

AGEING OF POLYPROPYLENE

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jméno

ABSTRACT

This bachelor thesis is dedicated to ageing of polypropylene. The first part comprises the basic information about processing of polypropylene and its features. Special attention is focused on its polymorphism. The second section is devoted to the various ways of polypropylene degradation (biological, thermic, termooxidative and photooxidative). Whereas the photooxidative degradation is the most important, it is described intimately and the effect of morphology on the degradation process is discussed. The last part deals with the life prolonging additives.

ANOTACE

Tato bakalářská práce se zabývá stárnutím polypropylenu. První část obsahuje základní informace o výrobě polypropylenu, o jeho vlastnostech a podrobněji se zaměřuje na strukturu. Druhý oddíl se věnuje různým způsobům degradace polypropylenu (biologická, tepelná, termooxidační a fotooxidační), přičemž je největší důraz kladen na degradaci fotooxidační a vliv morfologie polypropylenu na míru degradace. Poslední část se zabývá aditivami, která prodlužují životnost polypropylenu.

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INTRODUCTION

Polymers are relatively new class of materials. They have been developed to take place of some natural materials for their low cost and advantageous and specific properties. Initially the polymers were produced without the exhaustive knowledge of their properties. The result was the financial loss, which inspired distrust to this material. One of the causes of ineffectual applications of polymeric materials is the bad knowledge of their resistance in their surrounding environment. The plastics are not suitable for the universal use. Applicability of their use depends on their chemical composition, structure, the amount and the composition of the fillers, impurities and admixtures. The way of processing, chemical composition and specifications of the environment have to be also considered.

The plastics may be devalued during the action of the high temperatures especially in presence of the aerial oxygen, solar radiation, ionizing radiation, various chemicals and microorganisms. These factors may act not only during the use, but over the course of the processing and storage too. That is why the grasp of polymer devalue processes is important both for the producer and the user. The elevation of the resistance of the polymeric materials leads to the economy of finances and the natural resources.

This work is addressed to the ageing of isotactic polypropylene (iPP). Polypropylene is the one of the largest sales volume polymers. This material is largely used in many industrial branches and that suggests a lot of modifications and adjustments, such that the study of its possible applications and its limitation is important. Considering the polypropylene structure, the main cause of PP ageing is the photo-oxidative degradation.^[56] Since isotactic polypropylene is a polymorphic material, it exhibits several modifications (α -, β - and γ - crystalline phases).^[1] The monoclinic α - phase is the most common in melt-crystallized or solution-crystallized samples.^[1-5] The trigonal β - phase is observed only occasionally during crystallization of neat PP from a melt. The relative amount of β -phase can be considerably increased by crystallization in shear fields, in temperature gradients, or by adding specific nucleating agents.^[4, 5] It has been shown that the presence of β -phase significantly influences important properties of the material: it highly enhances its toughness and drawability but lowers E-modulus.^[6-10] Consequently, isotactic polypropylene containing the β - phase (β - iPP) is currently classified among common polymeric materials, and for specific applications it is rated as a suitable alternative to the conventional (α) polypropylene (α - iPP).

Photooxidative degradation of iPP has been the subject of investigation of many studies,^[11-17] but there are still many unanswered questions. For example, the photooxidation process was rarely related to initial supermolecular arrangement. Utterly sporadic are studies dealing with the interrelations between the polymorphism of iPP and its degradability. And yet, the effect of specific structures in both amorphous and crystalline phases of α - iPP and β - iPP could and should be expected.^[18]

This work summarizes main knowledge of isotactic polypropylene and its degradation behavior. Attention is also devoted to polypropylene containing β - phase and to its influence on degradation process.

1 POLYPROPYLENE

One of the major polymers is polypropylene (PP). This material was introduced to the large scale production in 1957 as a plastic and fibre forming material. ^[19]

1.1 PRODUCTION

Polypropylene is made of propylene monomer ($\text{CH}_2 = \text{CH} - \text{CH}_3$). Propylene is colorless gas, practically odorless (boiling point -47.6°C , melting point -185.2°C). It is produced primarily as a by product of petroleum refining and of ethylene production by steam cracking of hydrocarbon feedstocks. Propylene is major chemical intermediate. In the environment, propylene occurs as a natural product from vegetation. ^[20]

The polypropylene was first made in 1869 by Barthelot. It was sticky sediment and had no possible application for industry. At the beginning of the 1950s Karl Ziegler discovered possibility to use group of aluminium and titan - based compounds which lead monomer to the fast polymerization at the low pressure. His work was extended by Giulio Natta who successfully prepared semicrystalline polypropylene. This method is called Ziegler - Natta (ZN) polymerization because of it (Fig.1) and the catalysts as well (TiCl_3 , TiCl_4 , ZrCl_2 and others). ^[21]

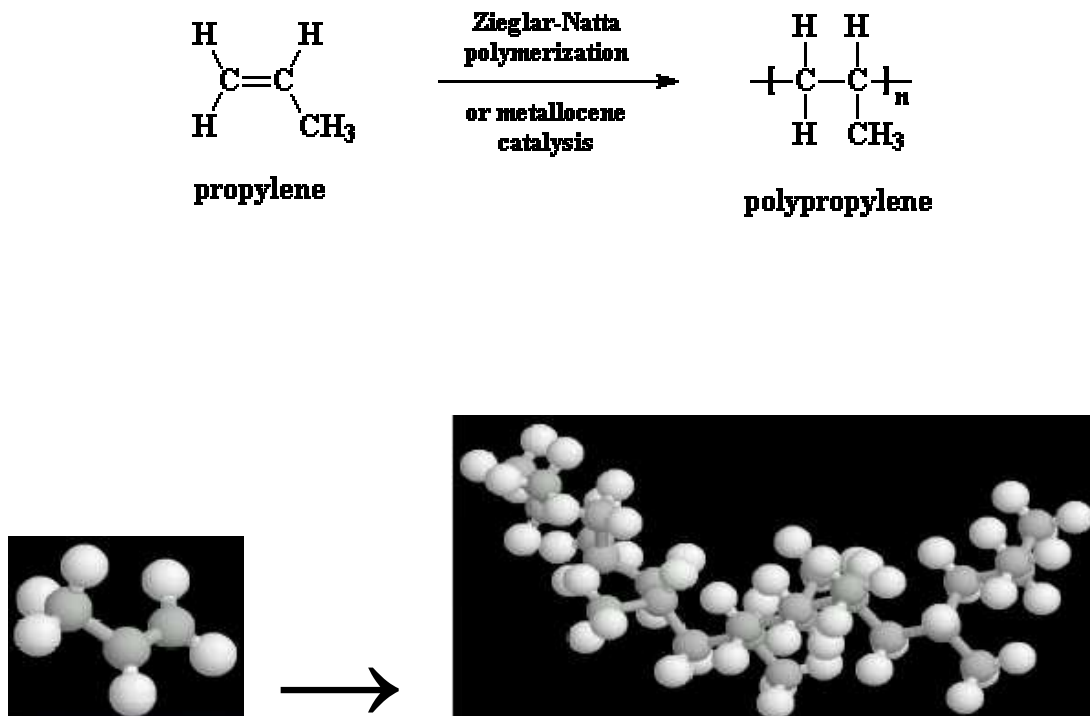


Fig. 1. Ziegler - Natta polymerization ^[22]

The use of ZN catalysts makes possible the production of highly stereoregular polymer. The aim is to produce isotactic polypropylene (iPP) or syndiotactic polypropylene. Small amounts of atactic polypropylene are also produced but are separated by their solubility in *n*-hexane, so the product contains from 2 to 6% of atactic portion. ^[19, 23]

1.2 STRUCTURE

The basic building unit is a repeating unit of propylene. The main chain is composed of the carbon atoms. Every other of them carries a methyl group. There are three types of PP according to the position of the methyl group - isotactic, syndiotactic and atactic.

The stereochemical structure of PP is demonstrated with the planar form trans. The atoms of the chain are stowed in a basic chain plain sandwiching.

1.2.1 Atactic polypropylene

Generally atactic polymers are characterized by their tacky, amorphous behavior (they are unable to crystallize) and low molecular weights. Atactic portion provide the same effect as a plasticizer, by reducing the crystallinity of the polypropylene. A small amount of atactic polymers in the final polymer can be used to improve certain mechanical properties. This provides properties to the final polymer, such as improved low temperature performance, elongation, processability and optical properties (transparency), but sacrifices flexural modulus or stiffness, and long-term heat ageing properties. Configuration of atactic polypropylene is randomly distributed in the repeat units. The structure is irregular, the polymer is weak rubbery compared with isotactic polypropylene, which is hard and stiff. It has found some uses as a carpet backing and road surfacing material. ^[19] Atactic polypropylene is viewed in Fig. 2.

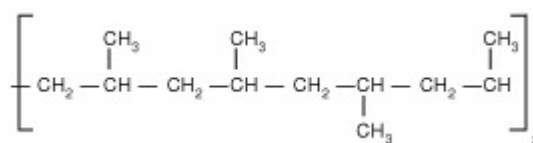


Fig. 2. Atactic polypropylene ^[24]

1.2.2 Syndiotactic polypropylene

Much is already known about the structure of semi-crystalline syndiotactic polypropylene (Fig. 3). Syndiotactic polypropylene (sPP) forms both hedrites and spherulites, depending on the crystallization temperature (T_c). Going to lower T_c , an increasing tendency of branching and splaying of growing lamellae continuously changes the hedrites into spherulites.

Sequence for each syndiotactic unit, setting up a helix with two syndiotactic units per turn with a period 0.74 nm. The stable structure of sPP has a unit cell which includes 2 left - and 2 right - handed helices in a regular alternation along both the *a* and the *b* axis. In real crystals the regular left - right packing is often perturbed, leading to lattice disorder. This disorder is known to increase with decreasing T_c . ^[25]

This polymer may be synthesized by the use of certain ZN catalysts, such as $\text{VCl}_4 + \text{AlEt}_2\text{Cl}$ at -78°C . The polymer crystallizes with a melting temperature value (T_m) of 183°C (or 134°C) and has a glass transition temperature (T_g) value of about 0°C .

Syndiotactic polypropylene has finally found the exercise in adhesives, caulks, and cable-filling compounds. ^[19]

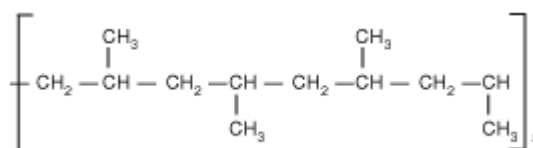


Fig. 3. Syndiotactic polypropylene ^[24]

1.2.3 Isotactic polypropylene

From a commercial viewpoint, isotactic polypropylene (Fig. 4) is very important. In comparison to atactic and syndiotactic, isotactic polypropylene is the most stereo - regular structure of polypropylene. Therefore, a higher degree of crystallinity (60-70%) is achieved. As a result, the level of isotacticity and thus crystallinity heavily determines many of polypropylene mechanical properties and processability.

Although the increased crystallinity of polypropylene makes the material less tough than polyethylene, it also provides polypropylene with a higher flexural modulus, and tensile properties much higher than polyethylene. This allows polypropylene to be used as a replacement for engineered thermoplastics, such as ABS. ^[26]

Isotactic polypropylene (iPP) is an important polymer also scientifically, because of its different morphological behavior. The chain conformation of iPP is a threefold helix (3_1 or $3/1$ helix), that means that one coil is created from three monomer units, which can be either right or left - handed, with periodicity of 0.65 nm and methyl groups are turned round about 120° . The position of methyl group with respect to the chain axis can be either up or down. ^[22, 27-34]

Molecular weight is from 100 000 to 600 000, $T_m \approx 170^\circ\text{C}$, and the density is $\rho = 0.905 - 0.912 \text{ g/cm}^3$.

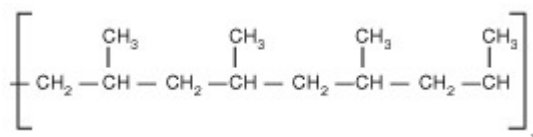


Fig. 4. Isotactic polypropylene ^[24]

On the crystal lattice, iPP exhibits three different morphological forms, α (monoclinic), β (hexagonal), and γ (orthorhombic), distinguished by the arrangement of the chains. ^[63-68] This variety in morphology is called polymorphism. Each of these forms is for example identified with specific peaks in the X-ray pattern. Another form of iPP with degree of order between crystalline and amorphous phases was first reported by Natta,

who named it the „smectic“ form. Each of these forms was prepared with different preparation procedures. [2, 39, 40]

1.2.3.1 α - form

The predominant crystal structure of pure isotactic polypropylene at atmospheric pressure is monoclinic α structure (α -iPP). Unit cell parameters are: $a = 0.665$ nm, $b = 2.096$ nm, $c = 0.650$ nm with $\alpha = \beta = 90^\circ$, and $\gamma = 99.3^\circ$. [30]

The α form of iPP exhibits three types of spherulites:

- (α_I) can be developed at an isothermal crystallization temperature below 132°C . These are positive birefringent spherulites.
- Negative birefringence spherulites (α_{II}) exist at a temperature greater than 138°C .
- However the most common spherulites are of mixed birefringence type (α_{III} or α_m); they possess no distinct Maltese cross and are revealed as radiating arrays of intermingled areas of positive and negative birefringence. This type of spherulite has been observed at any temperature up to 152°C .

The presence of one type depends not only on the crystallization temperature, but also on the film thickness. The birefringence change of α -form spherulites has been directly related to the relative amounts of tangential lamellae branching, inside the spherulites. An amount of branching lamellae is relatively higher than that of the negatively birefringent α_{II} . The angle between branched lamellae for twin crystals grown by crystallization in solution is about 80° . [40]

The melting behavior of α spherulites of iPP is complicated by presence of thin lamellar branches inclined at 80° to the dominant radial lamellae. During a heating cycle the branches melt at lower temperature than dominant lamellae, causing an increase in the birefringence of the spherulites and, hence, of the specimen. Values of the melting temperature (T_m°) reported in the literature fall into two groups, one around 186°C and the other around 210°C . It was observed, that there are changes in melting temperature with crystallization time for different molecular weights and fractions of iPP. At the same crystallization temperature the degree of shift is proportional to the crystallization time. The changes in melting temperature with time are independent of molecular weight and its distribution. In addition, using small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques for determining the lamellar thickness, equilibrium melting temperature (T_m°) was extrapolated to the value of 186.1°C . Such that it is believed that the value 210°C is inaccurate since it is caused by lamellae thickening phenomenon. [21]

1.2.3.2 β - form

The β - form of iPP was first identified in 1959 by Keith et al. [41] It is normally referred to as „hexagonal iPP“.

In the crystallization of conventional iPP grades, a small amount of β - form occurs sporadically at high supercoolings ($T_c < 130^\circ\text{C}$) or in quenched samples. It is possible to produce a high amount of β - form using special crystallization conditions, when temperature gradient method and selective β -nucleating agents (for example quinacridone dyes or triphenodithiazine produce even 100% of the β - form). [21]

The derivation of the unit cell of the β - form of unoriented specimens has been attempted by many researches. [21] For example Keith et al. [41] suggested a four chain unit cell with $a = b = 1.274$ nm and $c = 0.635$ nm with $\alpha = \beta = 90^\circ$, and $\gamma = 99.3^\circ$, Turner - Jones

et al.^[35] declare it to have hexagonal (or trigonal) lattice with $a = b = 0.636$ nm and $c = 0.649$ nm. All the investigations in the more recent literature agree on this basic model.^[21] However, when additional reflections are taken into consideration, this model is not sufficient. A more satisfactory model is model with $a = b = 1.103$ nm and $c = 0.649$ nm.^[21] Another possible unit cell, suggested by Turner-Jones^[35, 36, 42] is orthorhombic with $a = 1.103$ nm, $b = 1.910$ nm and $c = 0.649$ nm.^[43] The calculated density of the hexagonal unit cell is $\rho = 0.92$ g/cm³.^[29, 36, 42]

An interesting feature of the growth of the β - phase is the β to α modification transition. It can be generally stated that this transition always takes place if the growth rate of the α - phase (G_α) is higher than that of the β - phase (G_β). It was found that G_α is higher than G_β above defined temperature marked $T(\beta\alpha)$.^[44-46] The low - temperature $\beta\alpha$ - growth transition also evidences that $G_\alpha > G_\beta$ below $T(\alpha\beta)$, but the experimental proof of that is very difficult due to the extremely high-growth rate. The phenomenon of β to α growth transition above $T(\beta\alpha)$ and below $T(\alpha\beta)$ which takes place on the growing β - crystal front evidences that the formation of pure β - iPP has a theoretical upper ($T(\beta\alpha) = 140$ - 141°C) and a lower limit temperature ($T(\alpha\beta) \sim 105^\circ\text{C}$). Within this temperature interval different types of supermolecular structure (SMS) of β -iPP can be formed. The types and structural features of SMS formed are markedly influenced by the thermal conditions of crystallization, by the melt history,^[47] by mechanical stresses to the crystallizing system and by the presence of extraneous materials. In a quiescent melt, β - spherulites can be formed. Depending of the crystallization temperature, negative radial (grow below 128°C) or negative banded (grow between 128 and 135°C) β - spherulites of iPP might form during the melt crystallization. The β - spherulites have strong negative birefringence in comparison with the α - spherulites.^[48, 49]

Similar to the α - form, many values of the equilibrium melting point have been reported;^[21] it varies between 170°C and 200°C . Recently the value of 174.4°C for T_m° is reported using the same procedure for determining the most accurate value T_m° of the α - form.^[21]

Padden and Keith^[48] demonstrated that β - spherulites recrystallize into α - modification ($\beta\alpha$ recrystallization) when heated and, finally, they melt from this form. Hence, due to this recrystallization phenomenon and melting of the α - and β - phase of iPP with mixed polymorphic content, the melting curves have a complicated melting profile.^[50-52] According to Varga,^[44, 49, 53] the melting characteristics of β - iPP are highly sensitive to the post - crystallization thermal history (melting memory effect). It can be stated that β - iPP samples are susceptible to $\beta\alpha$ - recrystallization only if they were cooled below a critical temperature before melting. This critical recooling temperature was $T_R^* \sim 100$ - 105°C . It should be suggested, that the critical recooling temperature (T_R^*) corresponds to the lower limit temperature, $T(\alpha\beta)$, of the formation of pure β - iPP.

1.2.3.3 γ - form

This form was noted during the 1960s. It was produced by crystallization at elevated pressures from high molecular weight homopolymer. Other procedure is crystallization from the melt of high molecular weight stereoblock copolymer with small amounts of ethylene or but-1-ene. When the pressure is varied, only the α - and γ - forms are observed. With growing pressure the γ - form becomes dominant.

The lattice parameters of the orthorhombic cell are $a = 0.854$ nm, $b = 0.993$ nm, $c = 4.241$ nm.^[21]

The melting point of this form is mostly reported from 125 to 150°C for low molecular weight samples. In the case of pressure crystallized samples, the melting occurs above 150°C .^[21]

1.2.3.4 Smectic form

It is prepared by quenching thin sheets of iPP from the melt into the ice water. The density of the smectic form has been reported by Natta to be 0.88 g/cm³. The interpretation of the structure is still disputed in literature. ^[21]

1.3 PROPERTIES

Commercial PP is 90 - 95% isotactic and has a number average molecular weight of 40 000 to 60 000 with polydispersity of 6-12. The crystalline region which constitute about 82% of the material has density 0.94 g/cm³ and the amorphous 0.85 g/cm³ (overall 0.90 g/cm³). PP is stiffer than PE, having tensile modulus strength of 1000-1300 MPa. Its elongation at break is 50-300% and its impact strength is 0.3-4.3 J. Generally, the melting temperature is 160-171°C PP is highly solvent resistant and environmental stress cracking resistant. It has very high electrical resistance. However, the presence of a tertiary hydrogen on each repeat unit makes it very susceptible to oxidative degradation. As a plastic material PP is mainly used as an injection moulding material. ^[19]

Many studies deal with the comparison of the mechanical properties and fracture behavior of α - iPP and β - iPP during the deformation. In experiments with highly pure β - form iPP, this structure resulted in lower elastic modulus and yield stress at a given strain rate, but had a higher ultimate tensile strength and strain (Tab. 1). The impact strength, breaking strain and toughness of β - iPP exceeds that of α - iPP. ^[54, 55]

Table 1. Static tensile characteristics of α - and β - iPP ^[47]

Property	α - iPP	β - iPP
E-modulus [GPa]	2.0	1.8
Yield stress [MPa]	36.5	29.5
Elongation at yield [%]	~ 12	~ 7
Necking stress [MPa]	27.5	28
Elongation at necking [%]	~ 22	-
Tensile strength [MPa]	39.5	44
Elongation at break [%]	~ 420	~ 480

2 DEGRADATION

Ageing of plastics is defined as an aggregate of irreversible changes of material characteristics caused by chemical, physico-chemical and physical processes, leading to undesirable non-reversible changes of the features of the polymers. Deterioration of polymeric materials is effected by light, weather conditions, temperature, ozone, oxygen, chemical attack or mechanical stress. But likewise the biological ageing might lead to the improvement of some characteristics of the material. For example at the beginning the termooxidation might lead to the enhancement of some characteristics of polymers as a consequence of hardening.

Degradation-breakdown is defined as a whole of destructive reactions of polymers. It includes processes which lead to the splitting of macromolecule to the smaller elements, mainly to the monomers and low oligomers (depolymerization). The processes which manage to the change of the chemical structure of polymeric material allied with the production of low-molecular substance (for example H_2O , HCl and others).

There are several types of degradation: ^[56]

- Thermic and termooxidative degradation is caused by thermic stress without oxygen or in presence of oxygen
- Photodegradation is destruction caused by the light
- Photooxidative degradation is similar to the photodegradation but in presence of the oxygen
- Biological degradation
- Mechanodegradation (mechanical stress)
- Chemodegradation is degradation influenced by the chemicals
- Ionizing degradation

PP is with respect to the other polymeric materials unstable to weather conditions. PP especially comes under the oxidative degradation beside the sun (ultraviolet) radiation. Failure is usually by brittle fracture resulting from surface embrittlement. Chemical stabilizers added to the polymer can increase the lifetime very considerably and should be used even if the component is to be exposed to sunlight only occasionally. ^[24]

2.1 BIOLOGICAL DEGRADATION OF POLYPROPYLENE

The resistance to the microorganisms and especially to the mould depends on its relative molecular weight M_r . If the M_r reaches the certain number it is not attacked by mould anymore. The growth of *Aspergillus oryzae* and the others moulds causes the change in crystallinity at the surface layer and it creates the yellow marks.

There were no mechanical or electrical changes in the characteristics noted. When PP was buried into the ground it proved the good resistance of the PP to the affect of the ground bacteria.

The weak growth of the mould was observed at the neat PP and at the stabilized PP. Polypropylene containing ZnO is not attacked. The changes of the characteristics were not noted. Acrylic resin modified PP gets attacked by moulds. ^[24]

2.2 THERMIC AND TERMOOXIDATIVE DEGRADATION OF POLYPROPYLENE

From polypropylene heated for 30 minutes in the vacuum to the temperature 328°C are isolated about 8.2 % of desultory products. The desultory products of the thermal degradation of PP are saturated and nonsaturated aliphatic hydrocarbons. Activating energy of the thermal degradation in vacuum is 242.8 kJ/mol. Table 2 shows the desultory products of the thermal degradation at 150°C, quantity released from 1 mol of the polypropylene after the four hours of oxidation.

Table 2. Desultory products of the thermal oxidation ^[56]

Desultory products	Amount [mmol]
Basics -COOH	110-130
Esters -OCOCH ₃	35-36
Unsaturated compounds	40-42
Peroxides	4-5
Formaldehyde	15-25
Acetaldehyde	5-8
H ₂ O	670-750
CO ₂	100-120
CO	40-50
H ₂	17-20

The PP is considerably less resistant to the termooxidative degradation. After the short heating to the temperature 100°C the mechanical properties of unstabilized PP get suddenly worse. At the same time the electrical properties are changed. Comparing to PE there is produced more desultory products and PP absorb more oxygen than PE. During the termooxidation, carbonyl and carboxyl groups are formed.

Termooxidative degradation of PP is going with the increase of amorphous portion. Activating energy of termooxidative degradation is 91.3 kJ/mol. Resistance of PP against the termooxidation gets worse in the presence of the metals or metal salt. Stabilization is provided by using stabilizers such as derivatives of amines, phenols, organic substances containing sulphur, organic phosphites etc. Stabilized PP is suitable for use up to 100°C in the long term and up to 140°C in the short term. ^[56]

2.3 PHOTOOXIDATIVE DEGRADATION OF POLYPROPYLENE

The reason that the PP is not resistant to the solar radiation is the presence of the tertiary carbons in polypropylene macromolecule which are vulnerable to the oxidative destruction.

The neat polypropylene does not absorb the light above the wavelength 200nm. The photolysis of the commercial PP by the light about 290 nm is caused by the chromophores, which are developed during the polymerization or the thermal processing. Chromophores are sensitive to the photolysis by the light above the wavelength 300nm. Greatest changes in the PP are evoked by the spectra from 300 nm to 340 nm. The photodegradation is accelerated by the damp and the warmth. The 10°C raise of the temperature cause two time quickened photooxidative degradation of PP. ^[56]

In the natural atmospheric conditions insulating of PP generally causes:

- Embrittlement of the material
- Cracking of the surface (the cracks are oriented across the orientation of the macromolecules; during the exposition the number of the cracks increases, the cracks leak deeper in the material and link)
- The change of the color (PP gets yellow or brown, over the further ageing the color gets darker; the color is changed before any chemical changes appear in the sample thence it follows that the coloration is caused by the impurities or the presence of the foreign chemical groups in the chain)
- The contraction of the material (length 0,5-1% and thickness 0,1-0,2%)
- The chemical changes (growth of the content of the carbonyl and peroxide groups which absorb the solar radiation in field of UV, absorption increase with their quantity)
- The decrease of the mechanical features ^[56]

2.3.1 Photophysics

Visible light, infrared, UV, and γ -rays are each a distinct form of electromagnetic radiation. Each propagate in space as waves of electronic and magnetic fields. Electromagnetic waves carry a discrete amount of energy depending on their frequency, as stated by Planck's Law:

$$E = hf \quad (1)$$

where E...energy of radiation [J]
f...frequency of radiation [1/s]
h...Planck's constant [J.s].

The frequency of radiation depends on the conditions in which this radiation was formed. With temperature increase, the light spectrum is shifted to the left, meaning that more UV and visible light is emitted (the frequency of radiation depends on conditions of emission, mainly temperature). Table 3 presents the wavelengths and energies of given radiation.

Table 3. Energy of radiation ^[57]

Type	λ [nm]	Energy [kJ/mol]
Far UV	100	1196
Vacuum UV	200	598
UV	300	399
	350	341
	390	306
Blue-green	500	239
Red	700	171
Near IR	1000	120
IR	5000	24
Hard X-rays, soft γ -rays	0.05	2.4×10^6
Hard γ -rays	0.005	2.4×10^7

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 photodegradation of exterior plastic materials is caused mainly by UV light.

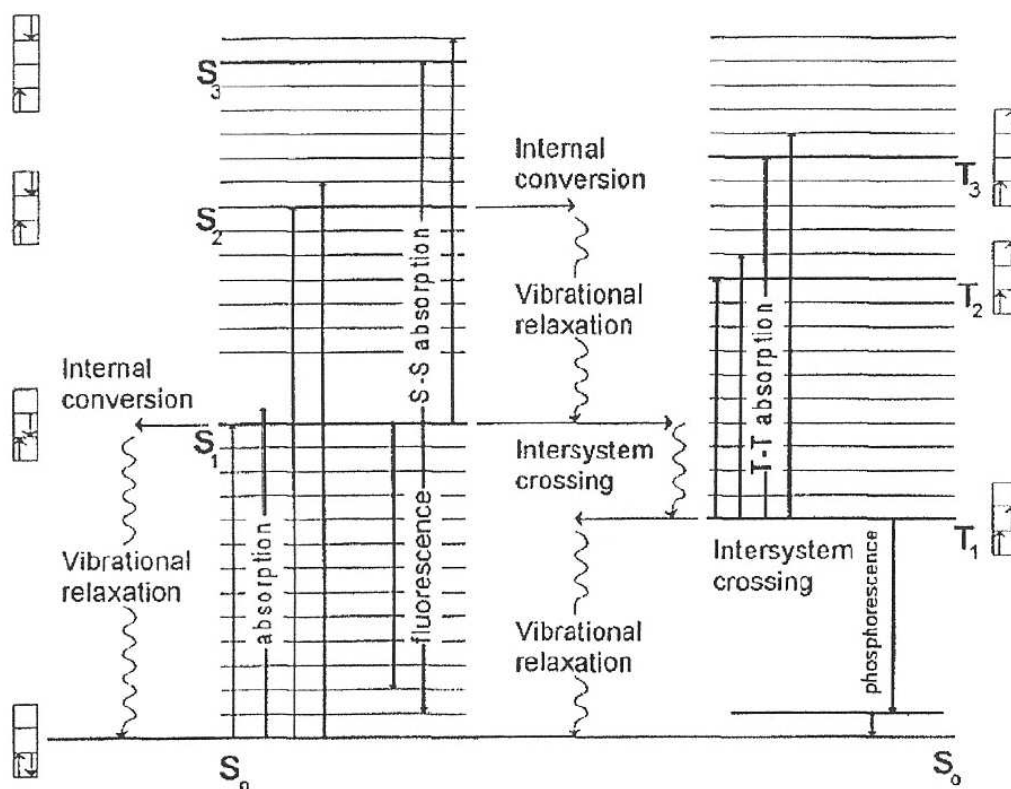
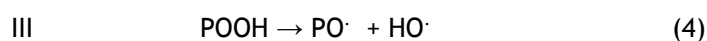
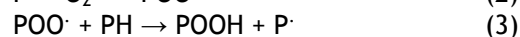
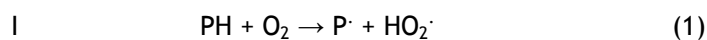


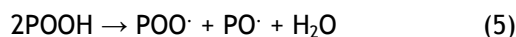
Fig. 5. Jablonski diagram ^[57]

The outcomes of energy absorption by molecules are well demonstrated in Jablonski diagram (Fig. 5). 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. 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. These primary photochemical reactions are mostly followed by secondary reactions. A mostly reaction with oxygen or ozone and photooxidation is realized.

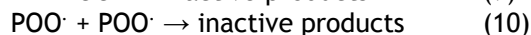
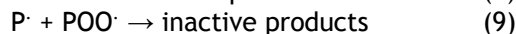
2.3.2 The photooxidative processes

Polypropylene weathering involves mainly oxidative degradation, proceeding as a radical reaction with branched kinetic chains. This chain reaction is composed of four main stages: initiation (I), propagation (II), chain branching (III) and termination (IV). ^[58]





Radicals formed in (3) then re-enter the propagation phase via the following reactions:



Initiation is promoted by photon in the UV part of the solar spectrum and it is caused by collision of a photon with an impurity. Further molecular degradation occurs because the radicals are unstable and may undergo scission or crosslinking reactions. Scission dominates, but both reactions lead to deterioration of the engineering properties of the material.

Hydroperoxides produced by reaction (2) and (3) can be decomposed by UV radiation with wavelength below 360 nm giving a $\text{PO}^\cdot$ radical (4) and (5). Hydroperoxide decomposition is central in the degradation of PP. Carbonyl groups are produced during PP oxidation and are themselves photolabile. There are aldehyde and keton groups produced and may influence the subsequent photodegradation behavior. ^[58]

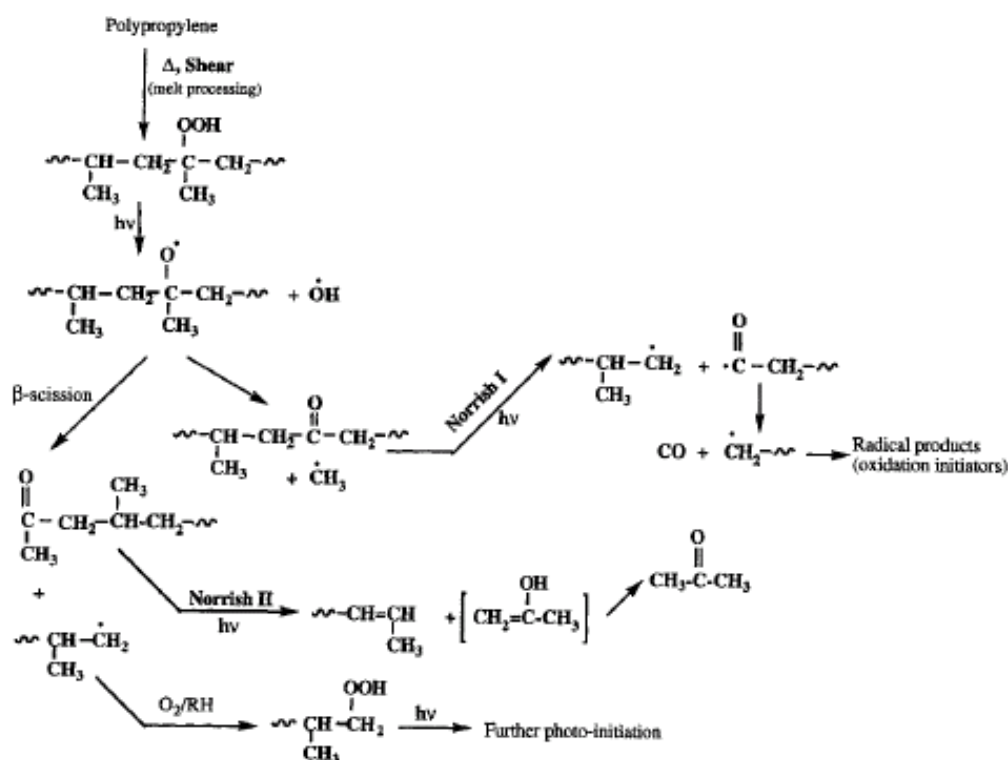


Fig. 6. Polymer hydroperoxidation during processing and further photoinitiation by the hydroperoxides and the derived carbonyl compounds ^[59]

Polymer hydroperoxidation and further processes leading to the polypropylene degradation are schematically arranged in Fig. 6.



Fig. 7. Cracks in the surface of polypropylene samples during tensile testing after 12 weeks laboratory UV exposure while held in bending ^[58]

The major failure mode with weathered PP is fracture nucleated in an embrittled surface layer. Photodegradation is concentrated strongly in the surface zone partly because the UV intensity is greatest there, but mainly because of the ready supply of oxygen. The reaction near to the surface is so rapid in sunny conditions that oxygen diffusing in from the surface is consumed before it can penetrate far into the polymer and no more oxidation is possible in the interior as long as UV irradiation continues. Chain scission releases molecule segments from entanglements and assists secondary crystallization. Weathered PP often develops tensile residual stresses in the surface as a consequence of the volumetric contraction caused by crystallization, further enhancing its vulnerability to cracking. When the surface is put into the tension cracks form readily in the embrittled layer and often propagates into interior, leading to failure (Fig. 7,8). ^[58]

Even though the interior may be relatively undegraded chemically, a crack in the embrittled layer may provide sufficient stress concentration to cause brittle fracture or a ductile tearing instead of deformation and drawing. If UV exposure is prolonged the surface may become so degraded that it is no longer effective in supporting a critical crack that propagates into the interior. The strength of polypropylene may recover somewhat after a period of exposure. Failure may nucleate at the surface facing away from the UV source after prolonged exposure because similar damage develops at this surface, but more slowly. Eventually the surface facing away from the UV source becomes ineffective also and failure may occur from an internal site.

If the UV source is applied only intermittently the oxygen level may recover during the dark periods. The presence of stabilizers has an important effect on the depth-distribution of degradation. Stabilizing system slows the reaction near the surface so much that oxygen diffusion into the interior is possible and the level of degradation there may be higher than in an unstabilized system. ^[58]

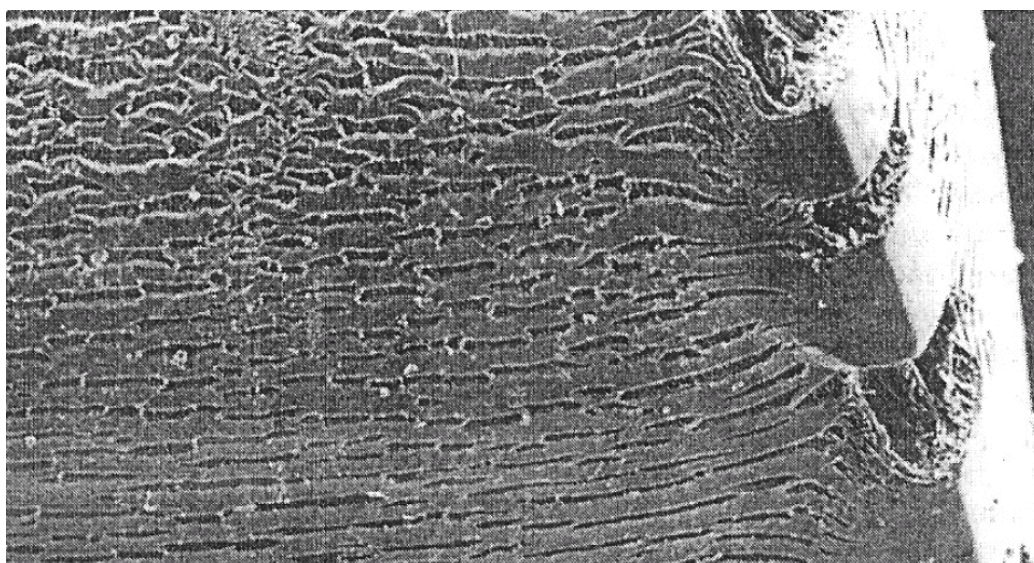


Fig. 8. Cracks in the surface of polypropylene samples during tensile testing after 4 weeks laboratory UV exposure while held in bending ^[58]

2.3.3 Effect of morphology on photodegradation kinetics

The mechanical properties of degraded PP were shown to depend not only on the extent of chemical degradation but also on the character of the polymer (chemical structure, physical structure), especially the spherulite size. According to the experiments ^[43, 60] the spherulite size plays a major role in determining the properties of these materials. The higher spherulite size in slow cooled samples in comparison with normal cooled samples makes these specimens particularly vulnerable to the weathering effects due to the expected lower concentration of tie chain molecules. As well as the spherulite size the crystal size is important. If the lamellar thickness of the slow cooled sample is large, as expected, then there will be relatively small number of chain folds available for reaction at the crystal surface. It is expected that the extent of degradation will decrease with the increase in the degree of crystallinity and molecular orientation, following the effects of these parameters on oxygen diffusion. On the other hand, the crystallinity and the molecular orientation determine the mobility of the radicals and therefore reduce the rate of termination, allowing an increase in the propagation of chemical reactions leading to molecule scission, and this effect is opposite to that caused by reduced oxygen mobility. ^[61]

As is written above, it is accepted, that degradability of semicrystalline polymers is significantly influenced by their morphology. Therefore, the effect of physical structure on the degradation of polypropylene (especially induced by UV irradiation) has been studied in many works. ^[e.g. 11, 12, 13] However, these works deal only with α - iPP. While β - polypropylene (β - iPP) is more suitable material for some application and it has become to be used, some studies focused on degradation of β - iPP have been published. ^[17, 62-64] It was found, that the β - nucleation specifically affects the processes of UV degradation of isotactic polypropylene. The molecular degradability of β - PP is lower as compared to α - iPP, reflecting higher opacity of β - iPP for UV light; the degradation mechanism, however, is similar for both materials. Fig. 9 shows the molecular degradation of both the neat (α - iPP) and β - nucleated (β - iPP) polypropylene as a function of ageing time (it means the time, for which the samples were exposed to UV irradiation). Molecular degradation is characterized by carbonyl index. ^[64] It is clear from this picture, that the degradation is more pronounced for α - iPP and particularly evident at higher aging times. It indicates a more intensive molecular degradation of α - iPP. Macroscopically, the degraded α - iPP containing larger spherulites is characterized by more severe surface cracking.

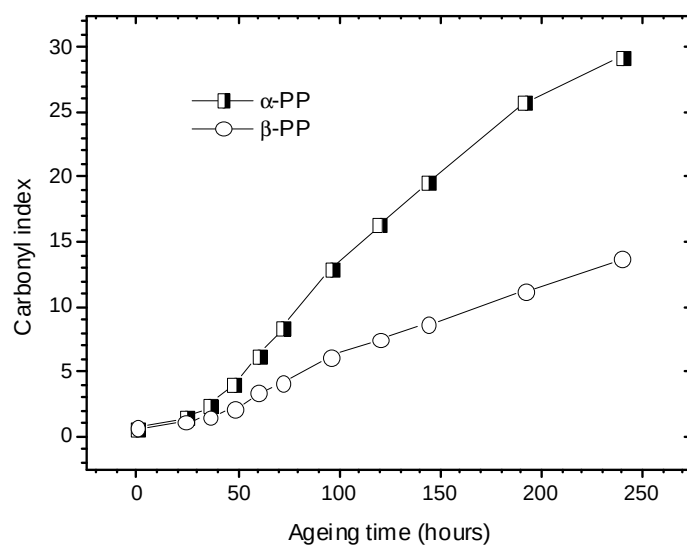


Fig. 9. Effect of UV exposure on the carbonyl index of α -iPP and β -iPP specimens ^[51]

3 PHOTOSTABILIZATION

The outdoor performance of polymers depends largely on their photooxidative (combined action of ultraviolet (UV)-light and oxygen) stability, although generally the overall effect is that of a combined photo- and thermal-oxidation of the polymer. Fortunately, the vulnerability of PP to the deleterious effects of their outdoor service environment can be greatly controlled, and the outdoor performance can be markedly improved, by appropriate choice of photostabilizers used either separately or in synergistic combinations. ^[65]

Photostabilizers are incorporated in PP during its melt processing and are generally used at higher concentration levels than that of thermal antioxidants (up to 1 wt.%). The effectiveness of photostabilizers is assessed by first subjecting the stabilized polymer to accelerated weathering and/or outdoor exposure conditions. To be effective photostabilizers, these compounds must satisfy not only the basic chemical (i.e. intrinsically active) and physical (i.e. solubility, low diffusion and volatility, nonextractability) requirements, but must also be stable to UV light and must withstand continuous periods of exposure to UV light without being destroyed or effectively transformed into sensitizing products. ^[58] Other factors that can affect the ultimate photostability of the polymer are sample thickness, polymer crystallinity and presence of other additives, e.g. pigments and fillers. ^[65, 66]

It ensues from the mechanism of photooxidation, that the presence of the peroxide and carbonyl groups in the polymer negatively influences the degradation. These groups arise during the processing of PP and that is the reason to choose the processing parameters not to corrupt the disruption of the mass. The abstract of the durability of PP with the diverse stabilizers is represented by the Table 4. ^[56]

Table 4. Durability of PP exposed to the solar irradiation ^[56]

Polypropylene	Durability (h)	
	Tropics	Great Britain
No additives	135	590
Brown colored	920	1730
Black	3500	>3000
Clearly yellow	600	1330
No additives under the glass	380	-
2 % of clack carbon	>6000	-
UV stabilized	1900	-
Brown with the UV stabilizer	1880	-
Clearly yellow with the UV stabilizer	2100	-

There is a lot of stabilizing effect compounds which protect the polymer against the oxidative ageing: ^[67]

1. Ultraviolet screening can be provided by pigments, including carbon black. ^[58] The influence of pigments may diverse. Some pigments decelerate the degradation, some have no influence at all and some of them accelerate the degradation. The pigments have the ability to reflect or absorb the radiation and avoid the penetration of the radiation inside the material. The efficacy of pigments depends on their concentration, the size of the elements. There are several kinds of pigments

using for the stabilization of the PP. For instance the white (titanium dioxide and zinc oxide), yellow (cadmium yellow), red, blue and green pigments. The best defense against the atmospheric ageing is provided by the black carbon. The standard amount of the black carbon in PP is 2.5 %. This amount differs from the weather conditions in which is PP used. ^[56]

2. Ultraviolet absorption can be provided by additives that are transparent to the visible light and do not alter the appearance of the product, but the energy that they absorb must not be available for transfer to and breakage of nearby polymer bonds. The tendency for carbonyl photolysis to lead to backbone cleavage can be reduced by deactivating carbonyl species using transition metal chelates. As with UV absorbers, the quencher must be able to dissipate the acquired energy. Radical scavengers break the oxidation chain, so limiting the damage. The scavenger is often a free radical that is relatively stable and does not itself initiate reactions with the undamaged polymer, reacting with alkyl radicals when they are produced by photooxidation. Examples are nitroxyls and phenoxyls (see Fig. 10). ^[58]

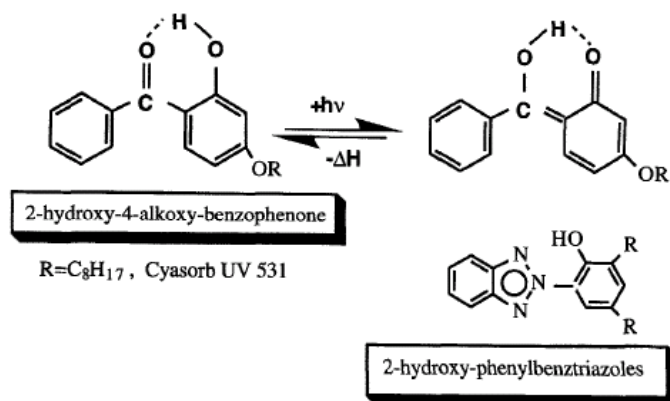


Fig. 10. The main photostabilizing reaction of ultraviolet-absorbers exemplified with substituted hydrobenzophenones. The structure of hydroxyphenylbenztriazole is also shown. ^[65]

3. Hydroperoxide decomposition into inactive products is an important method of stabilization for it prevents generation of radicals by reactions such as (3) in chapter 2.3.2. Hydroperoxides are more potent photoinitiators than carbonyl groups and may be produced during processing as well as by photooxidation. Decomposition of hydroperoxides can be achieved by reaction with phosphite esters or nickel chelates, or by catalytic action by a range of compounds including mercaptobenzothiazoles. ^[58]
4. The latest class of photostabilizers developed commercially is based on hindered amines (known as HALS, hindered amine light stabilizers) which have proved to be amongst the most effective photostabilizers. HALS are a unique class of photostabilizers which do not subscribe to the general mechanisms of photostabilization; they are not UV absorbers, do not quench singlet oxygen or triplet carbonyls, and do not catalyze hydroperoxide decomposition. Their effectiveness, however, is due to their transformation product, the corresponding nitroxyl radicals, which is the real stabilizing species, (Fig. 11(a)). Hindered nitroxyl radicals are effective chain breaking-acceptor (CB-A) antioxidants which act by

trapping the macroalkyl radicals to give hydroxylamines (Fig. 11(b)) or /and alkylhydroxylamines (Fig. 11(c)); the former regenerates the nitroxyl radical via a CB-D process (Fig. 11(d)). The overall high efficiency of HALS as photostabilizers in polymers is attributed to the regeneration of nitroxyl radical and the complementarity of the CB-A/CB-D antioxidant mechanisms involved. ^[26, 58]

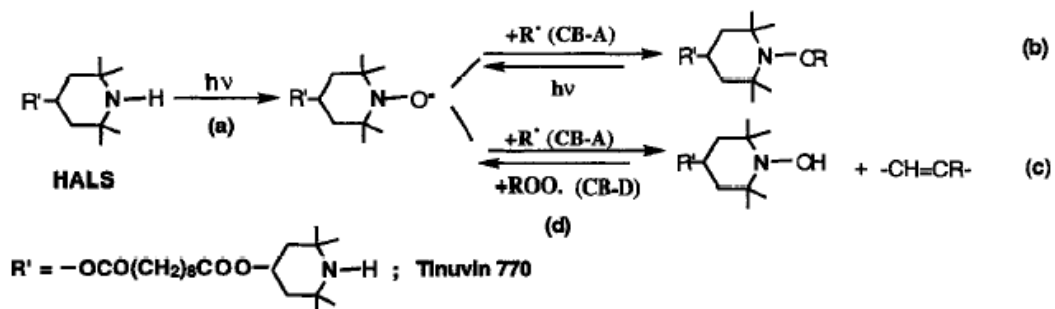


Fig. 11. Simplified antioxidant mechanism of hindered amine light stabilizers (HALS) ^[65]

Some molecules often migrate within a polymer, which is an advantage when they diffuse to replenish those lost by reaction in the surface region but it is a disadvantage if they diffuse to the surface and are lost by processes other than those in which they provide sacrificial protection. HALS (and other stabilizers) may be copolymerized with PP to reduce mobility, as may be required in films. A mixture of low molecular weight stabilizer and polymer/bound stabilizer sometimes appears to be the best option. ^[58]

CONCLUSION

Bachelor thesis is engaged in the degradation of isotactic polypropylene and influence of its morphology on the extent of the degradation.

There are several types of degradation which more or less change the properties of the polypropylene. The activity of the microorganisms (biological degradation) is inconsiderable in comparison with thermic, termooxidative and mainly photooxidative degradation.

Termooxidative degradation leads to the deterioration of the mechanical and electrical features of the polypropylene. The termooxidative degradation causes serious damages of the material but the effect of that is suppressed using the material in certain temperature scale or by using different, temperature-resistant, materials.

Whereas the polypropylene is applied in ordinary conditions the act of the UV irradiation is irremissible. The photooxidative degradation manifests itself by the embrittlement of the material, surface cracks, the change of the color, the decrease of the mechanical features etc. The degradability of the polypropylene just as other semicrystalline polymers depends among other things on the spherulite size (physical structure). The current studies have shown that the photooxidative degradation is more pronounced for α -PP which contains larger spherulites than β -nucleated PP.

All these adverse attributes of polymeric materials are mitigated by using of various additives such as stabilizers.

Finally, it should be overall noted, that the research of ageing of the isotactic polypropylene, favourable polymeric material due to its low cost and good mechanical properties, is still in progress. The improving of its photostability has to lead to enlargement of its use outside.

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REVIEW OF SYMBOLS

PP	Polypropylene
iPP	Isotactic polypropylene
aPP	Atactic polypropylene
sPP	Syndiotactic polypropylene
α	Monoclinic crystalline phase
β	Trigonal crystalline phase
γ	Orthorhombic crystalline phase
α-iPP	Polypropylene containing mainly α -phase
β-iPP	Polypropylene containing mainly β -phase
ZN	Ziegler - Natta
T_c	Crystallization temperature [$^{\circ}\text{C}$]
T_m	Equilibrium melting temperature [$^{\circ}\text{C}$]
T_g	Glass transition temperature [$^{\circ}\text{C}$]
T^*_R	Critical recooling temperature [$^{\circ}\text{C}$]
$T(\beta\alpha)$	High-temperature $\beta\alpha$ -growth transition
$T(\alpha\beta)$	Low-temperature $\beta\alpha$ -growth transition
ρ	Density [kg/m^3]
SAXS	Small-angle X-ray scattering
WAXS	Wide-angle X-ray scattering
G_α	Growth rate of α -phase [s^{-1}]
G_β	Growth rate of β -phase [s^{-1}]
SMS	Supramolecular structure
M_r	Relative molecular weight
UV	Ultraviolet
IR	Infrared
E	Energy of radiation [J]
f	Frequency of radiation [$1/\text{s}$]

h	Planck's constant [J.s]
λ	Wavelength
HALS	Hindered amine light stabilizers

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