorb radiation above 300 nm and in the subsequent reaction they are mostly converted to carboxylic acids and vinyl groups. Carboxylic acids accumulate in PE during photooxidation because they apparently do not undergo further reactions. Vinyl groups cannot absorb UV radiation above 300 nm but they can react with the singlet oxygen generated photochemically in PE and then they are susceptible to free radical attack. During photolysis, ketones and vinyl groups increase linearly with time of exposure.

The crystalline structure of the polymer has a very strong influence on its stability. Crystallinity changes during the course of degradation. In the initial stages of photodegrada-

tion, chain scission prevails which reduces molecular weight. Shorter chains are more mobile and are thus able to crystallize more readily. Therefore, embrittlement of PE is controlled by two associated processes: reduction of molecular weight and increased crystallinity [7].

During the lifetime polyethylene mulching foils are exposed to the most of degradation factors included in weather conditions. Between factors with great influence belong UV radiation, atmospheric oxygen, ozone, microorganisms and chemical attack in the form of fertilizers. These main factors are supported by other weather processes like temperature changes, different air humidity, rains, location and many others. Combination of all these factors causes negative changes in the structure of polymeric material generally called ageing. This process is followed by changes in mechanical properties and often in visual changes too. At beginning they are visible color changes. For example white foils start to be yellow and colored foils lose their colorfulness. During the ageing they are visible cracks on the foils and in the end this cracks leads to loss of mechanical properties and disintegration of the foil.

3 ACCELERATED AGEING

As it was already mentioned, PE mulch foils are attacked by many degradation factors during the exposition to natural conditions. Prediction of durability for these foils present problems. Tests of natural ageing where the polymeric material is exposed to real conditions in real time are time consuming. Better alternative is method of artificial ageing called accelerated ageing employing weatherometers through alternating modes of e.g. UV radiation (simulating sunlight), water shower (simulating rains and watering), air humidity and temperature changes (simulating changing of day and night). Disadvantage of this method is possibility of difference between setup of artificial ageing and natural ageing, caused by wrong compilation of experiment [8].

3.1 Artificial weathering equipment

Simulation of natural conditions presents problem due to some random factors in nature like rain, variable cloudiness, wind, microorganism attack, chemical attack and others. Therefore modern accelerated weathering equipment allows control of the following parameters of testing:

- wavelength of radiation
- radiation intensity
- irradiance uniformity
- energy dosage and exposure time
- temperature
- rain
- humidity

Radiation wavelength is controlled by the choice of source and filters. Radiation dosage and temperature are microprocessor controlled [7].

3.2 Sunlight

Sunlight is the main source of energy for planet but also for most polymeric materials is it the main cause of losing of properties due to photooxidative attack, that is the combined action of sunlight and oxygen on there chemical structure.

To define the stability or rate of deterioration of such materials on some meaningful scale three main approaches have been followed in an attempt to quantify sunlight as an agent of deterioration. They are based on measurement of three aspects of sunlight: sunshine duration, total solar radiation and ultraviolet radiation [9].

3.2.1 Light source

The most important parameter for weathering studies is relative photon energy vs. wavelength (shown in Fig. 6). Photon energy increases as wavelength decreases therefore photoreactions which require a particular amount of energy only occur at a certain wavelength. It is therefore imperative to assure that there is no wavelength in the radiation used in artificial weathering equipment which is lower than any wavelength in the daylight spectrum. This is the most important criterion used in the evaluation of light sources.

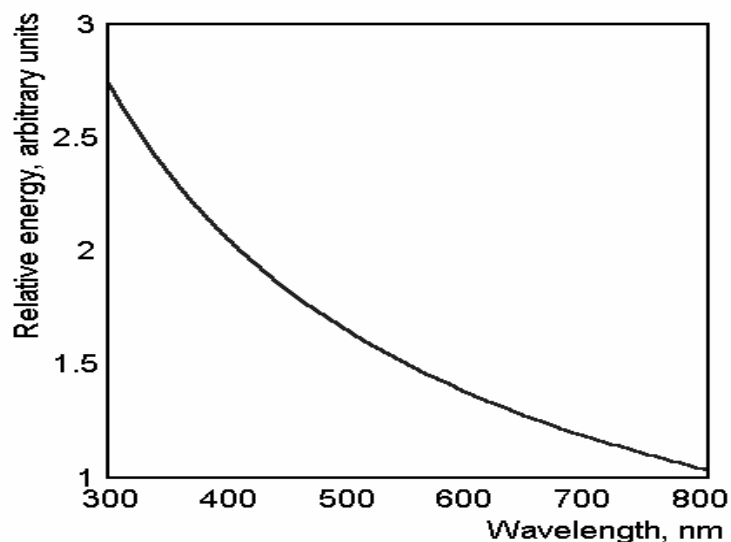


Figure 6: Relative photon energy vs. radiation wavelength

They are many possible light sources of UV and visible solar radiation that can be used for weatherometers like carbon arc, xenon arc, fluorescent UV lamps, mercury lamps, indoor actinic source and others. But many current devices are based on xenon arc.

Xenon arc was adapted for accelerated weathering in 1950's in Germany. Initially, there were several problems with the source stability over time and with the choice of proper filters, but, after these were overcome, the xenon arc lamp emerged as the source most closely resembling UV radiation in the daylight spectrum (see Fig. 7).

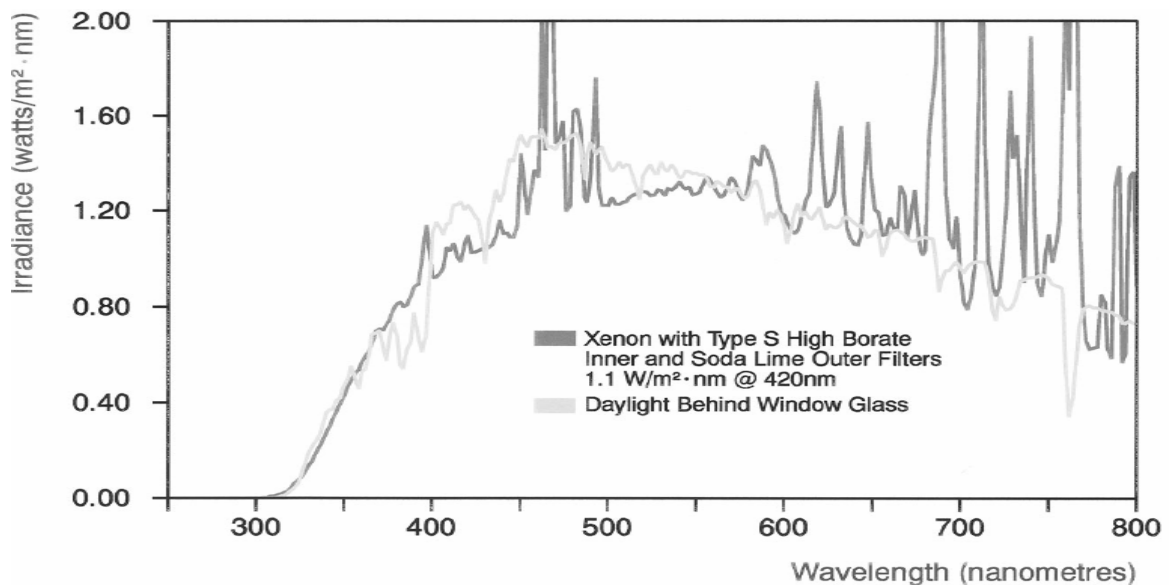


Figure 7: Spectrum of xenon arc vs. daylight behind window glass

Xenon arc light does not contain radiation below daylight wavelength and its radiation intensity is similar to that of daylight radiation. It is possible to adjust the radiation output by selecting the appropriate filters [7].

3.3 Water

In environmental conditions, water may have various physical and chemical effects. Liquid water may lead to the erosion of oxidized layers, swelling of matrix, and extraction of additives soluble in water. Liquid or gaseous water may also induce the hydrolysis of oxidation intermediates or of final products of photo oxidation.

Depending on the type of polymer, the nature of stabilizers (especially their solubility in water), and the climatic parameters, the relative importance of the different processes may be anticipated. The experimental design of a test should be based on the understanding of the prevalent effect of water:

- If the predominant effect of water is presumed to be rinsing, water sprays are relevant.
- If the predominant effect of water is presumed to be swelling and extraction of stabilizers, sprinkling should be limited to prevent exaggerated swelling or extraction.
- If the predominant effect is presumed to be hydrolysis of final photo oxidation products, post-immersion of the exposed samples in water is enough to lead to hydrolysis and to induce changes in optical properties.
- If water is able to react with intermediate degradation products, a combined effect of light, heat, oxygen, and water may be anticipated [10].

3.4 Chemicals

During the lifetime mulch foils can come into contact with some chemicals in the form of in/organic fertilizers which are combined with water at various concentrations.

But most of accelerated weathering equipments are not adapted for insert of chemical treatment to weathering process mainly due to oxidation properties of chemicals which can cut down their lifetime. Even though, effect of chemicals on original product can be small, effect on intermediates can be significant. Chemicals can influence also function of additives, e.g. stabilizers.

4 AGEING EVALUATION

For observation of process of photodegradation several analyses methods are useful. Influence of chemical and physical aging on thermal properties of mulch foils could be characterized using differential scanning calorimeter, while changes in mechanical behaviour can be recorded by the help of universal tensile test machine. Moreover infrared spectrometer, X-ray diffraction and spectrophotometer can be utilized for observation of molecular structure changes, and variations in optical properties, respectively.

4.1 Infrared spectroscopy

Infrared (IR) spectroscopy is a very important non-destructive technique for gaining structural information and identifying the chemical bonds in unknown in/organic compounds. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for qualitative as well as quantitative structural description and compound identification used in various scientific areas of research [11].

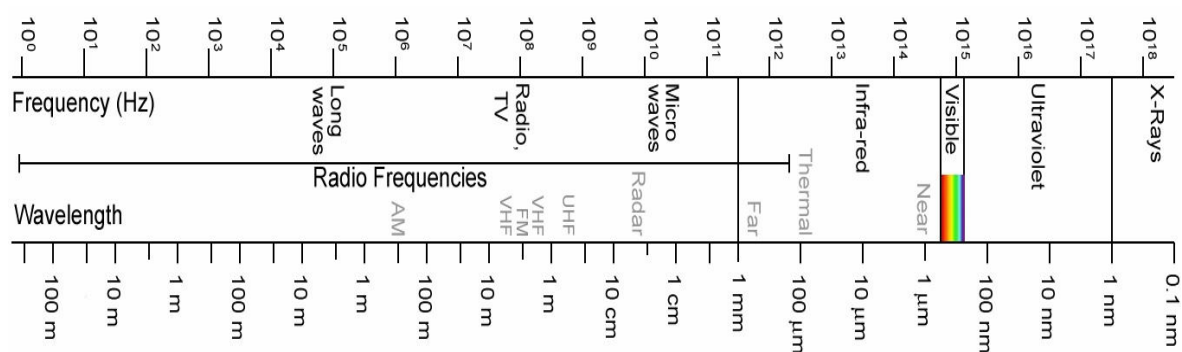


Figure 8: The electromagnetic spectrum showing the Infrared region

4.1.1 IR Frequency Range and Spectrum Presentation

Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly $13,000$ to 10 cm^{-1} , or wavelengths from 0.78 to $1000\text{ }\mu\text{m}$. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies.

IR absorption positions are generally presented as either wavenumbers ($\bar{\nu}$) or wavelengths (λ). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. The wavenumber unit cm^{-1} is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy. Wavenumbers and wavelengths can be interconverted via following expression:

$$\bar{\nu} [\text{cm}^{-1}] = \frac{1}{\lambda [\mu\text{m}]} \times 10^4 \quad \text{Eq. 1}$$

IR absorption information is generally presented in the form of a spectrum with wavelength or wavenumber as the x-axis and absorption intensity or percent transmittance as the y-axis. Transmittance (T), is the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T).

The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0 to 100% T whereas absorbance ranges from infinity to zero.

In IR spectroscopy two types of technique are used, transmission and reflectance [12].

4.1.2 Transmission

In transmission, the light source goes through the sample (embedded in an inert medium) to the detector. The sample is normally embedded in KBr or in CsI.

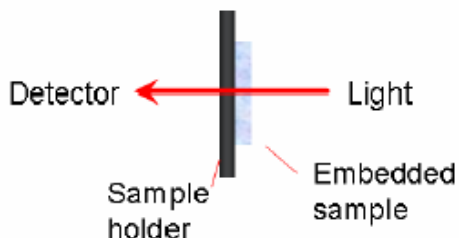


Figure 9: FT-IR transmission principle

4.1.3 ATR

The ATR (Attenuated Total Reflectance) technique is a surface examination technique. An internal reflecting element crystal is used to focus and direct the light beam to the surface of investigation. Usually the beam only penetrates about 1-5 μm into the sample. The beam is absorbed by the sample and is reflected back out to the crystal and the beam continues to the detector.

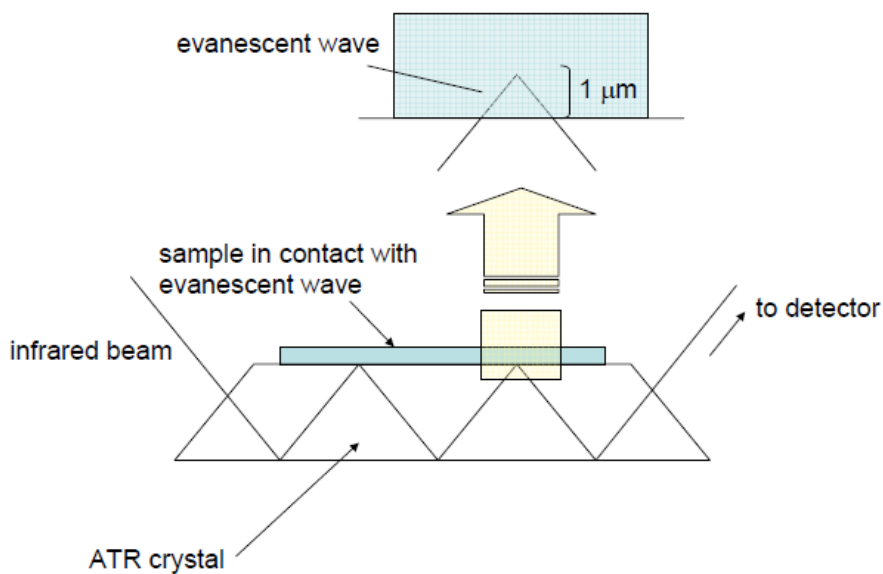


Figure 10: FT-IR/ATR principle

4.1.4 Benefits of ATR vs. Transmission for FT-IR Analysis of Polymers

Polymer samples presented for analysis are often too thick for measurement by transmission sampling techniques since the ideal IR beam path length for sample identification is typically less than 20 μm . However, the relatively thin depth of penetration of the evanescent wave (typically 0.5 to 2.0 μm) in ATR generally eliminates the need to do sample preparation [13].

4.1.5 Spectrometer Design

The basic instrument design is quite simple. The IR radiation from a broadband source is first directed into an interferometer, where it is divided and then recombined after the

split beams travel by different optical paths to generate constructive and destructive interference. Next, the resulting beam passes through the sample compartment and reaches to the detector. Most benchtop FT-IR spectrometers are single-beam instruments. Unlike double-beam grating spectrometers, single-beam FTIR does not obtain transmittance or absorbance IR spectra in real time. A typical operating procedure is described as follows:

1. A background spectrum is collected. The background spectrum includes the contribution from any ambient water (two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1}) and carbon dioxide (doublet at 2360 cm^{-1} and sharp peak at 667 cm^{-1}).

2. Next, a single-beam sample spectrum is collected. It contains absorption bands from the sample and the background (air or solvent).

3. The ratio of the single-beam sample spectrum against the single beam background spectrum results in a spectrum of the sample [12].

4.2 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) is an analytical technique in which a sample and a reference are subjected to a temperature program and where differences in heat capacity or heat of transitions are measured. Therefore, it is part of the group of analytical techniques called Thermal Analysis.

The aim of Differential Scanning Calorimetry experiment is to keep the sample and a reference (at constant pressure) at the same temperature throughout a temperature program. During the experiment the heat flow (heat transferred to or from the sample and the reference) is measured [14].

The main heater heats the sample and the reference equally and at a rate slightly less than the preset heating rate. Individual sample and reference heaters add heat to maintain the preset heating rate. The difference in energy to individual heaters is the heat flow plotted in the thermogram [15].

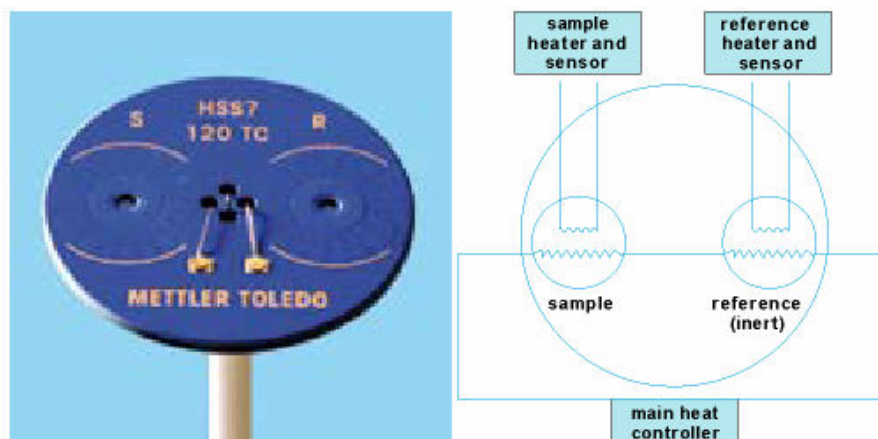


Figure 11: Diagram of heating and temperature sensing units for differential scanning calorimetry.

4.2.1 Melting and recrystallization

During the heating the sample will begin to melt. But to keep the temperature of the sample and reference the same, more heat is needed for the sample. In a plot of heat flow against temperature an endothermic peak (increase of heat flow) will become visible. An exothermic peak (decrease of heat flow) will appear when solidification occurs analogously.

4.2.2 Melting point

A first order transition is characterized by its baseline and the peak. In such a curve there are a couple of characteristic temperatures: the beginning of melting, the peak temperature and the return to the baseline. And none of these is the same as the melting point. To determine the melting point, one has to extrapolate the baseline and the left tangent of the temperature peak.

4.2.3 Glass transition

Glass transitions of polymers can also be determined by DSC. Below the glass transition temperature T_g the sample is amorphous. At higher temperatures the molecules have enough energy to become crystalline. The heat capacity increases when you go from below to above the T_g . In a plot of heat flow against temperature (with constant heating rate) this is visible as an increase in the baseline.

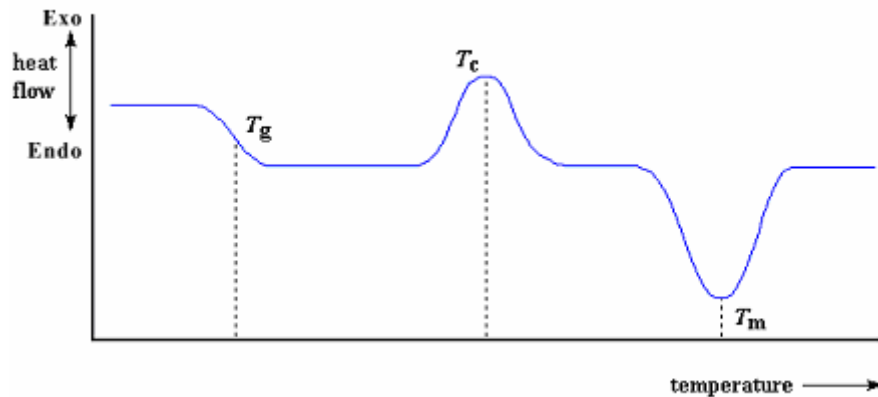


Figure 12: A standard features of output for a polymer from a DSC machine (T_g - glass transition temperature, T_c - crystallization temperature, T_m - melting temperature)

This transition takes time, so in a plot of heat flow against temperature (with constant heating rate) the increase of the baseline is spread over a temperature range. For the glass transition temperature the middle of the incline is chosen [14].

4.3 X-Ray diffraction

X-ray diffraction (XRD) is the traditional and effective method of determining 3D structures in the solid state.

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength x-rays are used. Because the wavelength of x-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure [16].

Diffraction effects are observed when electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the wavelength of the radia-

tion. The inter-atomic distances in crystals and molecules amount to 0.15–0.4 nm correspond to these wavelengths.

Diffraction angle is given by Bragg's equation (shown in Fig. 13) where n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and ϑ is the angle between the incident ray and the scattering planes [17].

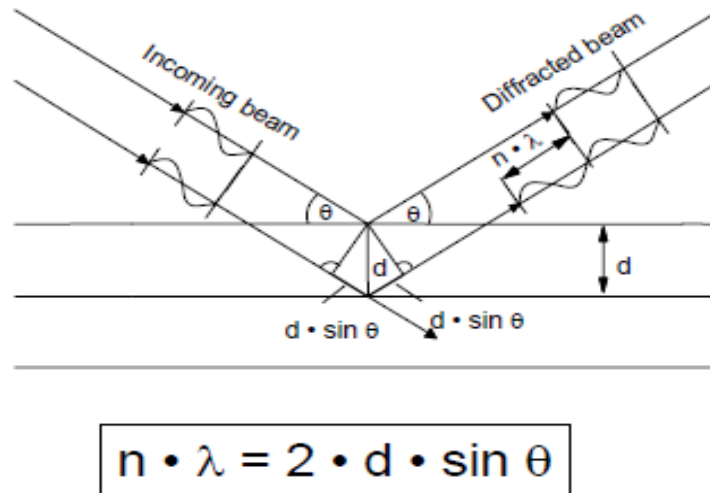


Figure 13: Scheme of X-ray diffraction and Bragg's equation definition [18]

XRD can be used to determine phase composition of sample where phase analysis gives relative amounts of phases in a mixture by referencing the relative peak intensities. Then is XRD used for determine unit cell lattice parameters, orientation, residual strain, crystal structure and crystallinity [19].

4.4 Mechanical properties

Today there are exist many methods to test mechanical properties of polymeric materials like a tensile, tear, shear, flexural, impact, compression tests and others. Tensile test belong to most widely used.

4.4.1 Tensile tests

Tensile tests are performed for several reasons. The results of tensile tests are used for comparison of mechanical properties of solid materials. Tensile tests are also useful for determination of mechanical properties of foils.

Foils are elongated and force necessary to maintenance of constant elongation is measured. End of test is presented by rupture of the sample. Resulting diagram of tensile test is shown in Fig. 14. Initially we find a viscoelastic, time-dependent, response that is considered to be fully reversible. For small loads the material behaviour is linear viscoelastic. From this part of diagram the Young modulus is calculated. With increasing load the behaviour becomes progressively nonlinear. At the yield point the deformation becomes irreversible and plastic flow occurs. End of test is presented by rupture of sample.

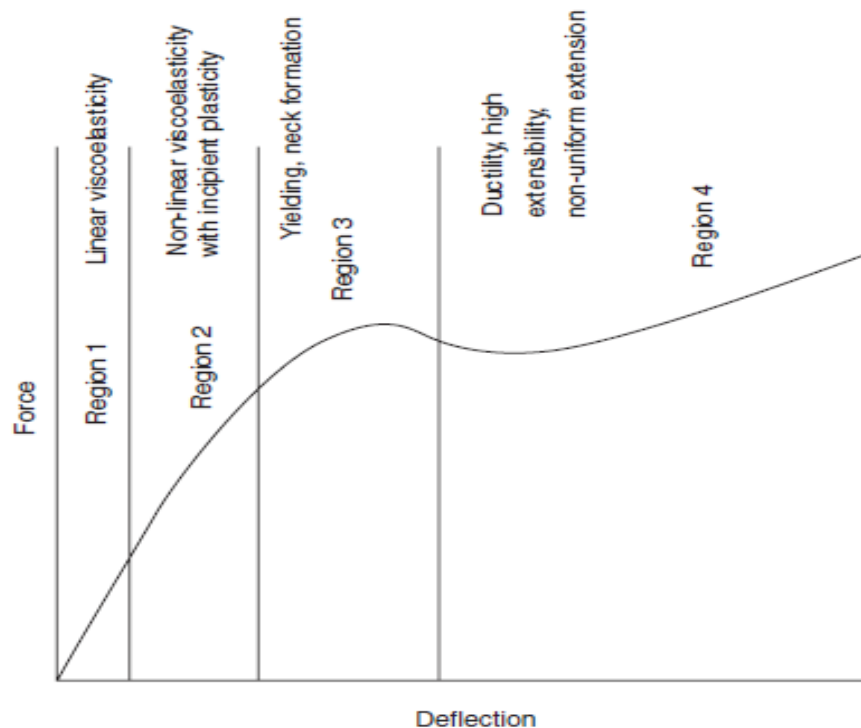


Figure 14: Tensile test diagram for polymeric material

The typical tensile specimen is shown in Fig. 15. It has enlarged ends or shoulders for gripping. The important part of the specimen is the gage section. The cross-sectional area of the gage section is reduced relative to that of the remainder of the specimen so that deformation and failure will be localized in this region.

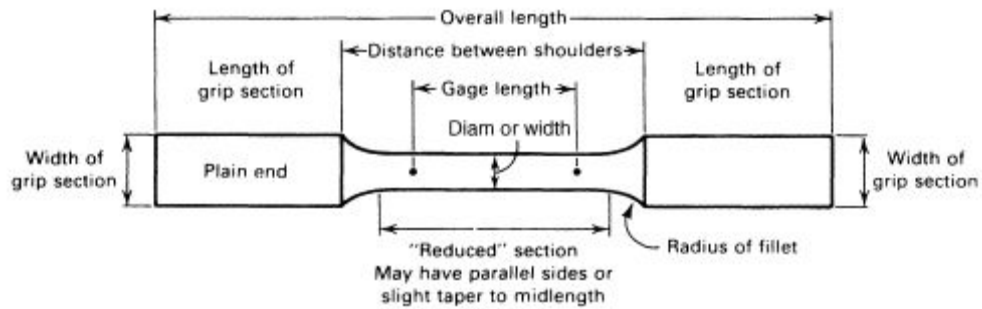


Figure 15: Typical tensile specimen, showing a reduced gage section and enlarged shoulders

The gage length is the region over which measurements are made and is centered within the reduced section. The distances between the ends of the gage section and the shoulders should be great enough so that the larger ends do not constrain deformation within the gage section, and the gage length should be great relative to its diameter. Otherwise, the stress state will be more complex than simple tension.

Tensile specimens must be without cracks and cells in the material. These defects influence results of tensile test. In these defects happens to decrease of strength of sample is ruptured early[20].

4.5 Reflectance spectrophotometry and colorimetry

Color is the human eye's perception of reflected radiation in the visible region of the electromagnetic spectrum (400–700 nm).

One of the most objective ways to measure color is to use diffuse-reflected spectrophotometry. Light reflected from the material is collected in an integration sphere, normalized to the source light of the reflectance, and calibrated with the measurement of a pure white standard (100% reflection) and a black box (zero reflection) over the entire wavelength spectrum of visible light [21].

For comparison of color difference CIELAB color scale is used. In a uniform color scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted. The CIELAB color space is organized in a cube form. The L^* axis runs from top to bottom. The maximum for L^* is 100, which represents a perfect

reflecting diffuser. The minimum for L^* is zero, which represents black. The a^* and b^* axes have no specific numerical limits. Positive a^* is red. Negative a^* is green. Positive b^* is yellow. Negative b^* is blue. Below is a diagram representing the CIELAB color space (see Fig 16).

There are used delta values associated with this color scale. ΔL^* , Δa^* , and Δb^* indicate how much a standard and sample differ from one another in L^* , a^* , and b^* . These delta values are often used for quality control or formula adjustment [22].

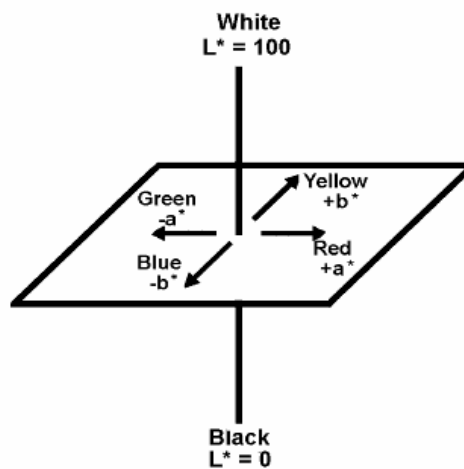


Figure 16: The CIELAB color system diagram

A light source is a physical emitter of radiation (i.e., candle, lamp, or sunlight) that can be characterized numerically by a spectral power distribution curve of power versus wavelength. For each light source, the wavelength tells us where light energy is present. The relative energy values (power) indicate how much energy is present at a particular wavelength.

The Commission Internationale de L'Eclairage (CIE) has codified the spectral power distributions of different types of white light sources and called them illuminants. An illuminant is a set of numbers (relative energy versus wavelength) that represents the spectral quality of a type of white light source and is used in the calculation of color measurements in colorimetric software. The choice of illuminant is independent of the instrument lamp. The most commonly used daylight illuminant norm is D_{65} representing daylight corresponds roughly to a mid-day sun in Western Europe/Northern Europe. Correlated

colour temperature of D_{65} is approximately 6504 K. D_{65} is used with two standard observers defined by CIE: the 2° or 10° observers [23].

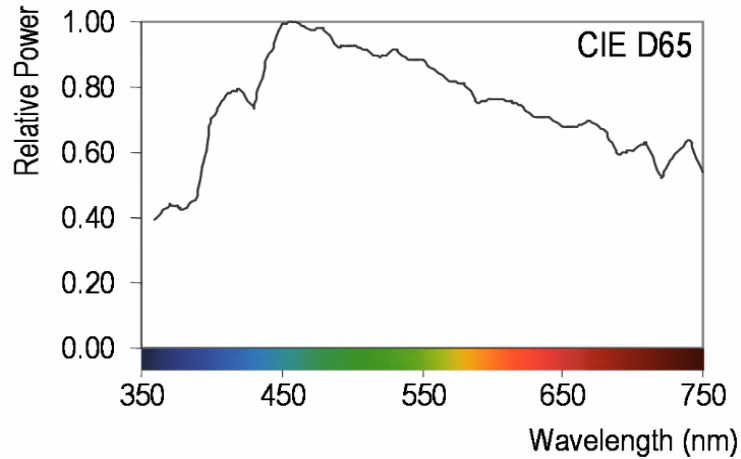


Figure 17: Spectral power distribution of D65.

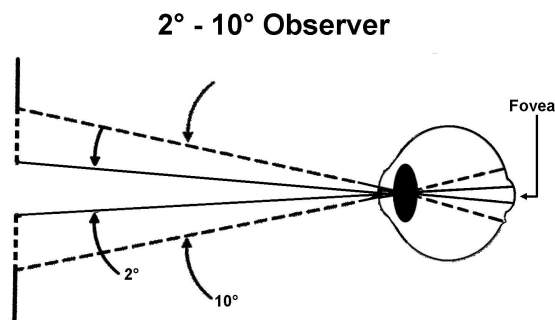


Figure 18: 2° and 10° observer difference

Yellowness index

Yellowness Index is a number calculated from spectrophotometric data that describes the change in color of a tested sample from clear or white toward yellow. This test is most commonly used to evaluate color changes in a material caused by real or simulated outdoor exposure. Yellowness is associated with scorching, soiling, and general product degradation by light, chemical exposure, and processing [24].

II. EXPERIMENTAL PART

5 ANALYSING METHOD AND DEVICES

Commercially produced polyethylene foils, loaded by extreme weather conditions during the real usage, mainly direct sun light (UV radiation), high air humidity and influence of chemical agents, were chosen for experiments. Selected PE foils are originally intended for usage in glasshouses, where foils are under direct sunlight filtered by glass and permanent high level of air humidity and increased temperature. These conditions are supplemented by chemical treatment in form of fertilizing and watering.



Figure 19: Tested PE foil

5.1 Sample preparation

Agriculture plastic foil of average thickness of 70 μm based on low density polyethylene was used for the investigation of the influence of commercially available nutrient agents on the kinetic of physical aging evoked by photodegradation.

Foil samples were cut into the rectangle form with dimensions of 150x45 mm and fixed on holders shown in Fig. 21.

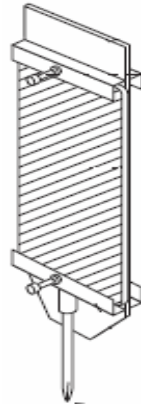


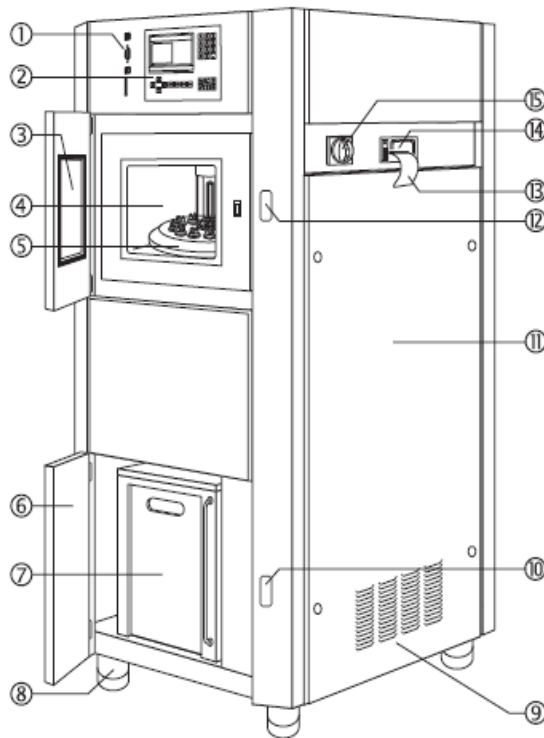
Figure 20: Sample holder

5.2 Accelerated ageing

Details of experimental setup employed for accelerated ageing of tested foils are given below.

5.2.1 Xenotest

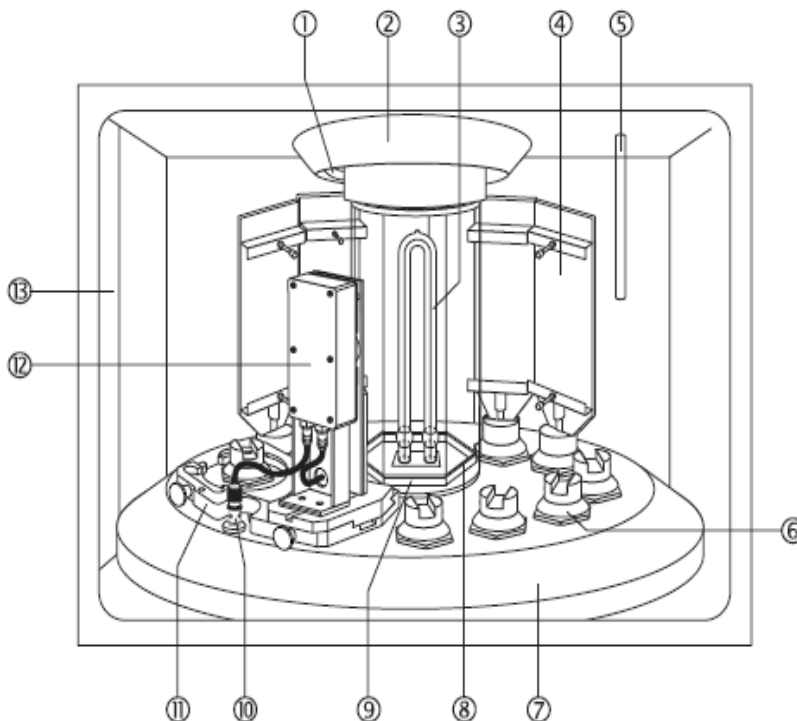
Xenotest Alpha+ (Atlas Material Testing Technology GmbH, Germany), universal weathering instrument, providing reproducible and repeatable test results of lightfastness using an air-cooled xenon arc light source was employed as a mean of accelerated weathering. For the weathering simulation purposes humidity conditions of 80 RH and chamber, and black standard temperature of 48, and 60 °C, respectively were chosen.



Atlas - Xenotest Alpha+ arrangement:

1. Communication ports
2. Operating panel
3. Test chamber door
4. Test chamber with rotating system and irradiation unit
5. Rotating system with sample holder bracket
6. Door to water supply system
7. Reservoir for treated water
8. Height-adjustable stand
9. Air inlet opening for lamp cooling and cooling of electrical components
10. Water supply system door release
11. Door to electrical supply unit
12. Test chamber door release
13. Print output
14. Optional printer for test data output
15. Main switch

Figure 21: Atlas Xenotest Alpha



1. Misting wand for misting samples
2. Air duct for air supply into test chamber
3. Xenon lamp for irradiating material samples
4. Sample holder for holding samples
5. Integral sensor for measuring test chamber temperature and relative humidity within test chamber
6. Sample holder retainer
7. Sample carousel for rotating samples around xenon lamp
8. Filter cartridge for creating specific light
9. Exterior cylinder
10. Socket for XENOSENSIV sensor
11. Sensor bracket for holding 2 sensors
12. XENOSENSIV sensor
13. Exhaust air opening for removing the heated test chamber air

Figure 22: Atlas Xenotest Alpha+ testing chambre

5.2.2 Chemical treatment

For the study of chemical effects of fertilizers on accelerated ageing of agriculture foil commercially accessible nutrient supplements: BN Nutri Nova A, BN Nutri Nova B, BN PH-, BN BioRoots, BN TML, BN-Zym, BN X-cel produced by Bio Nova (Netherlands) were selected.

Baths of nutrient agents were prepared according to their function of plants growing and were divided into four groups as given further. From each group were prepared two concentrations. First one corresponds to producer's instructions and second one exceeds ten times the recommended dosage.

Group A: basic nutrition for artificial substrates

BN Nutri Nova A

This product contains 7.5% NO₃; 0.7% NH₄; 10.6% CaO; 0.04% Fe (chelated).

This fertilizer is recommended with Nutri Nova B product.

BN Nutri Nova B

This product contains 3.5% NO₃; 4.7% P₂O₅; 5.5% K₂O; 1.0% MgO; 4.6% SO₄; 0,01% Mn; <0.01% B; <0.01% Cu; 0.2% Si. (Mn, B, Cu, Si are chelated).

BN Nutri Nova A+B together makes two component full mineral fertilizer with food grade ingredients for cultivating on artificial substrates such as rockwool slabs, polyurethane slabs

Group B: regulation pH

BN PH-

This product consists of 24,5% phosphoric-acid and it is intended for regulation of pH.

Group C: roots stimulators and plant stimulators

BN BioRoots stimulator

Stimulator consists of: 1.0% humic-acids; 3.0% ascophyllum nodusum; 3.0% ascorbin-acid (vitamin C); 0.3% thiamin (vitamin B1); 0.5 % myo-inositol; 1.0% L-glycine.

Stimulator improves the absorption of oxygen, quickens the root and cell development, and quickens the transport of ions. Stimulator consists kelp extract for healing of wounds and of chlorosis for increase the chlorophyll development - more root-hair development. Myo-inositol is there for the forming of cell walls and glycine for a better resistance and growth.

BN TML - The Missing Link

This product is composed of fulvic acid and colloidal minerals. Ultimate flower-booster stimulating the plant's natural defence system. The Missing Link consists of a great number of special trace elements that have become essential for the growth and flowering

Group D: growing stimulators

BN Zym

BN-ZYM is a natural bio-catalyst (process accelerator) based on specific enzymes. The main enzyme is cellulase, while pectinase and amylase are added to assist in breaking down all waste materials.

BN X-cel

BN X-cel is a biological growing and flowering stimulator and contains the following ingredients: various vitamins, natural growing and flowering stimulators, amino acids, bacteria, trace elements, enzymes, kelp and humic acids.

5.2.3 Time and ways of treatment

Prepared samples were treated in five various ways. Some samples were treated only by UV radiation (XUV). Other sets of samples were treated only by bathing at fertilizers from mentioned groups of fertilizers (Group A-D). Baths were prepared in two concentration (1 and 2) for determine of the influence of concentration of fertilizers. Finally, next samples were treated by combination of UV radiation and bathing at fertilizers.

Marking of samples corresponds to type (or combination) of treatment and it is shown in Table 1.

Table 1: Marking of samples

Group of fertilizers	concentration of fertilizes	UV treatment or without UV
A, B, C, D	1, 2	UV, ---

Times of chemical and UV treatment duration with corresponding radiation dosage per several cycles of ageing are shown at Table 2. One cycle includes two part of treatment, UV irradiation and bathing at fertilizers. Time data are divided in two groups according to concentrations: recommended (1) and ten times exceeded (2).

Table 2: Times of UV radiation and chemical treatment

	XUV		A1-D1	A2-D2
	UV time [hours]	radiation dosage [kJ/m ²]	Bath time [hours]	Bath time [hours]
1	35	3244	69	43
2	76	7153	117	85
3	121	11297	160	150
4	165	15401	229	194
5	208	19481	273	238
6	263	24658	320	306
7	287	26878	363	354
8	334	31275	410	401

5.3 Ageing evaluation methods

5.3.1 Infrared spectroscopy

FT-IR spectroscopy analysis - ATR method (Avatar 320, Thermo Nicolet, USA) was applied to determine chemical changes of the macromolecule. The whole mid-infrared spectrum (4000 – 550 cm^{-1}) was measured. The spectra were taken as an average of 32 scans.

5.3.2 Differential scanning calorimetry

Melting (T_m) and crystallization (T_c) temperatures of the un/treated plastic foil were determined using DSC 1 apparatus (Mettler-Toledo Inc., Switzerland) equipped with auto-sampler and intracooler. The testing temperature range from 25°C to 140 °C was used with a ramp rate of 20°C/min in the first scan in order to increase sensitivity of measurements, while the rate of 5 °C was chosen for the second temperature ramp in order to increase accuracy of the measurement.

5.3.3 X-Ray diffraction

X-ray diffraction was utilized in order to determine changes in crystallinity morphology structure of tested foils employing X'Pert PRO diffractometer (PANalytical B.V., Netherlands). Crystallinity content was evaluated using High Score software.

5.3.4 Mechanical properties

Tensile tests with speed of 100 mm/min, carried out using TESTOMETRIC M350-5CT universal testing machine (Testometric Company Ltd., UK) on the samples of the rectangular shape with the size of 8x45 mm approximately and initial grip length of 24 mm, were applied with the purpose to determine influence of accelerated aging on Young modulus, tensile strength and elongation at break.

5.3.5 Spectrophotometry

Colour changes were determined by using UltraScan® PRO spectrophotometer (Hunter Associates Laboratory Inc, USA) with standard D_{65} illuminant source and 10° observer.

From spectrophotometric measurement Δ values of L^* a^* b^* coordinates were used for Yellow index (YI) calculation. Samples were measured in opposite to white standard supplied to spectrophotometer. Yellow index were evaluated by spectrophotometer control software Easy MatchQ.

6 RESULTS

6.1 Infrared spectroscopy

Evaluation of photodegradation was determined via change of carbonyl peak at 1711 cm^{-1} . Experimental data values are represented in Fig 23. in the form of carbonyl index (CI), calculated through Equation 2 as a ratio of peak areas at interval $1590\text{-}1803\text{ cm}^{-1}$ and $2800\text{-}2866\text{ cm}^{-1}$ determined by the help of Omnic software originally supplied with IR spectrometr.

$$CI = \frac{a_{1711}}{a_{2847}} \quad \text{Eq. 2}$$

where is:

a_{1711} : peak area at interval $1590\text{-}1803\text{ cm}^{-1}$

a_{2847} : peak area at interval $2800\text{-}2866\text{ cm}^{-1}$

While the effect of nutrient agents on carbonyl index for tested PE foils was visible in the case of combination of UV treatment with chemical bathing, the evolution of CI for samples treated by nutrient agents baths only (samples A1-D1 and A2-D2) did not show enough changes for qualification of the influence of selected fertilizers.

Evolution of carbonyl index vs. the ageing time for samples exposed to UV radiation only (XUV) and samples exposed to combination of UV radiation and chemical treatment is shown in Fig. 23. It is obvious from results, that majority of bathed samples show lower value of CI in comparison with XUV samples that indicate possible retarding effect of nutrient agents on photodegradation of foils during the ageing.

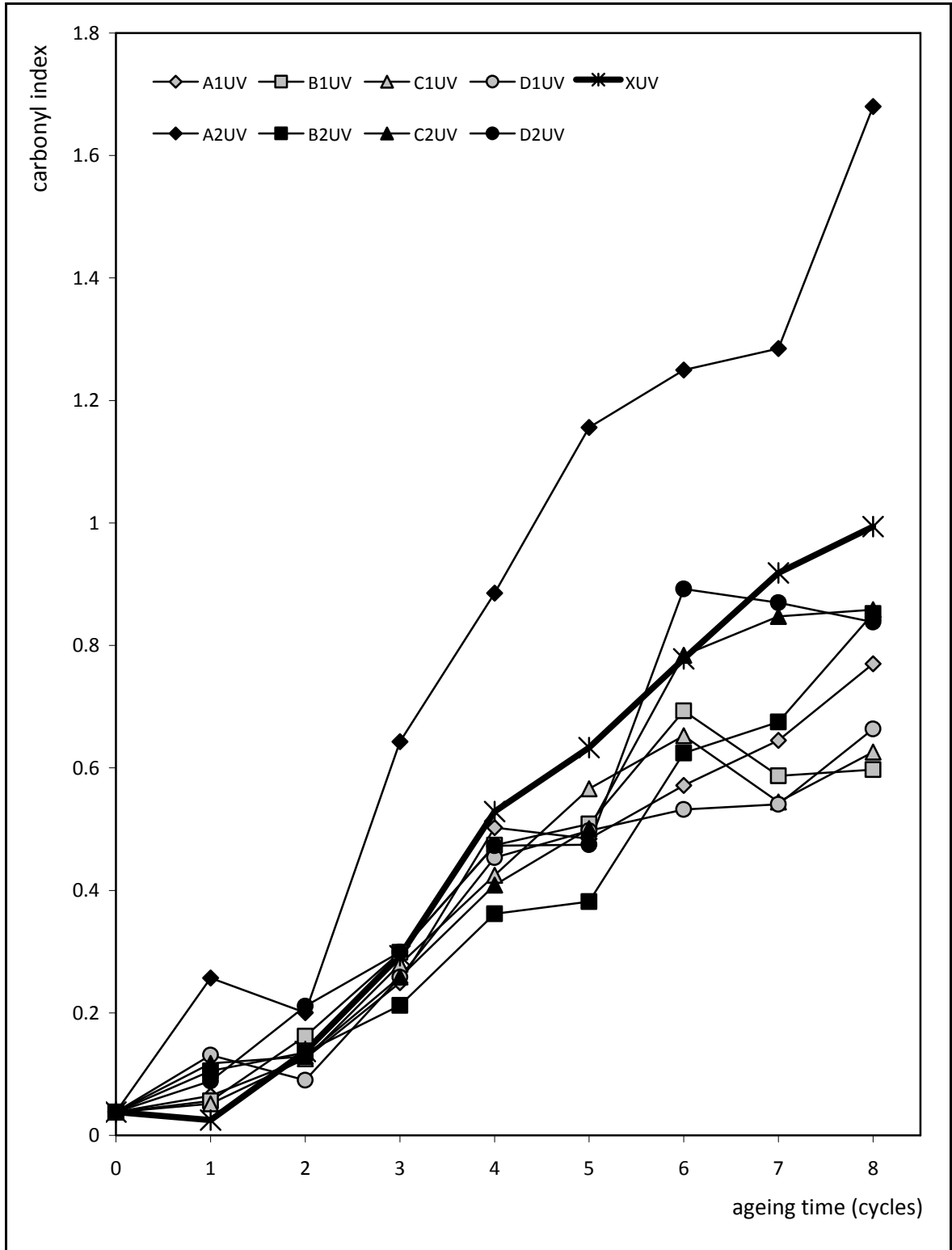


Figure 23: Time evolution of carbonyl index of samples exposed to UV radiation only (XUV) and samples exposed to combination of UV radiation with chemical treatment (in both concentrations)

Retarding effect of bathing is also visible in evolution of carbonyl index at appropriate segments of ageing cycles (alternating UV and chemical treatment), as it is presented in Figures 25 and 26, where decreases of CI on the curves in connection with alternating of foil treatment accompanying bathing are visible. In other words, there are lower values of carbonyl index after bathing compared to the previous UV part of cycle. Presented decreases of CI could be connected with chemical reaction between products of photo-degradation and components contained in fertilizers. Nevertheless, in spite of possible retarding effect of fertilizers, carbonyl index of samples treated by combination of UV and chemical treatment as well as samples treated by XUV grows up during the photodegradation.

Carbonyl index of samples treated by combination of UV irradiation and bathed at ten times higher fertilizer concentrations solution (A2UV, B2UV, C2UV, D2UV) comparing to samples A1UV, B1UV, C1UV, D1UV is higher. This dependence of CI on nutrient concentration is quite small in the case of B, C, D groups of fertilizers but strong influence of concentration on carbonyl index was determined for samples treated by group A (compare A1UV and A2UV in Fig. 23).

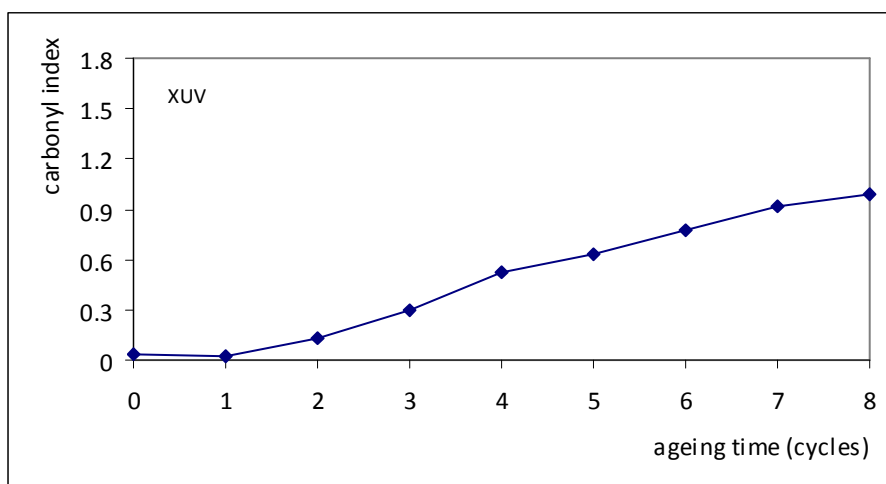


Figure 24: Evolution of carbonyl index for samples treated by UV radiation only (XUV)

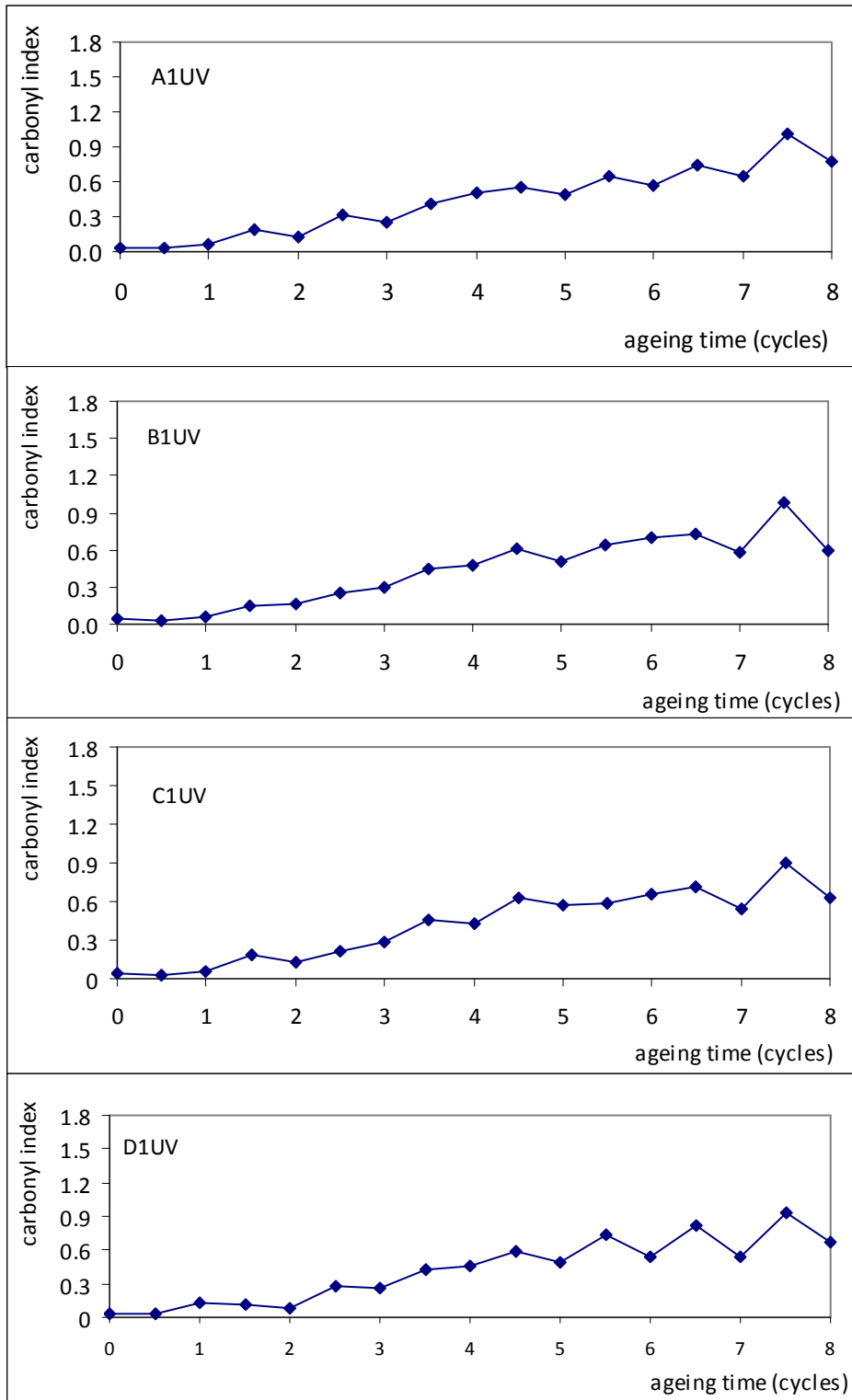


Figure 25: Time evolution of carbonyl index for samples A1UV, B1UV, C1UV, D1UV

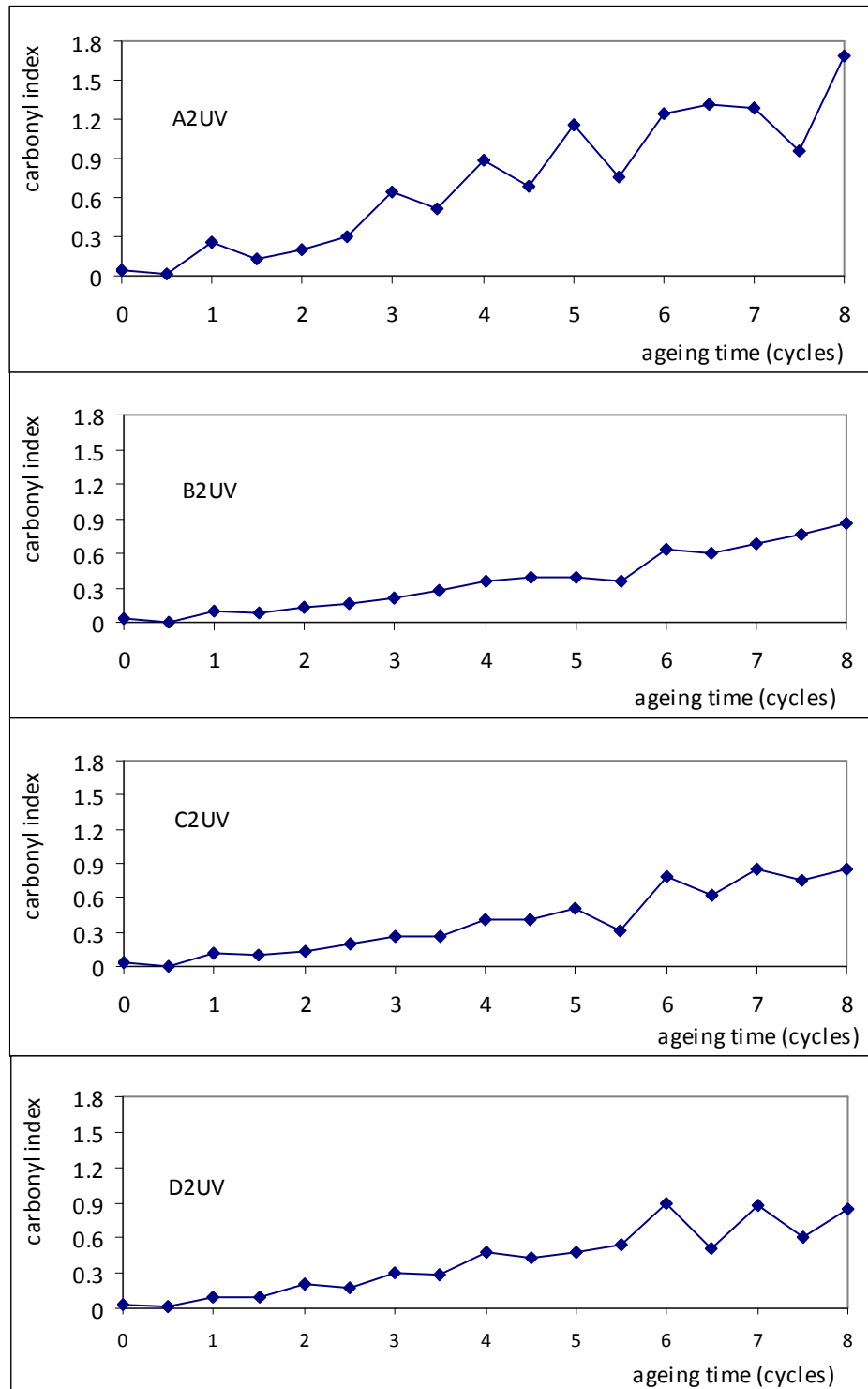


Figure 26: Time evolution of carbonyl index for samples A2UV, B2UV, C2UV, D2UV

6.2 Differential scanning calorimetry

The DSC analysis was employed in order to examine changes in thermal behaviour of tested PE foils. Temperature program consists of two heating/cooling scans between temperatures 25°C and 140°C was utilized. Ramp (heating/cooling) rate of 20°C/min was used in the first scan with the view of increase sensitivity to changes determination in foils, while 5°C/min was applied in the second scan improving resolution of observe changes in tested material.

Measuring of heat flow at first scan corresponding to structural changes of tested foils is presented in Figure 27. Major influence of photodegradation is proved by results of heat flow measuring of bathed only samples (unirradiated). In this case there is visible decrease of heat flow after first two bathing cycles, while there are no significant changes farther. Regarding irradiated samples it could be stated that, there is similar trend in thermal behaviour of the both types of samples - exposed to UV irradiation (XUV) and samples UV irradiated and bathed - increase of crystallinity follows initial decrease in beginning stage of ageing. It should be noted, that mentioned curve trends seems to be affected by chemical treatment, as heat flow grows up already after first ageing cycle in opposite to unbathed (XUV) samples where heat flow increase is not recognized until three cycles are repeated. Nevertheless differences between heat flow values revealed main influence of UV irradiation which is only partially affected by appropriate chemical treatment.

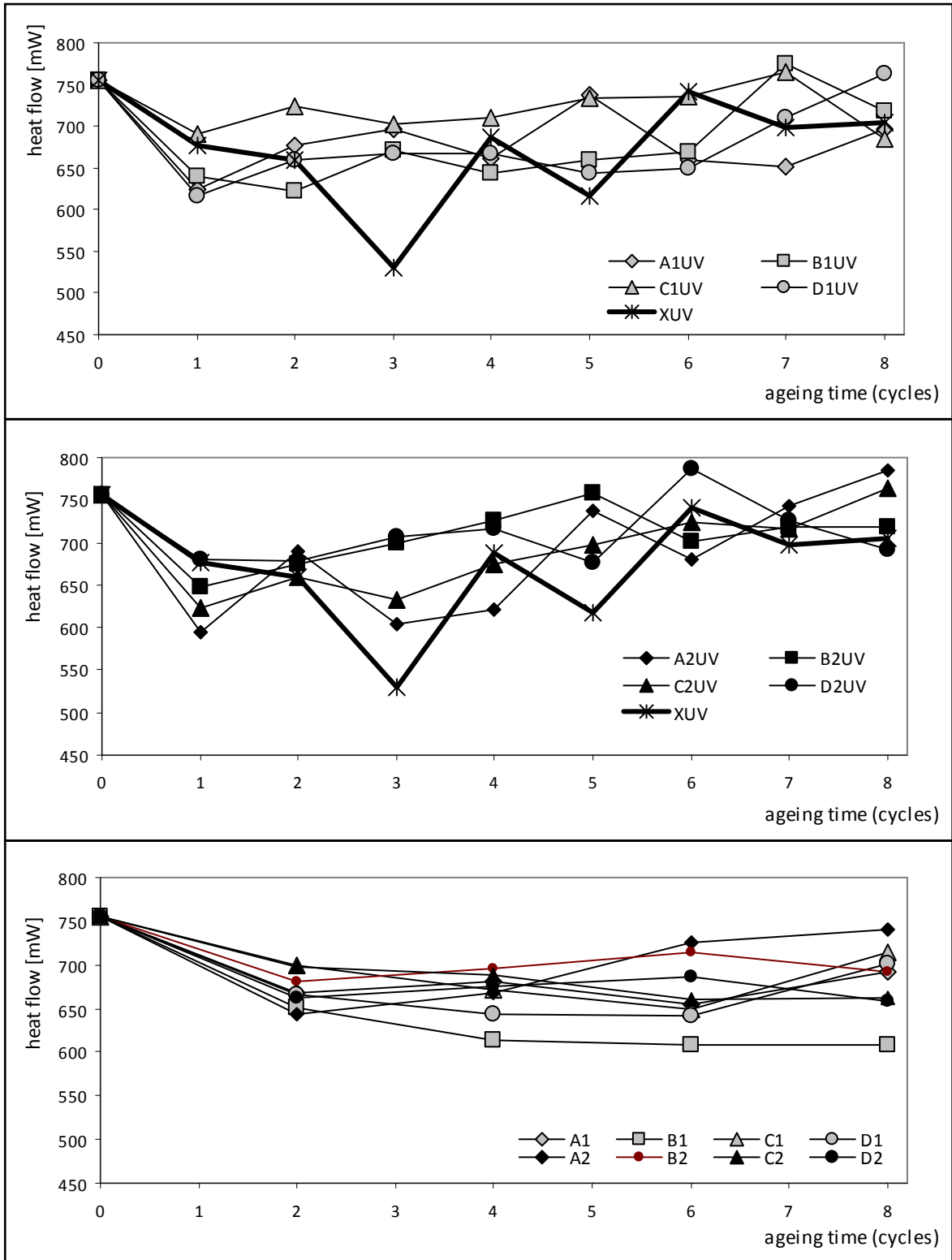


Figure 27: Heat flow at mW from first scan (first melting 20°C/min) for samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

Practically the same situation occurred after the second scan at ramping rate 5°C/min as it is visible in Figure 28. Second scan of UV irradiated samples is the similar as the first one but changes in structure of material comparing unbathed and bathed samples are more significant. Increasing value of heat flow of irradiated samples corresponds to expected increase of crystallinity as a consequence of (photo)degradation. The increase of crystallinity is connected with chain scission which produces higher amount of shorter chains that can crystallize more easily than longer ones.

Increase of crystallinity is supported by results shown in Figures 29 and 30 where crystallization temperatures of UV irradiated samples are presented. Increase in crystallization temperature of UV irradiated samples in the first scan at ramp rate 20°C/min could be connected with thermal annealing by increased temperature in UV chamber. Nevertheless this trend is visible also in the second scan at ramp rate 5°C/min that refer to supplementing effect of UV irradiation on material structure, since from measuring of crystallization temperature in the case of bathed samples without UV irradiation it is not evident any influence of chemical treatment (see Figures 29 and 30). First scan indicates increase of crystallization temperatures for all bathed (only) samples after first two ageing cycles, while this effect disappears in second scan.

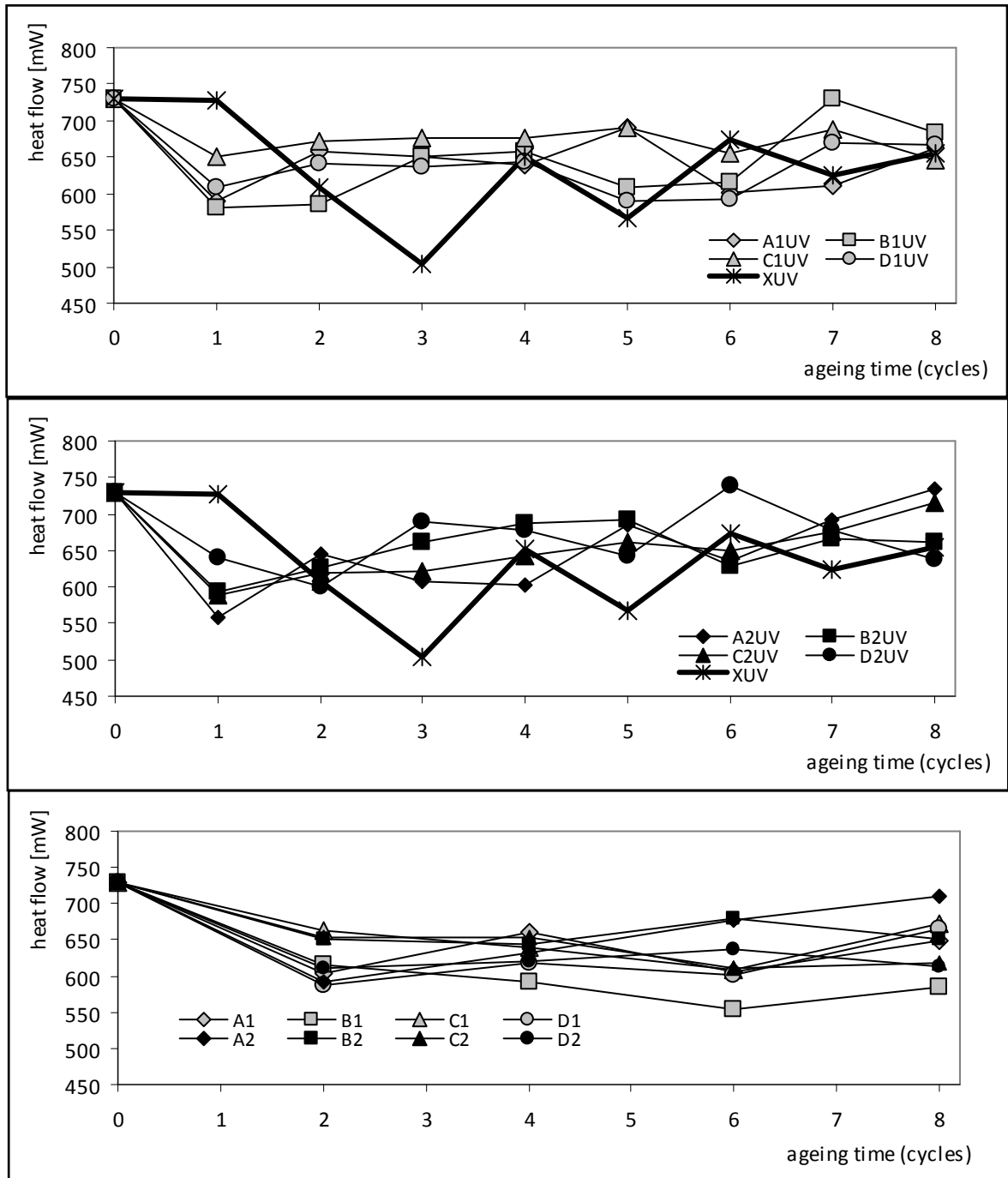


Figure 28: Heat flow at mW from second scan (first melting 5°C/min) for samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

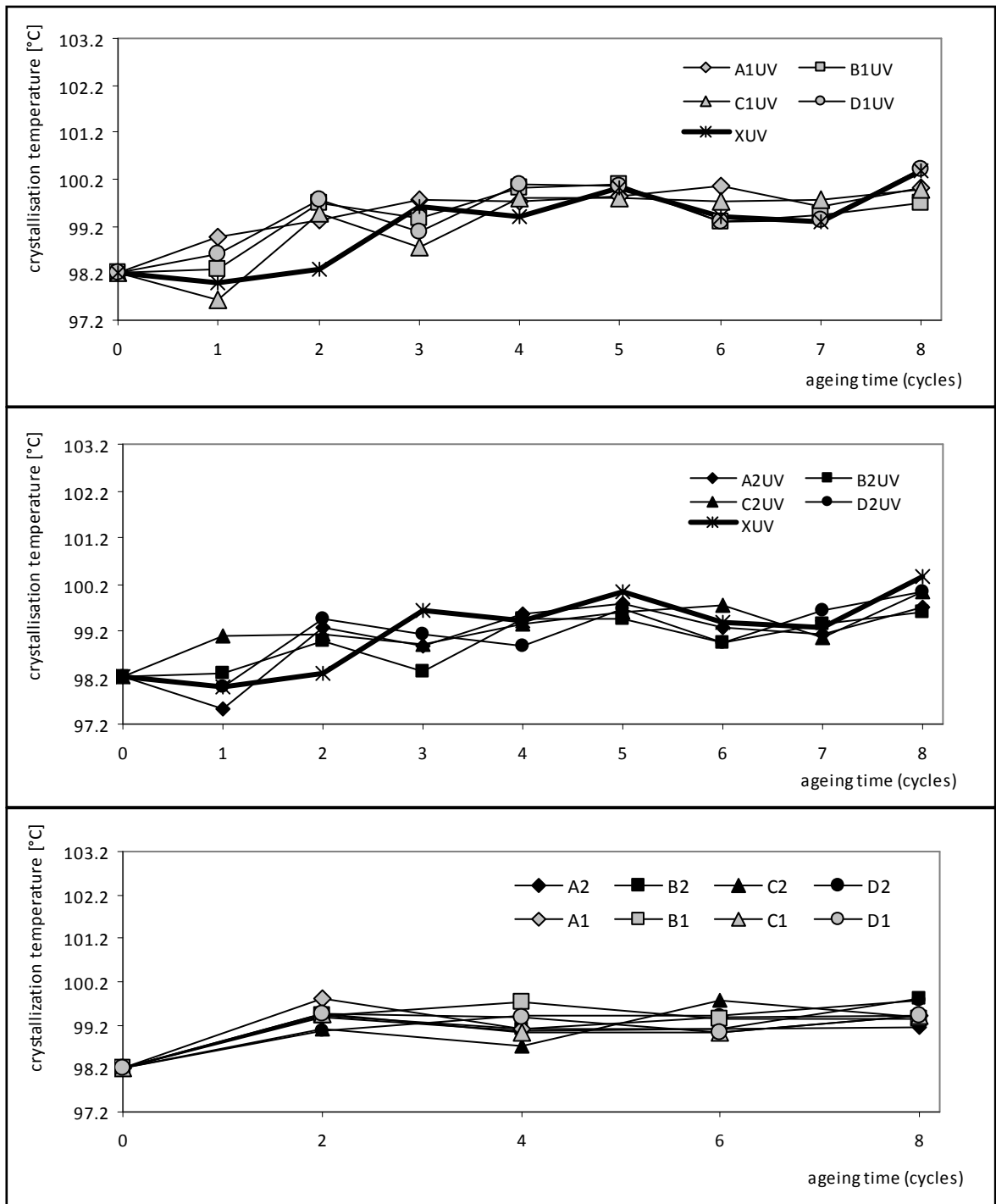


Figure 29: Crystallization temperature at cooling rate 20°C/min for samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

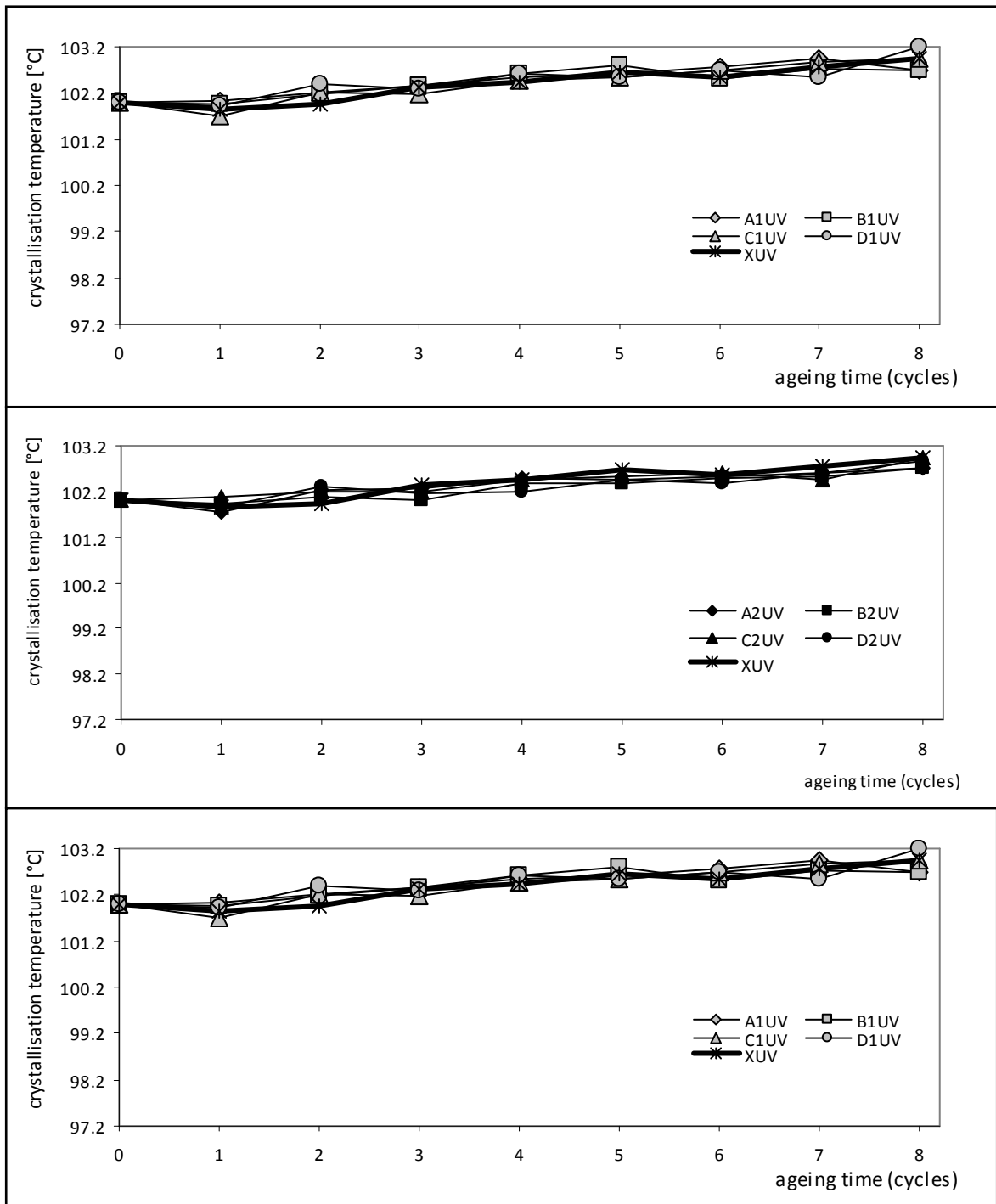


Figure 30: Crystallization temperature at cooling rate 5°C/min for samples of samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

6.3 X-Ray

X-ray diffraction was utilized mainly for determination of changes in crystallinity of samples during the accelerated ageing. Changes in crystallinity are connected with chain scission during the degradation as it was mentioned in previous chapter. X-ray spectra was measured in the 2-theta range from 10 to 45 degrees, while range of 10-26.5 degrees was employed for evaluation of crystallinity. This range includes two major peaks characteristic for polyethylene (21,35 and 23,8 degrees). For evaluation of crystallinity High Score software supplied with X'pert Pro Diffractometer was used. Calculated crystallinity of samples treated by UV irradiation only (XUV), bathing only, and combination of the both effects is summarized in Table 3 and Table 4.

Table 3: Crystallinity of samples treated by combination of UV irradiation and chemical treatment and samples UV irradiated only

cycles / crystall.	A1UV [%]	B1UV [%]	C1UV [%]	D1UV [%]	A2UV [%]	B2UV [%]	C2UV [%]	D2UV [%]	XUV [%]
0	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7
2	63.6	65.8	63.2	64.5	61.8	60.9	51.2	56.8	65.6
4	63.9	63.4	61.1	60.0	57.7	60.0	58.5	58.3	62.0
6	64.1	67.4	65.3	67.2	62.9	59.6	61.5	65.3	64.7
8	63.9	68.1	70.2	61.3	66.2	61.4	67.4	61.7	66.1

Table 4: Crystallinity of samples treated by chemical bathing

cycles / crystallinity	A1 [%]	B1 [%]	C1 [%]	D1 [%]	A2 [%]	B2 [%]	C2 [%]	D2 [%]
0	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7
2	66.5	71.4	73.4	76.3	60.6	64.6	66.7	65.2
4	71.7	69.0	70.9	80.2	63.9	62.2	67.1	69.8
6	73.5	67.0	73.2	73.7	60.2	67.6	68.7	65.6
8	69.3	71.1	71.8	71.8	61.0	62.9	68.5	67.6

As it is clear from the changes of crystallinity of UV irradiated samples (depicted in Figure 31), the same trend as it was observed in DSC analysis was described. Namely, development of crystallinity shows the same decrease and following increase similarly to evolution of heat flow values determined during the melting of samples (see Figures 27-28).

The effect of concentration of bath on samples exposed to combination of UV irradiation and chemical treatment was observable mainly during the first four cycles of ageing, when samples treated by recommended concentration reaches higher values of crystallinity in comparison with the samples treated using highly concentrated baths.

It is noticeable that changes in crystallinity of samples bathed only also correspond to results of DSC analysis. Crystallinity did not show any visible changes in trend and oscillate around starting value of about 70%.

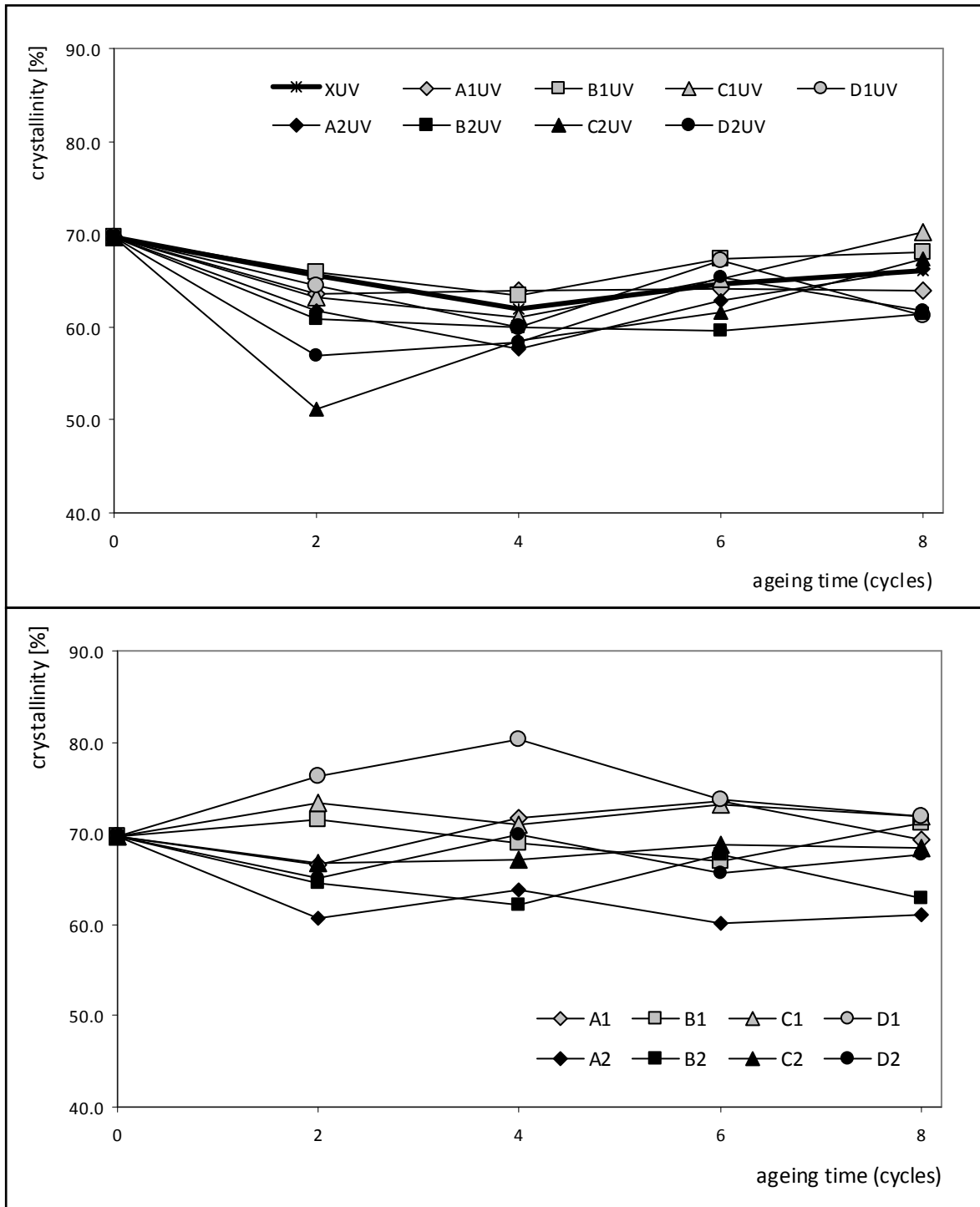


Figure 31: Crystallinity of samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

6.4 Mechanical properties

From results of tensile tests, presented in Fig. 32, it is obvious that there was no significant influence of bathing in fertilizers solution on elongation at the break. On the other hand, it is evident that the main effect on elongation at break of tested material had UV treatment. Although samples treated by combination of UV irradiation and bathing showed after two ageing cycles rather higher values of elongation than samples exposed to UV irradiation only, this effect was diminished in the following time of degradation. Increasing of drawability within the first two cycles of ageing could be connected with retarding effect of fertilizer baths on photodegradation already mentioned in previous chapters.

Moreover, significant decline of elongation from 300 to 80% after four cycles should be highlighted. During the rest of fourth ageing cycles elongation at break only slowly decrease from 80% to end value of about 40%. Fact that major influence on tensile properties of samples had UV irradiation is promoted by results of elongation at break for samples only bathed, while it could be stated that influence of bathing (without UV irradiation) on elongation at the break of samples was practically insignificant. During the ageing the values of elongation at break oscillated about original value without any dependency.

Similar founding was described also for the case of Young modulus of samples treated by bathing only (shown in Figure 33). Contrariwise another situation was documented for Young modulus of samples treated by UV irradiation. Obviously, Young modulus of UV irradiated samples seemed to be influenced by chemical treatment, since samples treated by combination of UV irradiation and bathing showed the same decrease and following increase of Young modulus like XUV samples during first four cycles of ageing but during the last four cycles Young modulus of XUV samples decayed in contrast to bathed samples which maintained their Young modulus to the end of test.

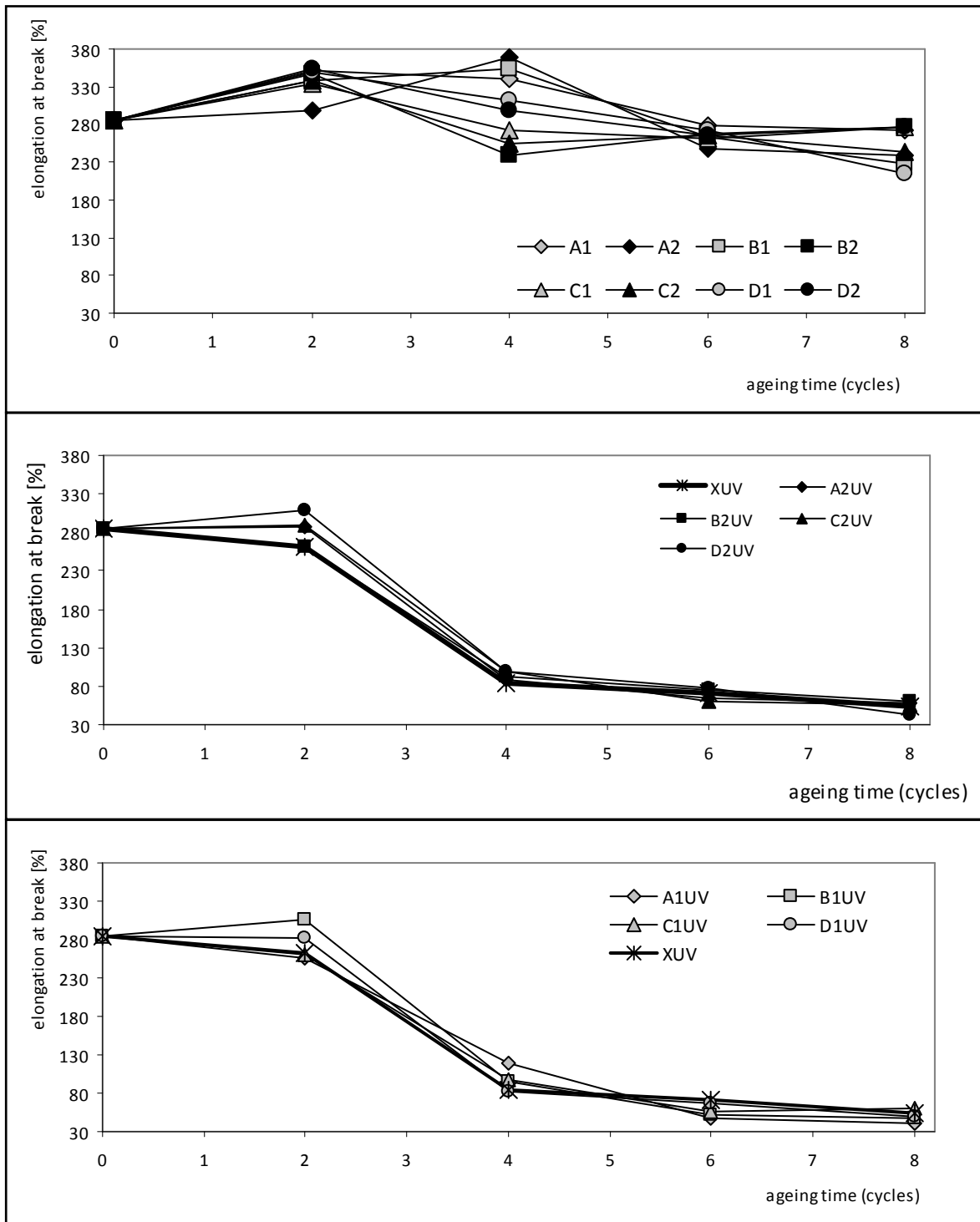


Figure 32: Elongation at the break for samples of samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

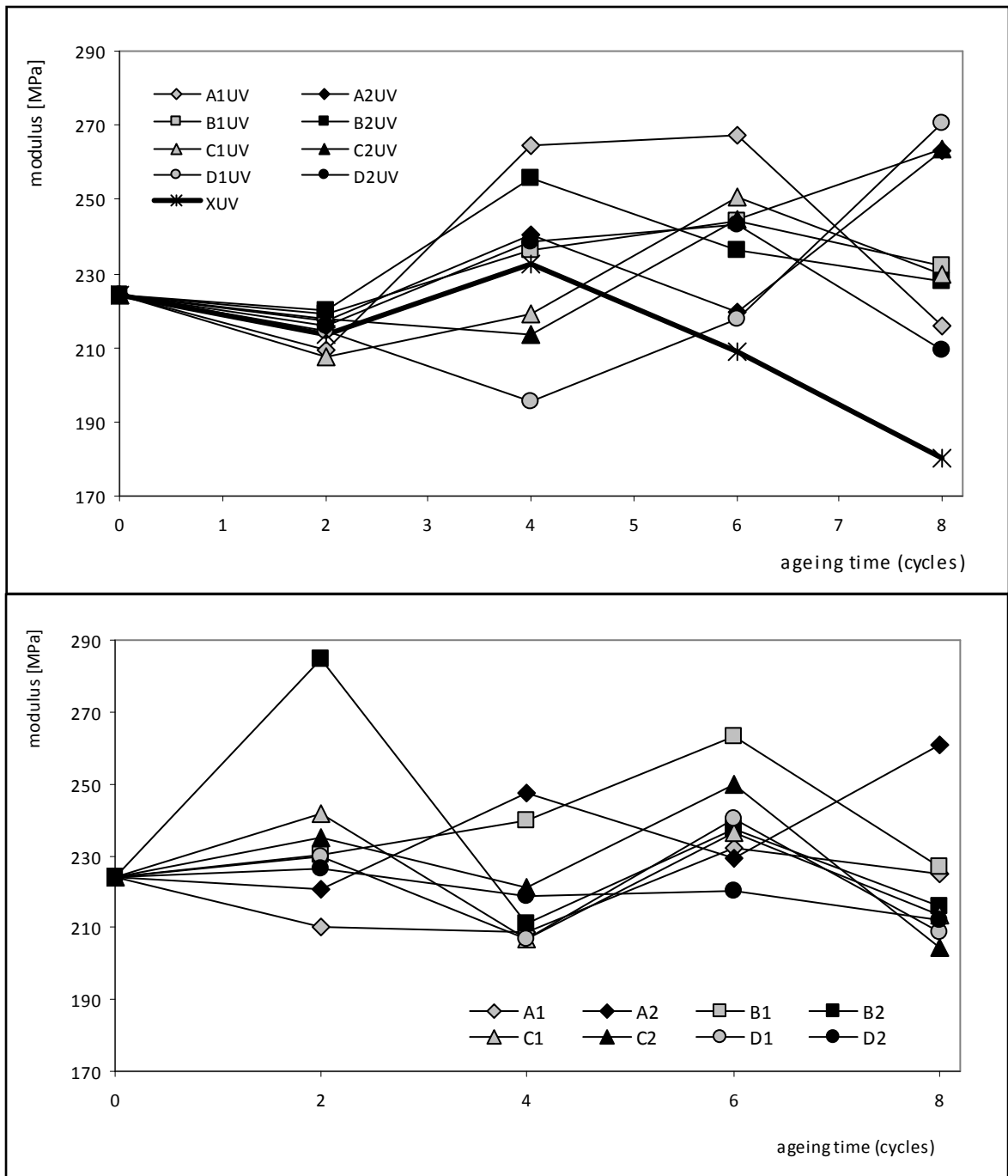


Figure 33: Modulus for samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

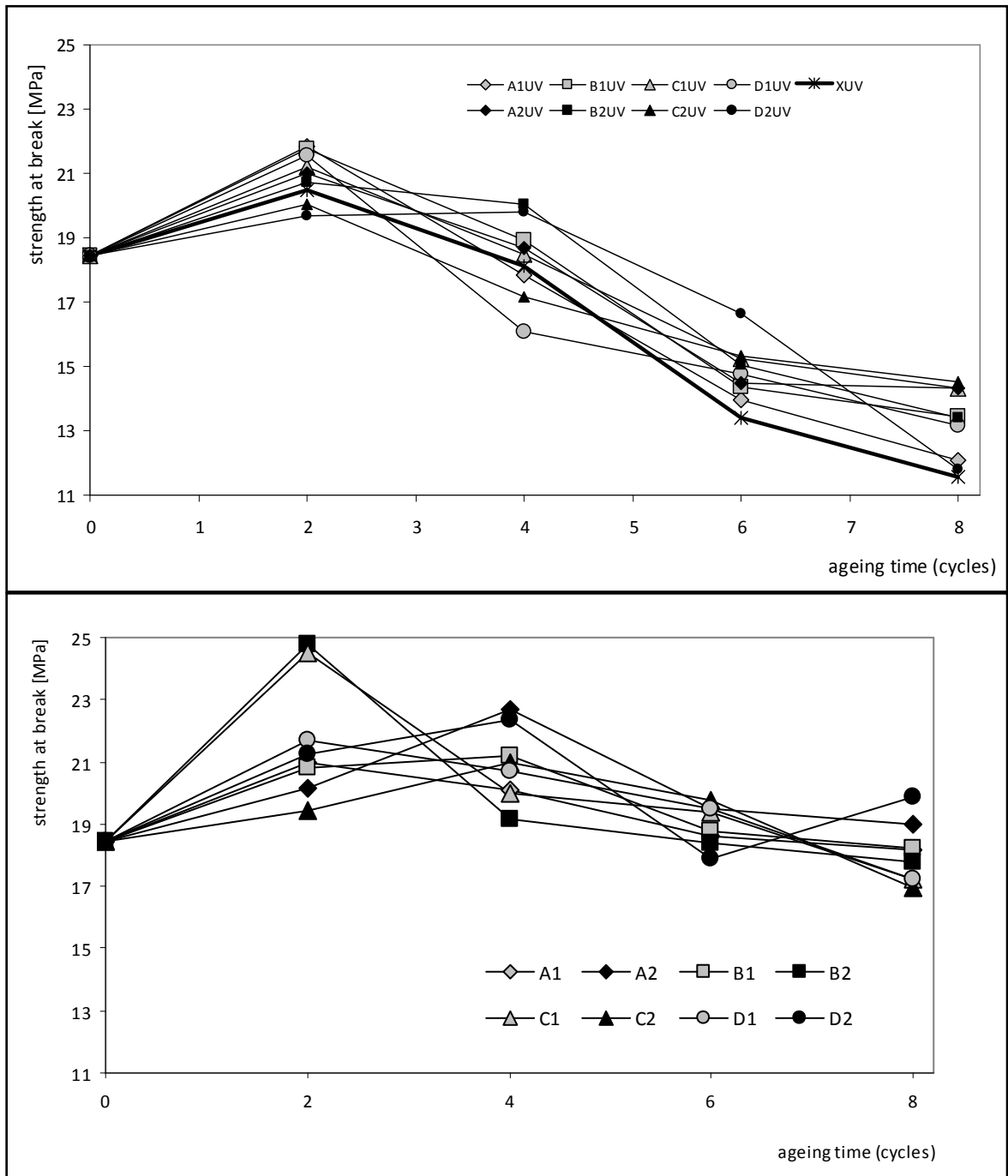


Figure 34: Strength at break for samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

Similarly in the case of strength at break the samples treated by UV radiation showed the greatest decline, which is retarded in the case of samples treated by combination of both ageing procedures (see Figure 34). As it is clear from the figure, increase of strength in first two cycles is obtained for all tested samples, which is followed by decrease during the rest of ageing. Additionally, it could be stated that the same curve profile - increase followed by decline - was determined for strength of samples bathed only. Nevertheless, this tendency is not intensive as in the case of irradiated samples.

6.5 Yellowness index

Changes in optical properties of aged samples, described in the form of Yellowness index, are shown in Figure 35, where comparison UV irradiated samples, bathed samples and samples treated by both procedures is presented.

From presented results, it is clear that both unbathed UV irradiated samples (XUV) and samples treated by combination of UV irradiation and bathing show variation in increase of Yellowness index in opposite to bathed samples only. Mentioned alternation could be caused by irregular change of optical properties reached at sample surface during the UV and chemical treatment, since indication of multicolour maps were observed on some of tested samples, and it could be moreover simultaneously magnified by the fact that optical measurement were carried out on the small fraction of sample only. While, the evolution of YI is uniform in the case of bathed samples, its increment is insignificant and hardly distinguishable for naked eye.

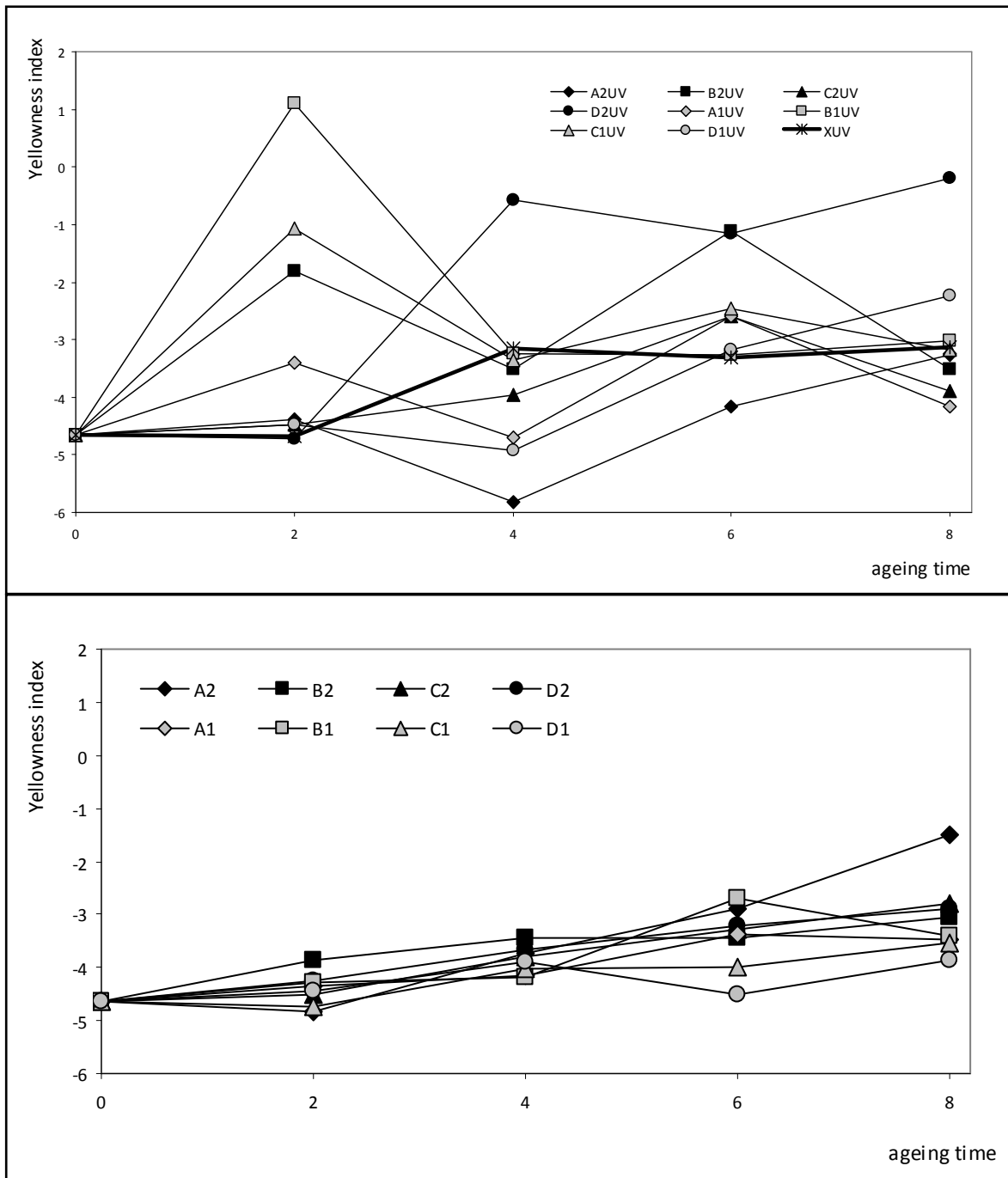


Figure 35: Yellow index of samples treated by UV radiation and fertilizer baths at normal concentration, treated by UV radiation and fertilizer baths at tenfold concentration (both in comparison with samples UV irradiated only), and for samples treated by fertilizer baths only at both concentrations

CONCLUSION

Polyethylene mulch foils are exposed to weather conditions all of their lifetime which can be simulated by method of accelerated ageing. Accelerated ageing studies usually do not include influence of chemicals so the aim of this work was evaluate the influence of fertilizers on photodegradation process of LDPE based mulch foil. Accelerated physical/chemical aging of studied foil was performed utilizing Xenotest apparatus in combination with baths in selected commercially available fertilizers.

From thermal analysis carried out by the mean of differential scanning calorimetry influence of chemical treatment on photodegradation process was determined. Obtained results indicated retardant effect of fertilizers on photodegradation kinetic and following changes in material structure namely during the beginning period of ageing. It should be highlighted that the most significant retarding effect of fertilizer bath on kinetic of UV ageing was however described via tensile testing. In spite of this fact all UV irradiated samples (even bathed ones) lost more than seventy percent of its mechanical performance during first half of chosen ageing time, while it was diminished by additional very fifteen percent tills the end of testing period. Even at that time all tested foils still held together, indications of samples destruction, as a small cracks and tendency to twist, were visible and more pronounced for irradiated samples. While significant colour changes were expected, mainly yellowing, these were not observed utilizing colourimetry measurements.

Even, thermal analysis and mechanical tests did not approve influence of fertilizers concentrations variation, this was confirmed through X-ray diffraction spectroscopy results. Noticeably concentration of fertilizers ten times higher than recommended one evoked higher inhibition potential to photodegradation process. The influence of concentration of fertilizer baths on retardant effect was moreover supported by results of infrared spectroscopy, where declines of carbonyl index of UV irradiated samples after bathing segments of ageing cycles were observed in comparison to unbathed samples presenting uniform increase of carbonyl groups in tested material during the ageing time only.

It was proved by performed experiments that even there are certain retardant effects of fertilizers on photodegradation, UV radiation is the main driving force of deterioration of tested LDPE based agriculture foils during the (accelerated) weathering.

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LIST OF ABBREVIATIONS

UV	Ultraviolet
PE	Polyethylene
LDPE	Third abbreviation meaning.
HDPE	High density polyethylene
UHMWPE	Ultra high molecular weight polyethylene
LLDPE	Linear low density polyethylen
IR	Infrared
$\bar{\nu}$	wavenumber
λ	wavelength
T	Transmittance
A	Absorbance
ATR	Attenuated Total Reflectance
FT-IR	Fourier transform infrared (spectroscopy)
DSC	Differential Scanning Calorimetry
T _g	Glass transition temperature
T _c	Crystallization temperature
T _m	Melting temperature
XRD	X-ray diffraction
d	the spacing between the planes in the atomic lattice
θ	angle between the incident ray and the scattering planes
CIE	The Commission Internationale de L'Eclairage
CIELAB	CIE (L*, a*, b*) color system
L*	CIE (L*, a*, b*) color system coordinate

a*	CIE (L*, a*, b*) color system coordinate
b*	CIE (L*, a*, b*) color system coordinate
D ₆₅	CIE standard illuminant
K	Kelvin
YI	Yellowness Index
BN	Bio Nova
XUV	sample UV irradiated only
CI	Carbonyl index

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