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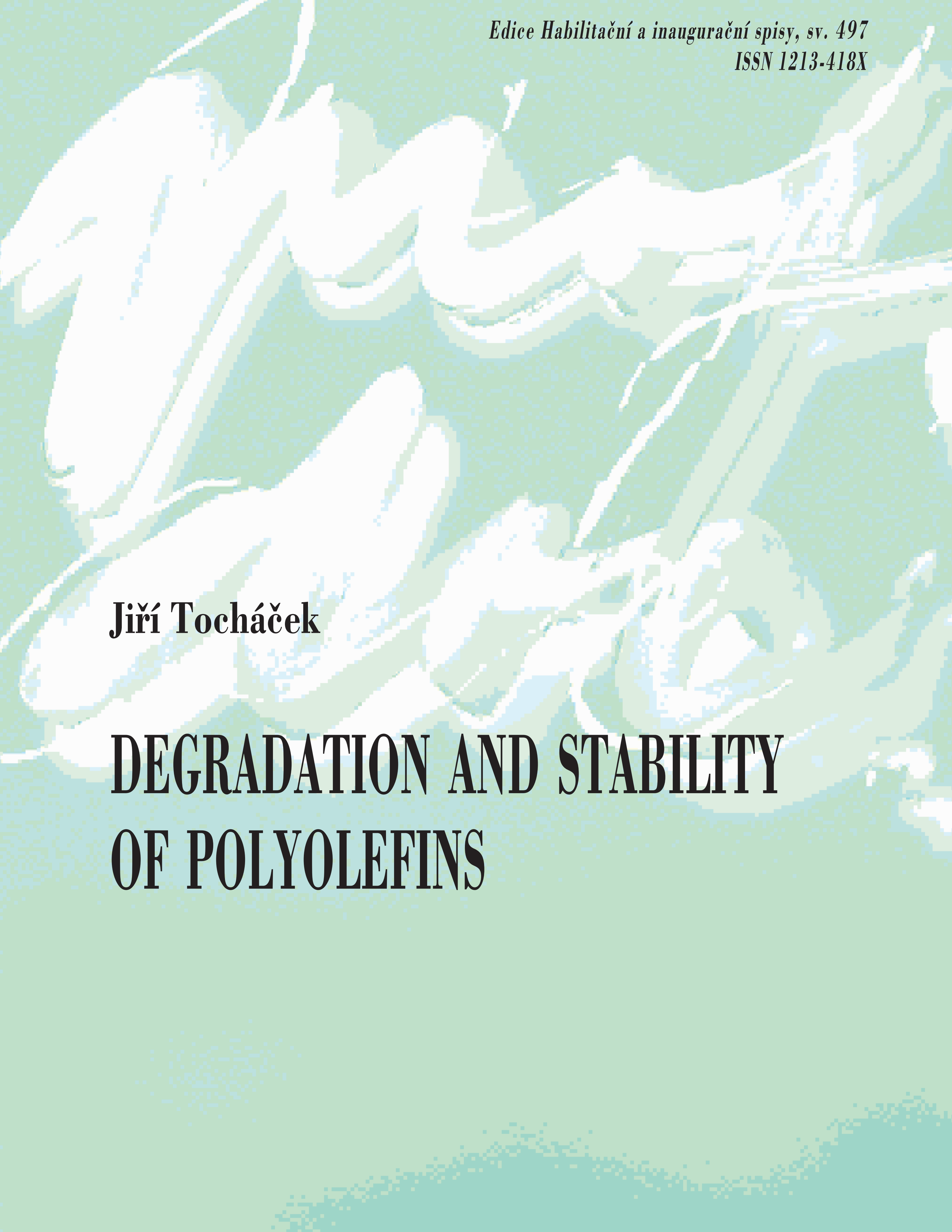

Jiří Tocháček

DEGRADATION AND STABILITY OF POLYOLEFINS

BRNO UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry
Institute of Materials Chemistry

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DEGRADATION AND STABILITY OF POLYOLEFINS

DEGRADACE A STABILITA POLYOLEFINŮ

Short version of Habilitation thesis
in Macromolecular Chemistry

VUTIUM

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KEYWORDS

Polymer, polyolefin, polyethylene, polypropylene, copolymer, degradation, thermo-oxidation, photo-oxidation, UV radiation, processing, extrusion, stabilization, stabilizer, antioxidant, accelerated ageing, life-time period, service life.

KLÍČOVÁ SLOVA

Polymer, polyolefin, polyethylen, polypropylen, kopolymer, degradace, termooxidace, fotooxidace, UV záření, zpracování, extruze, stabilizace, stabilizátor, antioxidant, akcelerované stárnutí, životnost.

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Zaměstnání

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Publikační činnost	11 záznamů na WOS, 82 citací (bez autocitací), h-index = 6 (aktualizováno 2/2015)

Výzkumná činnost	Uchazeč strávil většinu své profesní kariéry v aplikovaném výzkumu polymerů v Polymer Institute Brno (P.I.B.). Během této doby byl mimo publikovaných výsledků autorem nebo spoluautorem min. 36 výzkumných neveřejných zpráv, převážně z oboru aditivace a degradace polymerů a vývoje nových materiálů.
Projektová činnost	Mezi nejvýznamnější projekty, jejichž byl v P.I.B. manažerem, patřily “Stabilizers exudation from polyethylene and polypropylene“ projekt řešený pro Neste Chemicals Int. (Švédsko; nyní Borealis) v letech 1991-1992, “UV-masterbatch upgrade“ řešený pro Constab (Německo) v letech 1996-1998 a “Development of additive systems for UV-Protection of PE, PE/EVA films for agriculture with increased resistance to agrochemicals“ řešený pro Constab (Německo) v letech 2000-2002. K dlouhodobým projektům pak patří výzkumná činnost v oblasti vývoje aditivačních systémů a nových polymerních typů bázi HDPE a PP realizovaná pro Unipetrol RPA (dřív Chemopetrol Litvínov) v letech 1988-2008. Tato činnost byla součástí dlouhodobého výzkumného programu pokrývajícího přibližně třetinu rozpočtu instituce, uchazeč byl manažerem podprogramu – Aditivace a degradace PP a HDPE.
Grantová činnost	Na VUT v Brně byl členem řešitelských týmů projektů: Výzkumný záměr - Multifunkční heterogenní materiály na bázi syntetických polymerů a biopolymerů - MSM 0021630501 GAČR - Vliv tepelné historie na morfologii a lomové chování rázových kopolymerů polypropylenu 104/07/1631 Chempoint – vědci pro chemickou praxi CZ.1.07/2.4.00/12.0026 (jako koordinátor komunity PolymerPoint zorganizoval a řídil na fakultě chemické 6 kontaktních workshopů s firmami z českého průmyslu výroby a zpracování plastů) V rámci projektu SYLICA (FP7-REGPOT-2011-1) a ve spolupráci s MU zorganizoval mezinárodní Workshop “Polymer service-life: Estimation, durability and controlled performance“ (2014)

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Garant předmětu	MCO_DSA Degradace, stabilita a aditivace polymerů (FCh, CEITEC)
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Degradation and stability of polyolefins

1. Introduction

The polyolefins represent the most produced synthetic polymers of today. In the portfolio of synthetic plastics commercially produced, polyolefins reach nearly 70% of the overall world´s production. Polyolefins are almost represented by polyethylene (PE) and polypropylene (PP) grades, the production of which predominates over the niche olefin polymers, such as polybutylene-1, polyisobutylene, polymethylpentene and poly-α-olefins.

Polyethylene grades involve high-density polyethylene (HDPE; ρ= >0.940 g/cm^3), low-density polyethylene (LDPE; ρ = 0.910-0.940 g/cm^3), linear low-density polyethylene (LLDPE; ρ= 0.915-0.925 g/cm^3) and ultra-high molecular weight polyethylene (UHMWPE; ρ= 0.930-0.935 g/cm^3). Some grades such as MDPE (medium-density) and VLDPE (very-low density) are also defined. Polyethylenes, the melting point of which mostly ranges within 100-135 °C interval, are soft, flexible and easily processable by nearly all of the conversion technologies. They are most used in the packaging industry, but the spectrum of their applications is very broad, it varies from the few microns thick blown-films (HDPE), through injection-moulded consumer articles (LDPE, HDPE) up to the high-strength oriented fibres and artificial hip joints (UHMWPE). Polypropylene grades involve PP homopolymer and PP copolymers such as PP random copolymer and PP impact-copolymers, both with ethylene as co-monomer. Their melting points usually range within 155-170 °C. Polypropylene has also a very broad spectrum of use and since it is stiffer than polyethylene, beside packaging and consumer applications, it is also utilized as a construction material, especially in building and automotive industries.

Both PE and PP are the materials with very good physico-chemical properties – they are light, flexible, easily formable, resistant to non-oxidizing acids and bases and relatively cheap. That is why they became the most applied synthetic polymers of today. Their “high rated” properties, however, are ”not forever” and may be lost due to irreversible changes induced by environmental impacts, sometimes very easily and in relatively short periods of time.

2. Sensitivity to environmental impacts

Polymers utilized under the conditions of Earth´s troposphere are continuously attacked by many environmental impacts, varying in type, intensity and time, depending on the way, location and length of polymer application. Generally they may be as follows [1-10]:

1. Heat – in any of its form, during processing and/or during long-term exposure when applied
2. Light (UV+VIS+IR) – incident global solar radiation during outdoor application
3. Mechanical stress – mechano-chemical during processing or during end product application
4. Oxygen – present in the Earth´s atmosphere in any of its form (singlet, triplet, ozone)
5. Ionizing radiation (e.g. γ–rays)
6. Biological – selected types of bacteriae, fungi
7. Metal ions – catalyst residues, metal surfaces contacting polymer during the end use
8. Oxidizing chemicals – capable of oxidation of C-H bonds

In practice, usually at least two of these deteriogens attack polymer during its real existence. The development of polymeric materials capable of resisting these impacts and the ways of their testing were the major parts of the applicant´s research activities [T1-T23].

3. Mechanisms of polyolefins degradation

The chemical structure of polyolefin backbone is of a paraffinic nature and, thus, relatively sensitive to oxidation. The typical polyolefin chain features primary (CH_3-), secondary (-CH_2-) and tertiary (-RCH-) carbon functionalities, where especially the last one represent its most sensitive site [1,2].

Polyolefins degrade by means of a radical mechanism. If degradation is supposed to take place, initiation step has to precede. The most important factors capable of polyolefin initiation are heat, radiation (UV, ionizing) and mechanical stress. These deteriogens, acting either individually or simultaneously, usually cause homolytic splitting of C-H or C-C bonds in a hydrocarbon chain, giving rise to highly reactive alkyl radicals (C^*). According to the type of substitution, there may be defined primary, secondary and tertiary carbon radicals, differing in reactivity. Initiation is of a general scheme, where R stands for alkyl:

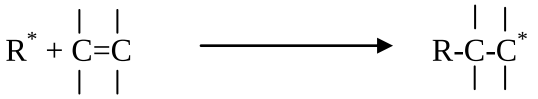
$$\begin{array}{l} \text{R-H} \\ \text{R-R} \end{array} \xrightarrow{\text{energy}} \begin{array}{l} R^* + H^* \\ 2\,R^* \end{array} \qquad (1)$$

If polymer initiation takes place in the surrounding atmosphere of oxygen, a fast reaction of alkyl radical with oxygen and a series of consequent propagation reactions follow:

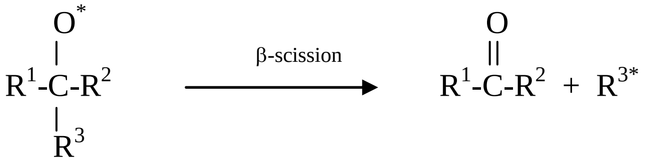
$$R^* + O_2 \longrightarrow ROO^* \qquad (2)$$

$$ROO^* + RH \longrightarrow ROOH + R^* \qquad (3)$$

$$HO^* + RH \longrightarrow H_2O + R^* \qquad (4)$$



$$R^* + \begin{array}{c} |\quad| \\ C{=}C \\ |\quad| \end{array} \longrightarrow R\text{-}\begin{array}{c} |\;\;| \\ C\text{-}C^* \\ |\;\;| \end{array} \qquad (5)$$



$$\begin{array}{c} O^* \\ | \\ R^1\text{-}C\text{-}R^2 \\ | \\ R^3 \end{array} \xrightarrow{\beta\text{-scission}} \begin{array}{c} O \\ \| \\ R^1\text{-}C\text{-}R^2 \end{array} + R^{3*} \qquad (6)$$

$$R^* \xrightarrow{\text{fragmentation}} \text{olefin} + R'^* \qquad (7)$$

Hydroperoxides ROOH formed in the propagation step are the most important intermediates of polyolefin radical scission. They are relatively sensitive both to heat and UV radiation and being homolytically decomposed, they cause chain branching responsible for the acceleration of degradation.

$$ROOH \longrightarrow RO^* + {}^*OH \qquad (8)$$

$$2ROOH \longrightarrow RO^* + ROO^* + H_2O \qquad (9)$$

When concentration of radical species in the system reaches up a certain level, the termination reactions between particular radicals become important.

$$R^{*} + ROO^{*} \longrightarrow ROOR \tag{10}$$

$$R^{*} + R^{*} \longrightarrow R\text{-}R \tag{11}$$

$$R^{*} + RO^{*} \longrightarrow R\text{-}O\text{-}R \tag{12}$$

$$2R^{*} \longrightarrow RH + \text{olefin} \tag{13}$$

$$2ROO^{*} \longrightarrow \text{ketone} + \text{alcohol} + O_2 \tag{14}$$

The degradation of polyolefins is a complex of subsequent radical reactions, where hydroperoxides, as degradation intermediates, play a crucial role [11-16]. As to the kinetics, three different phases may be described. An initial phase, also called an induction (or inhibition) period, where consumption of oxygen is moderate and hydroperoxide formation is low. Reaching a certain level of hydroperoxides, degradation is auto accelerated and oxygen consumption rapidly grows. In the third phase degradation rate slows down again due to termination, however, still continues, if there is enough substrate and access to oxygen. From the viewpoint of reaction kinetics and practical use, plastics products may successfully serve only during the induction period. When degradation rate is accelerated, usually the rapid loss of physical properties follows.

Mechanism of polyolefin degradation was intensively studied in the 60-ies and 70-ies of the last century. Based on its knowledge, critical points in the degradation process could be defined and the ways how to moderate the deteriorative radical scission were proposed and applied for stabilization [1,2,11-16].

4. Polymer protection and performance of stabilizer systems

The chemical structure of polyolefins is relatively vulnerable in terms of oxidation. Its sensitivity is increased by the traces of highly efficient catalyst systems (e.g. chromium, Ziegler-Natta, metallocene) remaining in ppm levels in the polymer matrix after polymerization [17-19]. Moreover, most of polyolefins leave the reactor in the form of a coarse fluff, with a relatively high specific surface allowing a good access to atmospheric gases, especially oxygen. All these factors cause that most polyolefinic grades must be additivated with efficient stabilizer systems before they leave the production unit. In most of technologies, stabilizers and other additives are dry blended with fluffy polymer and then converted into pellets. The presence of stabilizer system helps to prevent the loss of the original physico-chemical properties both during processing and subsequent application.

Stabilizers applied in synthetic polymers are of different chemical structures, dependent on the mechanism of action and site, where they enter and compete with the deteriorative processes. The following structure types are used [2,19]:

a) Hindered phenolics (primary antioxidants)
b) Organic phosphites (secondary antioxidants)
c) Thiostabilizers (secondary antioxidants)
d) UV absorbers (light stabilizers)
e) HALS (Hindered Amine Light Stabilizers)

According to the type of application, stabilizers may also be considered as processing and long-term acting. The role of processing stabilizers is the protection of polymer in melt during processing, usually extrusion, which is characterized by high temperatures (200-320 °C), increased mechanical stress and short exposure times (seconds to minutes). On the other hand, long-term acting stabilizers perform in the solid matrix, under the conditions of lower temperatures (up to 100 °C) and long-term periods of exposure (months to years). Despite this division has commonly been accepted and used, it is not fully rigorous, because some of the stabilizers act both as processing and long-term as well [3,19].

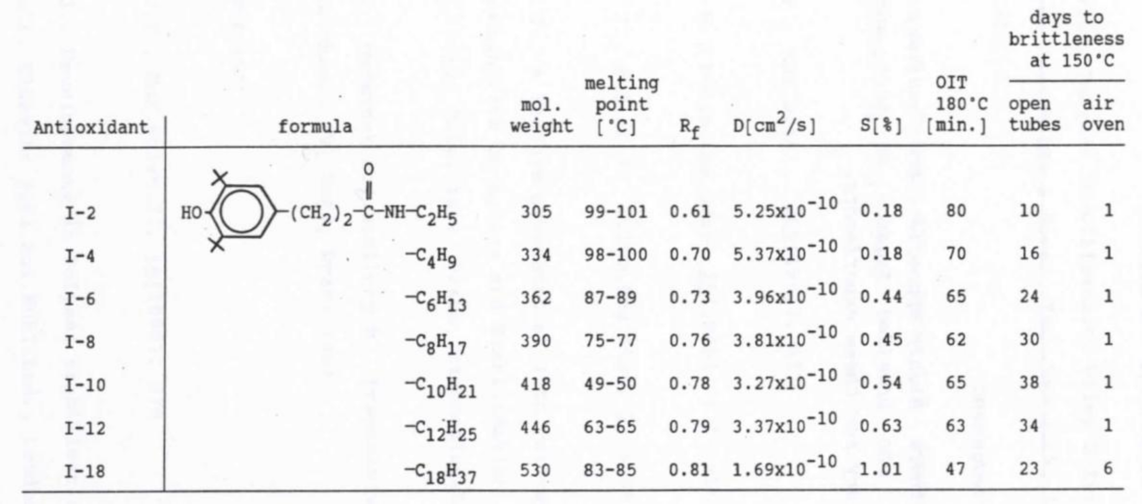
The core of applicant´s professional activity was the investigation of polymer degradation and the ways of its deceleration. He spent whole his previous professional career in Polymer Institute Brno, a specialized research facility dealing with the basic and applied research of polymers, especially polyolefins. The majority of results in applied research were mostly attained on a contract base, what did not allow publication in any way. The results submitted herewith, however, are those attained in other ways and, thus, may have been released in the public papers. Author´s most important deal in the branch was the contribution into the polymer protection and stabilization chemistry [T1-T8].

4.1 Hindered phenolic antioxidants

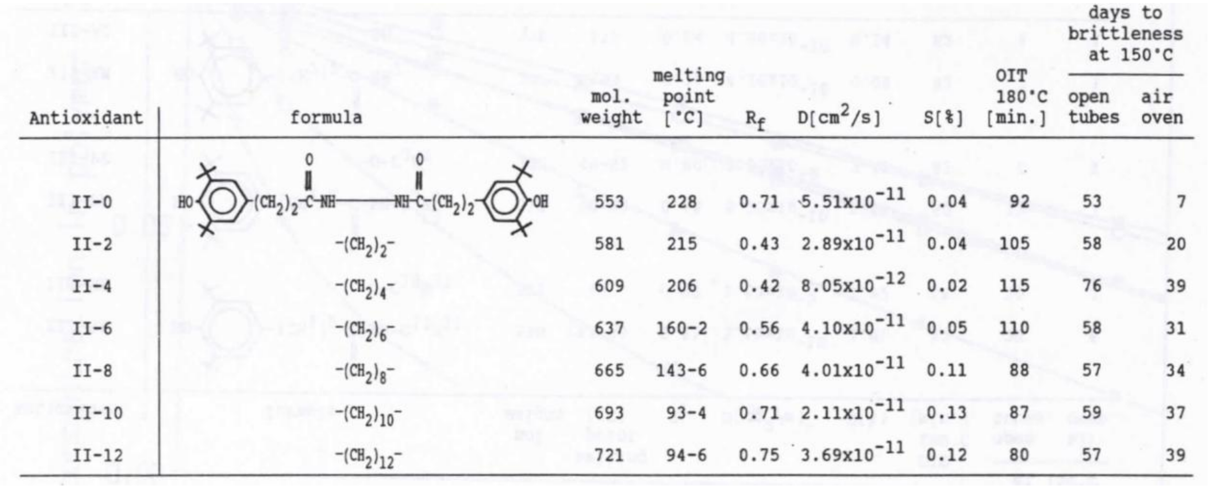
The prevailing majority of papers in literature deal with the investigation of stabilizers performance from the view-point of chemical reactivity [1-4, 20-24, 26-33]. Much less attention was given to the stabilizer physical behaviour within the polymer matrix, where the physical phenomena like diffusion, solubility, extraction and volatilization play an important role and basically influence the stabilizer performance as well [25,34-39]. One of the earliest applicant´s contributions to this field was the synthesis and investigation of the primary phenolic antioxidants having the same active 2,6-di-tert-butyl-phenol moiety, but different substitution in 4-position of phenol, denoted as “secondary structure”. Different variations in the secondary structure shown in Table 1 provided homological series, upon which the effect of molecular weight on stabilizer efficiency in polymer was investigated [T1, P1-7, P9, P11].

The performances and behaviour of the synthesized structures were tested in isotactic polypropylene by means of the long-term heat ageing in open test tubes (LTHA 150 °C), air-draft oven (HORO 150 °C), oxygen induction time (OIT 180 °C), diffusion coefficients and solubilities (80 °C), retardation factors (R_f) and monitoring the loss of stabilizers from the matrix due to volatilization at 150 °C. A correlation of the data attained with the secondary chemical structure modified by substituents was sought.

Table 1 Structures of hindered phenols based 2,6-di-tert-butyl-phenol functionalities substituted in 4-positon and their properties [T1].



Antioxidant	formula	mol. weight	melting point [°C]	R_f	D[cm^2/s]	S[%]	OIT 180°C [min.]	days to brittleness at 150°C	
								open tubes	air oven
I-2	$HO-C_6H_2-(CH_2)_2-\overset{O}{\overset{\|}{C}}-NH-C_2H_5$	305	99-101	0.61	$5.25x10^{-10}$	0.18	80	10	1
I-4	$-C_4H_9$	334	98-100	0.70	$5.37x10^{-10}$	0.18	70	16	1
I-6	$-C_6H_{13}$	362	87-89	0.73	$3.96x10^{-10}$	0.44	65	24	1
I-8	$-C_8H_{17}$	390	75-77	0.76	$3.81x10^{-10}$	0.45	62	30	1
I-10	$-C_{10}H_{21}$	418	49-50	0.78	$3.27x10^{-10}$	0.54	65	38	1
I-12	$-C_{12}H_{25}$	446	63-65	0.79	$3.37x10^{-10}$	0.63	63	34	1
I-18	$-C_{18}H_{37}$	530	83-85	0.81	$1.69x10^{-10}$	1.01	47	23	6



Antioxidant	formula	mol. weight	melting point [°C]	R_f	D[cm^2/s]	S[%]	OIT 180°C [min.]	days to brittleness at 150°C	
								open tubes	air oven
II-0	$HO-C_6H_2-(CH_2)_2-\overset{O}{\overset{\|}{C}}-NH-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_2-C_6H_2-OH$	553	228	0.71	$5.51x10^{-11}$	0.04	92	53	7
II-2	$-(CH_2)_2-$	581	215	0.43	$2.89x10^{-11}$	0.04	105	58	20
II-4	$-(CH_2)_4-$	609	206	0.42	$8.05x10^{-12}$	0.02	115	76	39
II-6	$-(CH_2)_6-$	637	160-2	0.56	$4.10x10^{-11}$	0.05	110	58	31
II-8	$-(CH_2)_8-$	665	143-6	0.66	$4.01x10^{-11}$	0.11	88	57	34
II-10	$-(CH_2)_{10}-$	693	93-4	0.71	$2.11x10^{-11}$	0.13	87	59	37
II-12	$-(CH_2)_{12}-$	721	94-6	0.75	$3.69x10^{-11}$	0.12	80	57	39

Systematic approach in this field has shown, that in contrast the structure of stabilizer active moiety being the same, the increasing size of aliphatic chain in phenol 4-position visibly impacted the overall stabilization efficiency. The chemical efficiency expressed by OIT 180 °C values attained in polymer melt was changed only in a limited extent, LTHA and HORO 150 °C, carried out with solid polymer, differentiated individual structures very well. There was found no expected linear or direct dependence of performance on molecular weight. In series-I, LTHA maximum performance at 418 and in series-II at 609 mol. wt. were observed. It followed that with increasing molecular weight and molecule lipofility, the solubility in non-polar polymer matrix was enhanced, while the tendency to physical loss due to volatilization was decreased. Superposition of these factors caused that within each row, some kind of their optimum combination induced the increased stabilization performance at a certain interval of molecular weights. We have observed similar phenomena also with another series, where a very good fit of performance maximum to permeation constant (P) at molecular weight 500-550 was attained [T2, 25, 37].

$$P = D_T \text{ x } S_T \tag{15}$$

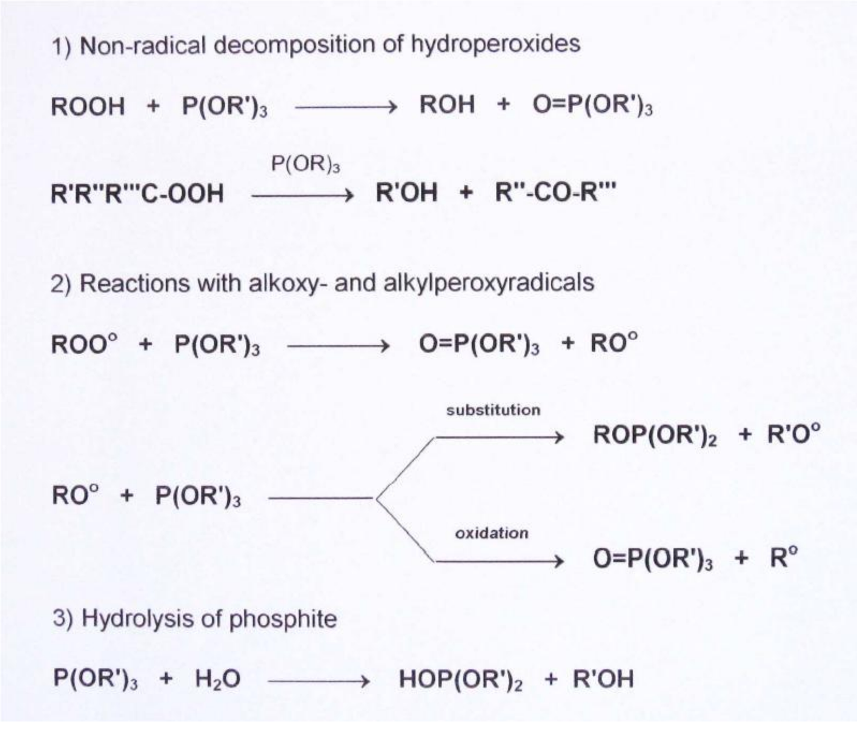
P …. permeation constant,
D_T …. diffusion coefficient at temperature T
S_T …. solubility in polymer at temperature T

In other paper published later it was shown that from the viewpoint of processing stability, when phenolic antioxidant performs in polymer melt (PP), the size of secondary structure plays a marginal role and the only effect is the "dilution" of molar proportion of 2,6-DTBP functionality by the remaining part of the molecule [T3].

Hence, considering the antioxidant performance in solid polymer, it was confirmed that there were especially the "non-chemical" phenomena stemming from the molecular structure, which control the stabilizer overall performance [T1-T5,40,41]. Applicant´s work provided fair explanations why some commercial stabilizers considerably differ in performances in semicrystalline polymers, like e.g. polyolefins, despite they have the same chemically reacting functionalities even at similar molar proportion. Some of the newly attained facts were applied in practice later, in the applied research carried out for Chemopetrol Litvínov, the only one Czech polymer producer (HDPE 300 kT/year, PP and copolymers 250 kT/year) [42]. An important part of applicant´s professional activity at Polymer Institute Brno up to 2008 was designing and developing the stabilizer and additive systems for the Chemopetrol production plant, both for HDPE and PP grades. Many of the formulations have still been in use at today´s Unipetrol RPA.

4.2 Organic phosphites

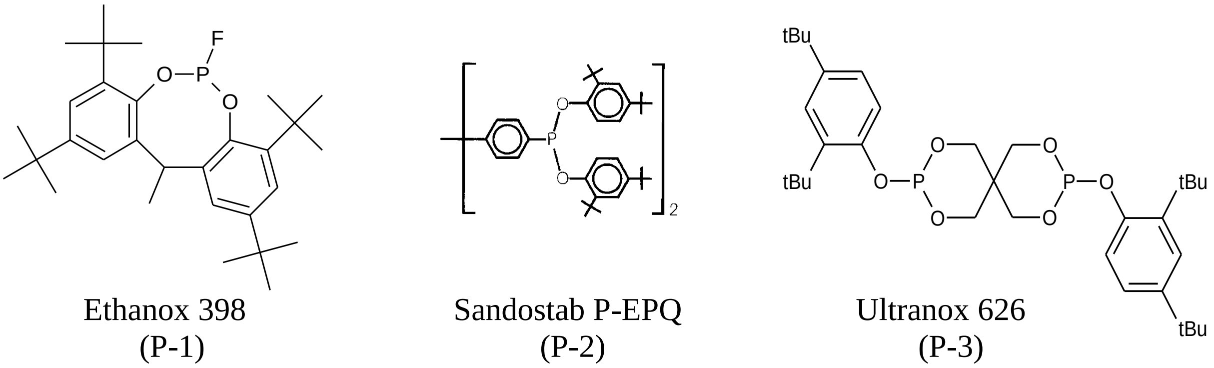
Another portion of applicant´s activity was focused to the investigation of mechanism of action and relationships between the structure and performance of organic phosphites. Currently, numerous organic phosphites are commercially available and used in the plastics industry. Phosphites act as efficient secondary processing stabilizers and in synergy with phenols, they provide powerful protective systems for polymers [43-51]. The performance of phosphites varies with structure. Beside the phosphite P^{3+} functionality, responsible for the main stabilizing mechanism – hydroperoxide non-radical decomposition, it is the secondary structure, which considerably impacts the performance as well. In general, phosphites may possibly react with oxidative degradation intermediates by means of three mechanisms, Scheme 1.



Scheme 1 Possible mechanisms of protective action of organic phosphite in polymer

It has been known, that phosphites more sensitive to hydrolysis are less stable during storage and during polymer processing often induce unwanted phenomena such as screen plugging or die drool, what limits their practical application. On the other hand, some of them, exhibit increased efficiency compared to the non-hydrolyzable ones.

Applicant was leading his research within the series of organic phosphites with a special attention to bis(2,4-di-t-Bu-phenyl)pentaerytrhrityl diphosphite (P-3), commercially known as Ultranox 626, which was launched by General Electric as a brand new product in the nineties. P-3 was found extremely efficient in polyolefins and its structure became the object of intensive investigations [T6-T8].



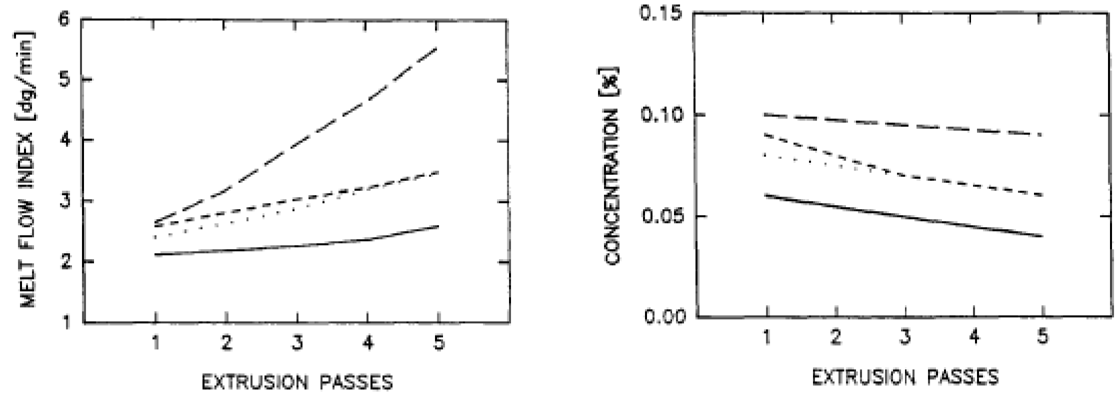
Ethanox 398
(P-1)

Sandostab P-EPQ
(P-2)

Ultranox 626
(P-3)

Figure 1 Structures of typical organic phosphites acting as secondary stabilizers (P-1 non-hydrolyzable, P-2 semi-hydrolyzable, P-3 hydrolyzable)

The investigations of P-3 were carried out together with 2,2′-Ethylidene-bis(4,6-di-tert-butylphenyl)fluorophosphite (P-1), tris(2,4-di-tert-butylphenyl)phosphite (P-4) and P,P′-distearyl pentaerythritol diphosphite (P-5). The processing performances were evaluated under the conditions of multiple extrusion in a laboratory twin-screw equipment in blends with a hindered phenol synergist – tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]methane (AO-1) in isotactic polypropylene.



a) Polymer melt viscosity during processing

b) Phosphite consumption rate

Figure 2 Processing stability of PP during multiple extrusion on a single-screw machinery Brabender extruder 19mm, L/D=30 at 260 °C/100 rpm; Formulation: 1000 ppm AO-1, 1000 ppm phosphite and 1000 ppm CaSt

P-1 --------- P-3_________ P-4 . . . . P-5 - - - - - - -

The performances of individual phosphites were correlated with structural features such as the molar proportion of trivalent P, presence of hindered phenolic functionality in the molecule and sensitivity towards hydrolysis. It was found that the high performance of P-3 may be accounted for its ability to perform efficiently via all the three mechanisms shown in Scheme 1. Higher reactivity of hydrolyzable phosphite leads also to its faster consumption and its "sacrification" in favour of a phenol, intended to remain in polymer after processing and act as the long-term stabilizer. Other phosphites, despite having the basic trivalent P functionalities, either did not possess suitable hindered phenolic functionality (P-5) or were not able to efficiently release it (P-1, P-4). In such cases, their stabilization efficiencies could reach only a limited level [T6].

Apart from this, it was revealed that the certain degree of P-3 hydrolysis positively contributed to its processing performance, which was increasing up to 7% of free 2,4-di-tert-Bu-phenol (2,4-DTBP) in P-3. Similarly, a certain increase in the long-term heat ageing efficiency (LTHA) was observed as well. The study of P-3 hydrolysis mechanism has shown that during the initial phases of hydrolysis preferably P-O_{phenol} bond is splitted and the maximum level of free 2,4-DTBP is released, Figure 3. Likely exhibiting some kind of "cage" effect while being released, 2,4-DTBP provides additional synergy with P^{3+} functionality and thus, significantly contributes to the P-3 overall performance [T7].

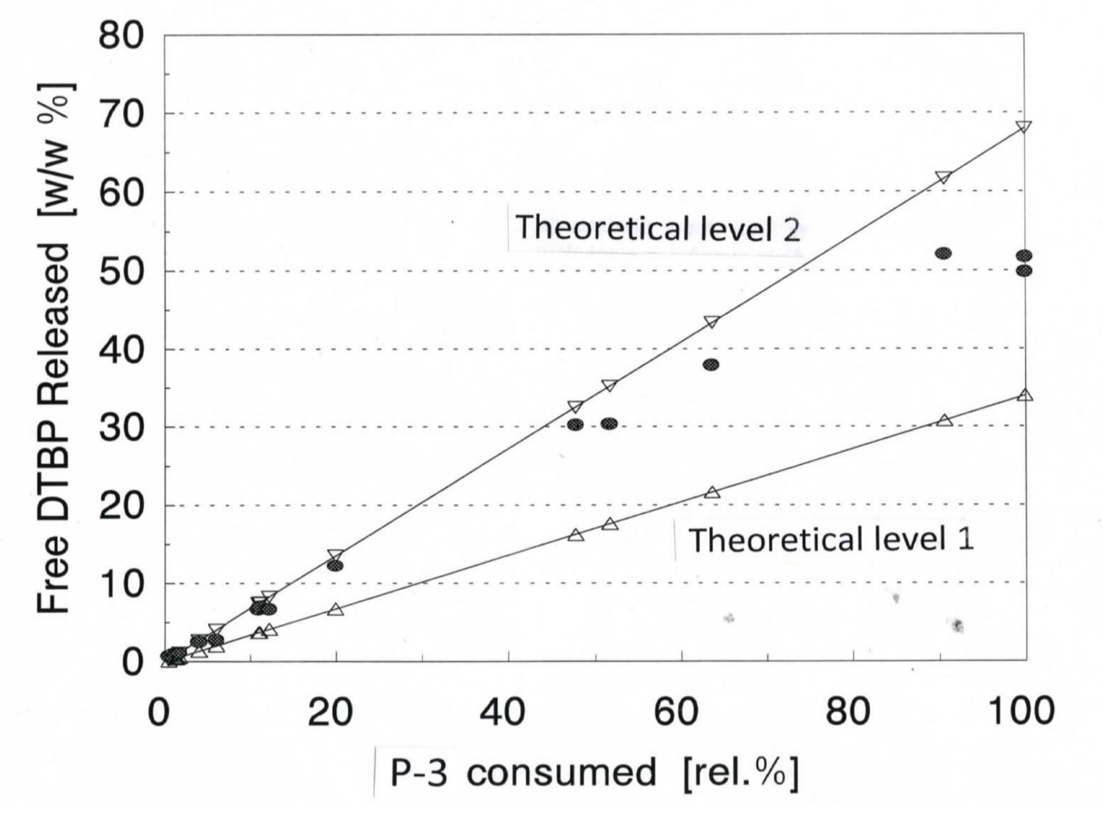
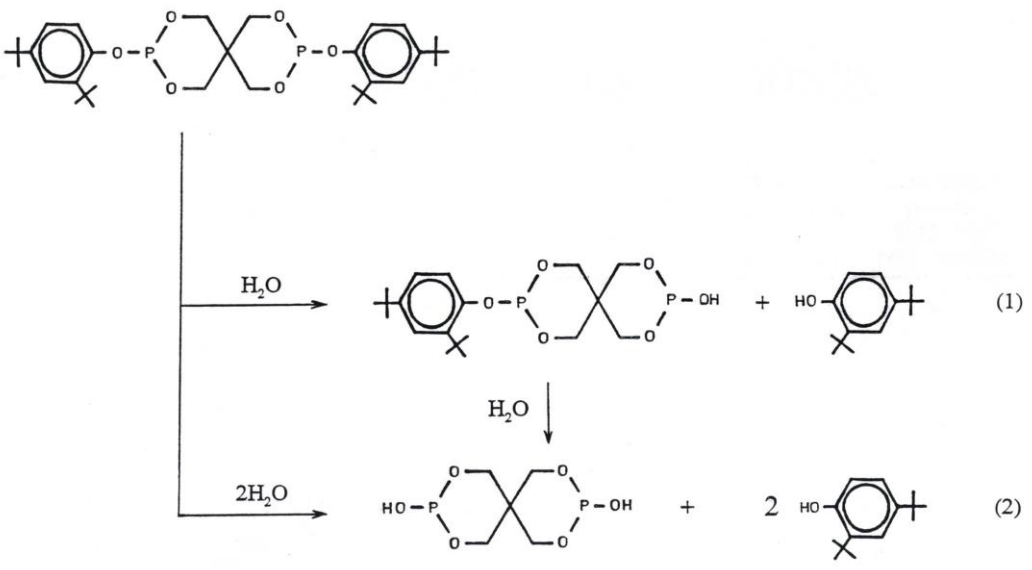


Figure 3 Formation of 2,4-DTBP during P-3 hydrolysis allowing the proposal of hydrolysis mechanism during the initial period (black marks = experimental).
Theoretical levels 1 and 2 are given by stoichiometry, where one or both 2,4-DTBP moieties are released during P-3 conversion.



The papers published by applicant contributed to the better understanding of mechanism of organic phosphites action. They showed that the phosphite performance is rather complex, not limited to one single mechanism and the role of secondary structure in the stabilization process is crucial [T6-T8].

5. Degradation and processing stability of polypropylene impact copolymers (ICPP)

ICPP are heterogeneous materials consisting of bulk PP homopolymer phase in which rubbery domains consisting of PE-homo and PE-PP random copolymer are statistically embedded. Such systems exhibit properties superior to PP homopolymer, e.g. higher impact resistance, especially at temperatures well below zero (°C) [52-56].

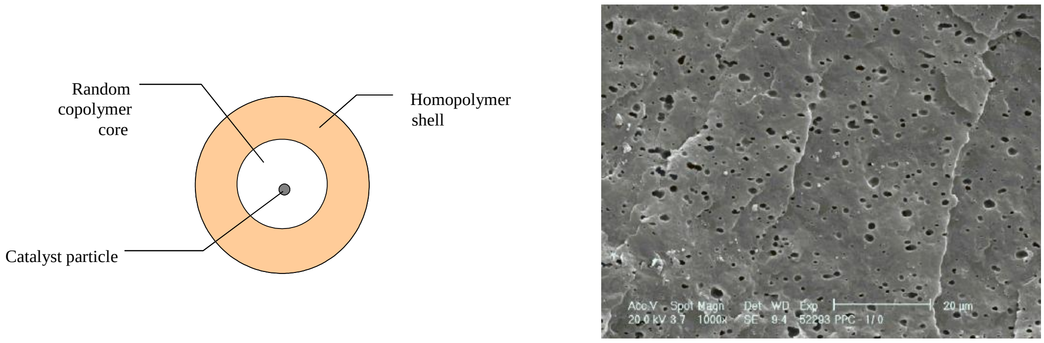


Figure 4 PP-impact copolymer – a model of original reactor particle and the SEM image of the real solid matrix after melt-processing.

The rubbery inhomogeneities and their interphases, despite providing improvement in toughness may act as points of thermo-oxidative instability. Several applicant´s papers were focused to ICPP degradation during processing and investigations of the related phenomena [T9-T14]. The results of the detailed studies using GPC analyses, SEM microscopy, FTIR, SSA, DSC analyses, preparative TREF analysis and successive solvent extraction techniques could have been summarized with conclusions, that processing of non-stabilized and commonly stabilized ICPP

irreversibly degrades both homopolymer (amorphous and crystalline) and rubbery phases. The biggest changes were observed in PP homopolymer phase, where the chain scission resulting in the drop in molecular weight was observed. In the rubbery PE-PP phase a certain degree of crosslinking was found. The changes in PP homo phase resulted in the decreased melt viscosity, while crosslinking lead to the partial drop in impact strength (Charpy at +23°C). Comparing the processing stabilities of the commonly available commercial grades, between ICPP and PP homopolymer no special difference in melt behaviour was found.
The ICPP processing stability may vary with the kind of technology, by which they were produced. In three PP impact copolymers produced by different polymerization technologies such as Innovene (INN), Spheripol (SPH) and Unipol (UNI), degradation due to processing was investigated as well. Processing stability under the conditions of multiple extrusion on a semi-pilot plant equipment at 220°C/200 rpm (Figure 5) provided the ranking as follows:

SPH > UNI ≥ INN

Where, SPH stands for the relatively most stable and INN for the least stable polymer.

Processing stability was correlated with the matrix composition. Using the analytical methods such as ^{13}NMR, DSC, GPC and SEM/EDX many structure parameters were determined. Direct dependence of processing stability, however, was found only on the Mg/Ti and Al/Ti molar ratios, the so called “catalyst parameters”, which reflected the reactivity of the catalyst active site. The traces of highly reactive Ti^{4+} ions originating from the catalyst system (catalyst residues) act as efficient prodegradants and seem to be the main factor responsible for the different sensitivities of ICPPs produced by different polymerization technologies. The protective stabilizer system used in this series was more efficient than that used in the previous experiments, so that the deterioration was well observable only in the PP homopolymer phase, crosslinking in the rubbery phase was not indicated (minimum differences in Charpy impact strength at +23 °C between 1st and 5th extrusion) [T13].

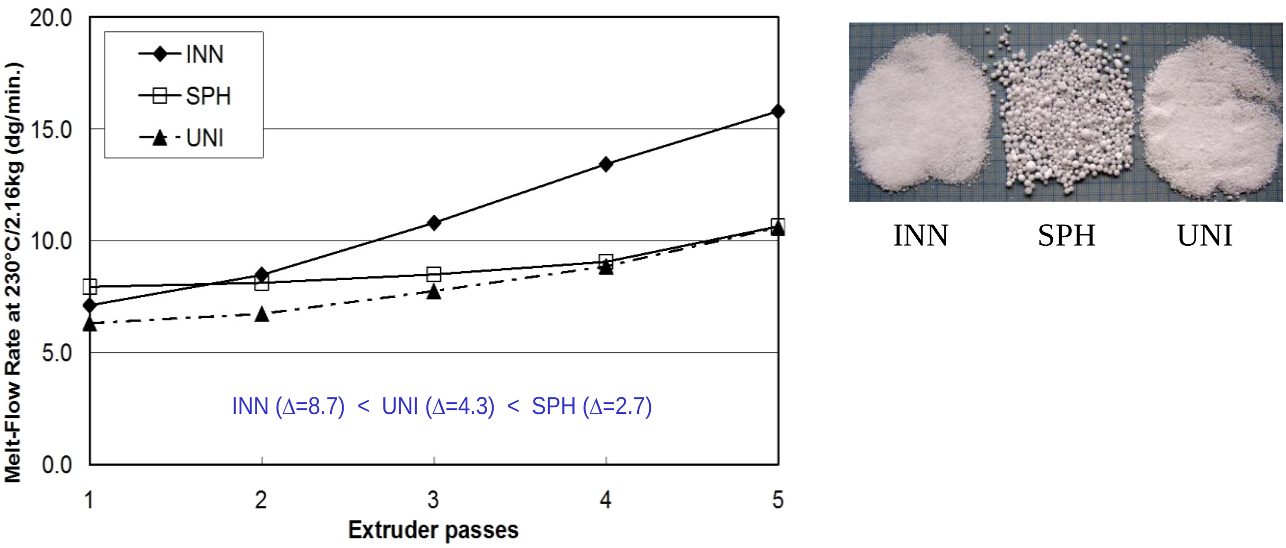
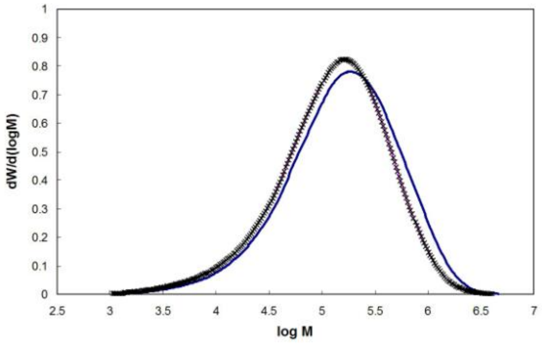
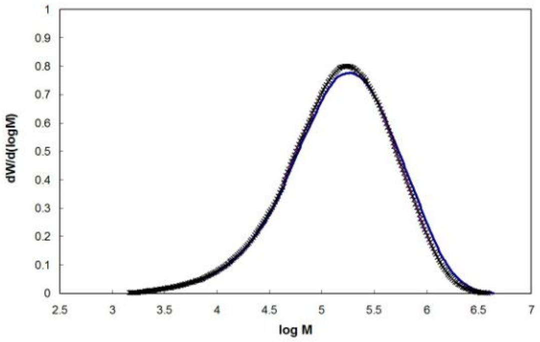


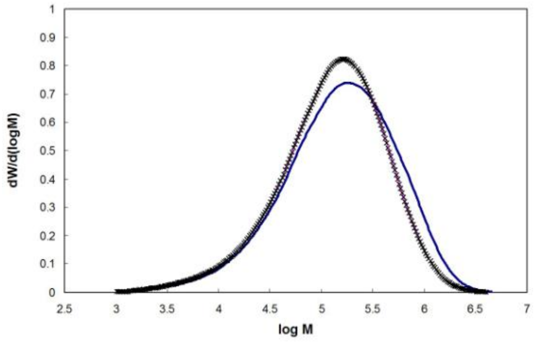
Figure 5 Processing stability of ICPPs tested by multiple extrusion on a twin-screw extruder W&P ZSK25 at 220 °C/200 rpm
Formulation: 400 ppm AO-1, 800 ppm P-4, 200 ppm DHT-4A and 200 ppm Cast



INN	M_n	M_w	M_w/M_n	Intrinsic viscosity (dl/g)[GPC]
1st extrusion	65 000	287 000	4.4	1.63
5th extrusion	53 000	228 000	4.3	1.32
Δ =	**12 000**	**59 000**	**0.1**	**0.31**



SPH	M_n	M_w	M_w/M_n	Intrinsic viscosity (dl/g)[GPC]
1st extrusion	66 000	286 000	4.3	1.71
5th extrusion	63 000	261 000	4.1	1.56
Δ =	**3 000**	**25 000**	**0.2**	**0.15**



UNI	M_n	M_w	M_w/M_n	Intrinsic viscosity (dl/g)[GPC]
1st extrusion	59 000	289 000	4.9	1.72
5th extrusion	48 000	243 000	5.0	1.48
Δ =	**11 000**	**46 000**	**0.1**	**0.24**

Figure 6 Molecular weight distributions of ICPPs after 1st and 5th extrusion on a twin-screw extruder at 200 °C/200 rpm

6. UV-stability and accelerated ageing

6.1 Correlation between accelerated ageing and outdoor exposure

Polyolefins, as well as other polymers, are during their service life exposed to the environmental impacts, which, due to their energetic nature, may basically affect their physico-chemical characteristics. Beside heat and atmospheric oxygen it is especially the UV portion of incident solar radiation, which induces irreversible changes in the polymer backbone [57-59]. Despite the solar radiation is filtered by atmosphere, its portion of 295-400 nm wavelengths, representing the part of UV-B and full UV-A range, is critical for many polymers. When testing polymers and their protective systems for outdoor applications, its simulation by means of accelerated tests is mandatory [60-63]

Applicant has long years been involved in the investigation of polyolefin performance under the conditions of outdoor exposure, proposed for application at various locations of the planet. His extended work in the qualified prediction of polymer service life consisted in generating the accelerated tests data, calculating the incident radiation energy balance and correlating the data with the chemical structure, composition and morphology of the material. Beside the incertitude - where, how and how long the plastics end product will be used, there also exist some system error of the presently used accelerated ageing techniques. It stems from the differences in spectral power distribution of radiant flux of commonly used light sources, compared to the incident outdoor solar radiation [64-71]. Presently most used light sources are xenon, fluorescent and carbon-arc [64]. Despite only the filtered xenon light source provide the best fit to the solar radiation, the latter two are also used and sometimes required even by some international standards [64, 67]. A comparison of suitability of individual techniques was an indivisible part of applicant´s activity in this field [T15,T17,T18].

Within the years 1994-2008 the applicant realized extended experimental activities in the field of accelerated ageing, carried out as parts of both domestic and foreign research contracts. Topics like designing new formulations, developing new materials, quality check or elucidation of material failure were the most common. Beside the profit of contract research itself, the experience acquired in this way was also utilized in the foundation of the small-scale production of stabilizer concentrates MAKROSTAB^{TM}, the production of which at P.I.B. has proven itself sustainable and exists up to now. The applicant was not only its founder, but provided especially the scientific background for the customer solutions up to 2008 [T16,72,73].

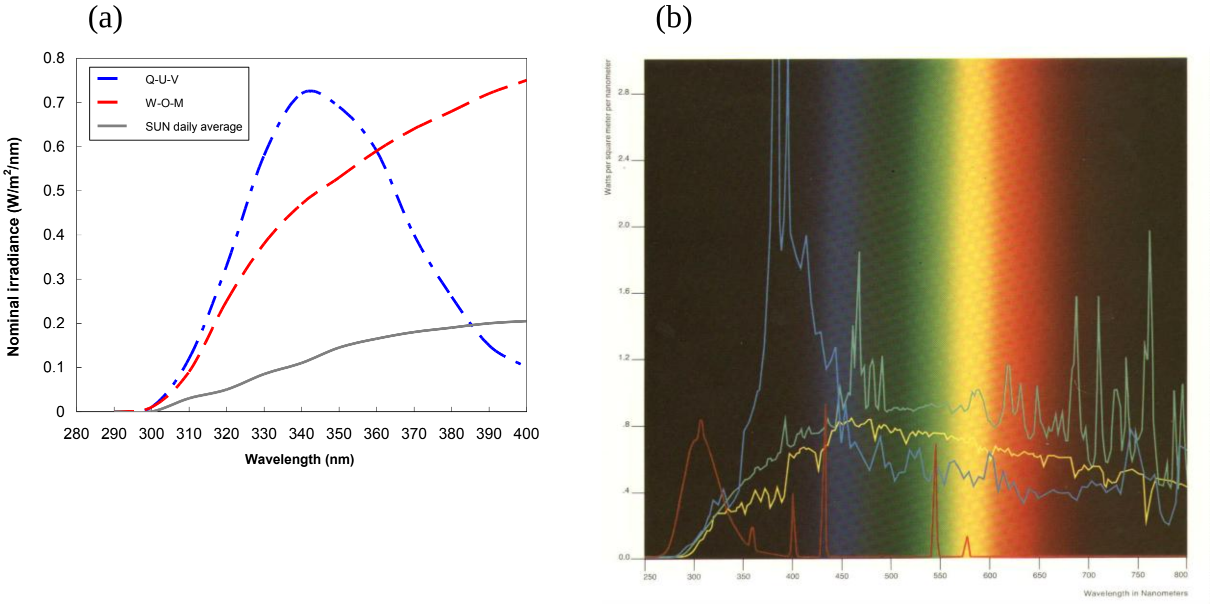


Figure 7 Distribution of spectral intensity (a) 295-400 nm range (TUVR) – comparison of artificial UV sources utilised for accelerated testing and UV portion of global solar radiation (diurnal+nocturnal average); (b) comparison of artificial UV sources and global noon solar radiation (middle Europe) in 250-800 nm UV+VIS range (curves: yellow stands for the solar radiation, red for UVB, green for filtered xenon, blue for carbon arc)

In the papers open to the public, the author contributed to the knowledge of sophisticated relationship between the outdoor and accelerated ageings [T15, T17, T18, 60-63]. With the selected materials aged to the same degree of deterioration, instrumental techniques such as Weather-Ometer Ci3000 using the Xe light source, Q-U-V tester (UV-A light source) and outdoor exposure were used and correlated. Reaching the different times to degradation at different temperatures of ageing, the absorbed radiant energies were found the only tool of comparison.

Independent of ageing temperature, the best relationships were observed between the W-O-M and mid-Eu outdoor exposure, where the incident energies in TUVR range needed for the same degree of deterioration were more or less comparable.

Under the conditions of Q-U-V tester using the fluorescent light source with an intensive maximum at 340 nm (UV-A light source) and decreased intensity at the upper part of 300-400 nm range, polymer deterioration was always reached much faster. In this case any rigorous correlation with the other ways of ageing was not found. It was accounted for the specificity of the Q-U-V spectral distribution, having higher irradiance especially at the lower end of the TUVR interval, coinciding with the PP activation spectra at 300, 330 and 370 nm. Here the catalyst residues based on Ti^{4+} (ε_{310nm}>1000 $Lmol^{-1}cm^{-1}$) and hydroperoxides with a high quantum yield of their homolysis ($Q^y \rightarrow 1$) absorb and promote polymer degradation [19]. High acceleration factors 25-31 reached with Q-U-V are irrational and cannot be used for the service life prediction in any case. Acceleration factors 5-8 reached with the xenon source are more rigorous and more reliably reflect the reality. Calculations of TUVR radiant energies needed for degradation are the most important parameters utilized for the polymer service life prediction. The interpretation, however, must be done with caution, because the calculated value may be considerably diminished, when polymer is in contact with water, organic solvents, chemical pollutions, exposed to elevated temperatures or mechanically stressed. Despite these factors in many cases may be quantified, the importance of their particular contribution to the overall rate of polymer degradation is still the matter of discussion (and still long time will be) [T15,T17,T18].

Beside the commonly used classical instruments, such as W-O-M and Q-U-V, applicant was involved in the introduction of a new instrumental technique – Q-Sun Xe-1 (Xe-light source; Q-Lab Ltd.) [74-76]. He introduced this instrument to Polymer Institute Brno, as one of the first units imported in the Czech Republic. Later on, he described its performance and advantages in many corporate reports and one public paper [T18].

Table 2 PP homopolymer degradation – outdoor exposure vs. accelerated ageing
Spun-bond non-woven textile 17g/m^2, PP Mosten 56.915 (MFI=27 dg/min.; 230 °C /2.16 kg)
Additivation: basic processing, no UV
Criterion of failure: loss of integrity in cross-direction

Settings: Q-U-V: IRR 0.72W/m^2@340nm, 20 hrs IRR at 50 °C, 4 hrs condensation dark cycle at 40 °C
W-O-M: IRR 0.47W/m^2@340nm, BST=65 °C, RH=70±3 %, 102/18 min. light/light+wet cycles
Outdoor exposure in Brno (CZ), mid-Eu climate, ~ 84 kLy/year

Ageing	Exposure time (hours)	Radiant energy (MJ/m^2)		Acceleration factor
		TUVR 295-400 nm	GLOBAL 295-3000 nm	
Q-U-V	79	11.1	→TUVR	7.6
W-O-M	124	23.7	n.a.	4.8
Outdoor exposure	600	26.1	435.5	1

Table 3 PP homopolymer degradation – outdoor exposure vs. accelerated ageing
Oriented slit-tape 1330 dtex, PP Mosten 58.512
Additivation: basic processing + 1500 ppm HALS
Criterion of failure: 50 % loss in tensile strength

Ageing	Stabilization	Exposure time	Radiant energy (MJ/m^2)		Acceleration factor
			TUVR 295-400 nm	GLOBAL 295-3000 nm	
Outdoor exposure	HALS-1	19.6 months	380	6326	1
	HALS-2	17.8 months	366	6104	1
Q-U-V	HALS-1	~ 457 hours	64.5	→ TUVR	31
	HALS-2	~ 515 hours	72.6	→ TUVR	25

Settings: Q-U-V: IRR 0.72W/m^2@340nm, 20 hrs IRR at 50 °C, 4 hrs condensation dark cycle at 40 °C
Outdoor exposure in Brno (CZ), mid-Eu climate, ~ 84 kLy/year

6.2 Property selection and polymer failure definition

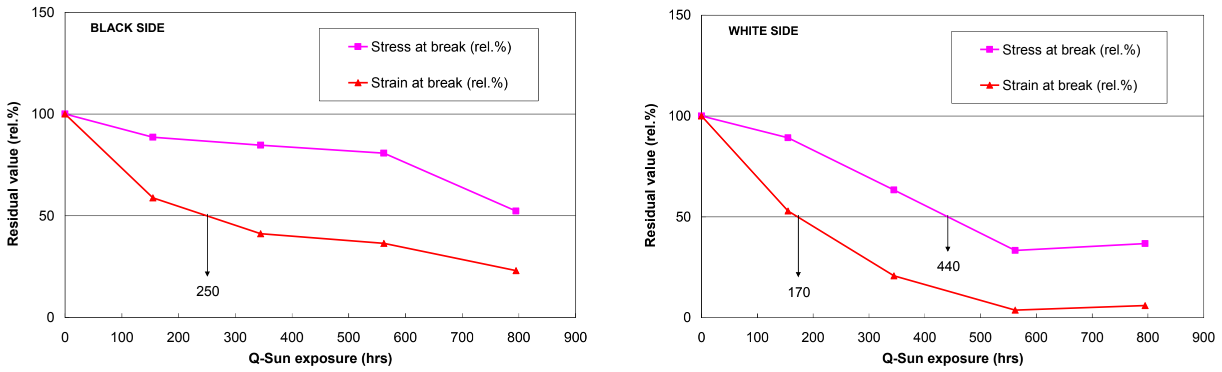
Nearly all the research activities in polymer stabilization chemistry are in their consequences directed to the determination of the length of polymer service life. The demands may vary according to application, in some cases they may strive for the maximum length [P13], in other cases only a limited period of time is demanded [P12]. In any case, the selection of property parameter, which is measurable and sufficiently reflects the degree of deterioration, is crucially important. The definition of the point when polymer is considered to be degraded or fails is a delicate matter, consisting in certain qualitative and quantitative aspects. There is a variety of properties which may be monitored and quantified. The principal ones are:

- Mechanical properties (tensile, impact, flexural ….)
- Optical properties (discoloration, surface quality, transmission ….)
- Chemical properties (presence of degradation products, organoleptics ….)

Usually, the polymer properties accessible to measurement undergo continuous changes during ageing, so that the drop in the property set as the main parameter of interest has to be exactly quantified and the critical point defined. The extent of selected property change may vary in dependence on the individual point of view and is often given by the intended end-product application [77-81]. It is often considered according to the generally accepted conventions or the corporate internal standards, defining the polymer failure point individually. Conventionally, polymer is considered to be degraded, when e.g. either some of the tensile properties drops by 50% or the surface gloss drops by 20% or the overall colour change dE surpasses value 1. However, many other individual criterions and requirements may exist. Considering the polymer useful life from the ecological view-point, polymer total disintegration would likely be accepted as the only solution.

a) Tensile strength (stress) at break

b) Elongation (strain) at break



c) Overall change in colour ΔE

d) Surface gloss at 85°

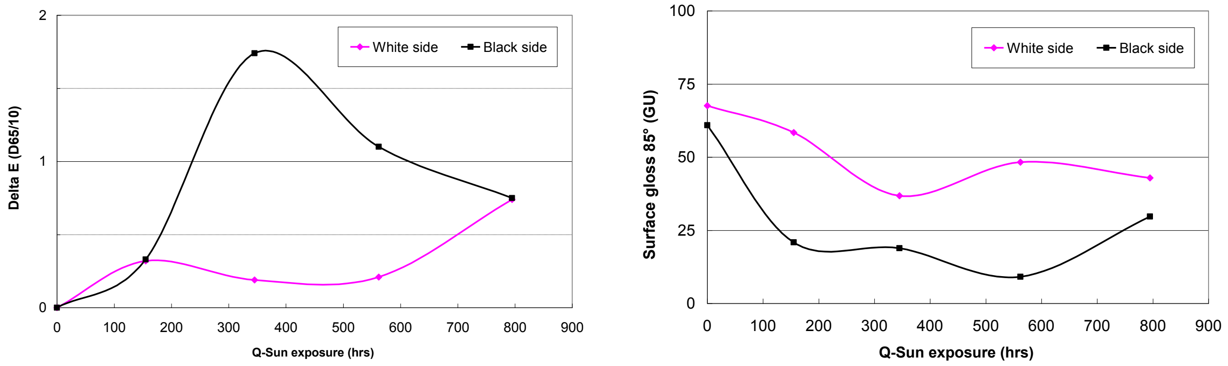


Figure 8 Photo-oxidation of 75 µm co-extruded black/white LDPE blown film (Retax) Q-Sun exposure, IRR 0.47 W/m^2@340 nm, BPT=65 °C, dry cycle

The importance of polymer failure definition has been well proven on a photo-oxidation of a three layer co-extruded LDPE blown-film, having one side black and one side white. The film was subjected to accelerated ageing in a Q-Sun exposure chamber and selected properties were monitored. According to the above mentioned failure criterions, different times to degradation were attained, when either the black or white side of the film was irradiated and different parameters taken as a measure of degradation, Figure 8.

Table 4 Photo-oxidation of 75 µm co-extruded black/white LDPE blown film (Retax) Q-Sun exposure summary – definition of times to failure as a base for the useful life-time calculations

Exposed side	**Time to defined failure**			
	Stress at break (drop by 50%)	Strain at break (drop by 50%)	Colour shift (delta E=1)	Surface gloss (drop by 20%)
White	440	170	>800	191
Black	>800	250	235	45

The results summarized in Table 4 indicate that the times to degradation attained by different approaches may substantially differ. In the case of this film, times to failure between 45 and >800 hours were reached. When TUVR energies inducing the described extent of deterioration were calculated and correlated with those of global solar radiation, assumed life-times under the Mid-European outdoor exposure (~ 90 kLy/year) varying from 3 weeks to more than 1 year were attained [T20].

Managing numerous applied research contracts and being in close contact with the real life needs, the experience committed the applicant to arrive at some more general conclusions. They have been expressed by the following statements [T19-T21] :

i) The useful life of polymer is not an unambiguous category and may be defined in different ways.

ii) The more parameters are taken into consideration, the more life-times may be attained.

iii) Especially with the bulk polymers having the higher mass/surface ratio, the use of more parameters for the description of the material behaviour is necessary.

iv) For the objective description of changes taking place in the polymer matrix exposed to the deteriorative conditions, there exists no general criterion of failure applicable for all plastics products. With one plastics product, more different life-times may be reached, sometimes very different, depending on the attitude of observer.

v) The polymer life-time period is a relative category and must always be related to the proposed application. The definition of failure criterions is of the same importance as the selection of polymer for a given application.

6.3 Prediction of polymer service life

The prediction of polymer service life-time period is a complex matter, very resembling the prediction of future itself [T15, T20, T24, 82-84]. The incertitude – “where”, “how” and “how-long” the plastic product will be serving - always exists. Nevertheless, the “reliability period”, during which polymer will serve for the given purpose has to be known and thus various stability tests and certain approximations were adopted. The physico-chemical factors most impacting the polymer stability are temperature, radiation, ambient oxygen, mechanical stress and environmental contact with chemicals in any of their physical form (gaseous, liquid, solid). Depending on conditions of application, these factors usually vary in intensity and time of action.

The applicant has been involved in the research activities issuing the prediction of polymer service life both under the thermo-oxidation and photo-oxidation conditions. Most efforts were focused to polypropylene, the importance and properties of which pushed it in the forefront. Some of the photo-oxidation stability issues applying weathering and accelerating ageing methods were mentioned in paragraphs 6.1 and 6.2.
In the cases when no UV but only the effect of temperature and oxygen is considered, accelerated thermo-oxidation tests are applied. They are used in two principal modifications, either with the

natural (open tubes) or forced circulation of air (air-draft ovens). Both provide good data for extrapolations to lower temperatures, giving rough information on how polymer would behave at given application conditions.

The accelerated thermo-oxidation ageing tests in open tubes (LTHA) were used for the evaluation of two polypropylene grades, where stabilities of polypropylene with a special prodegradant additivation and additive-free polypropylene were compared. Both polymers were investigated in the geometry of 0.5 mm compression moulded films. Induction periods (IP) defined as the time to brittleness characterizing the polymer stability at a given temperature were determined in the temperature range 90-150°C. Here, in the absence of UV radiation, there were temperature and ambient oxygen as the major deteriogens.

The data acquired in this way was processed according to Arrhenius (ln IP plotted against temperature reciprocal). Extrapolation down to typical application temperatures, such as 23°C, revealed the expected life-time periods - 40 years for the non-additivated PP and 7 years for prodegradation-additivated PP (Figure 9). In this study, the relatively low-stability materials were investigated and relatively short IP during accelerated tests attained. It follows that in the case of commonly stabilized plant-produced polypropylenes, much longer time-periods even during accelerated tests have to be expected. This indicates that common PP materials buried in the soil, with no access to solar radiation, may contaminate it for up to the hundreds of years [T20].

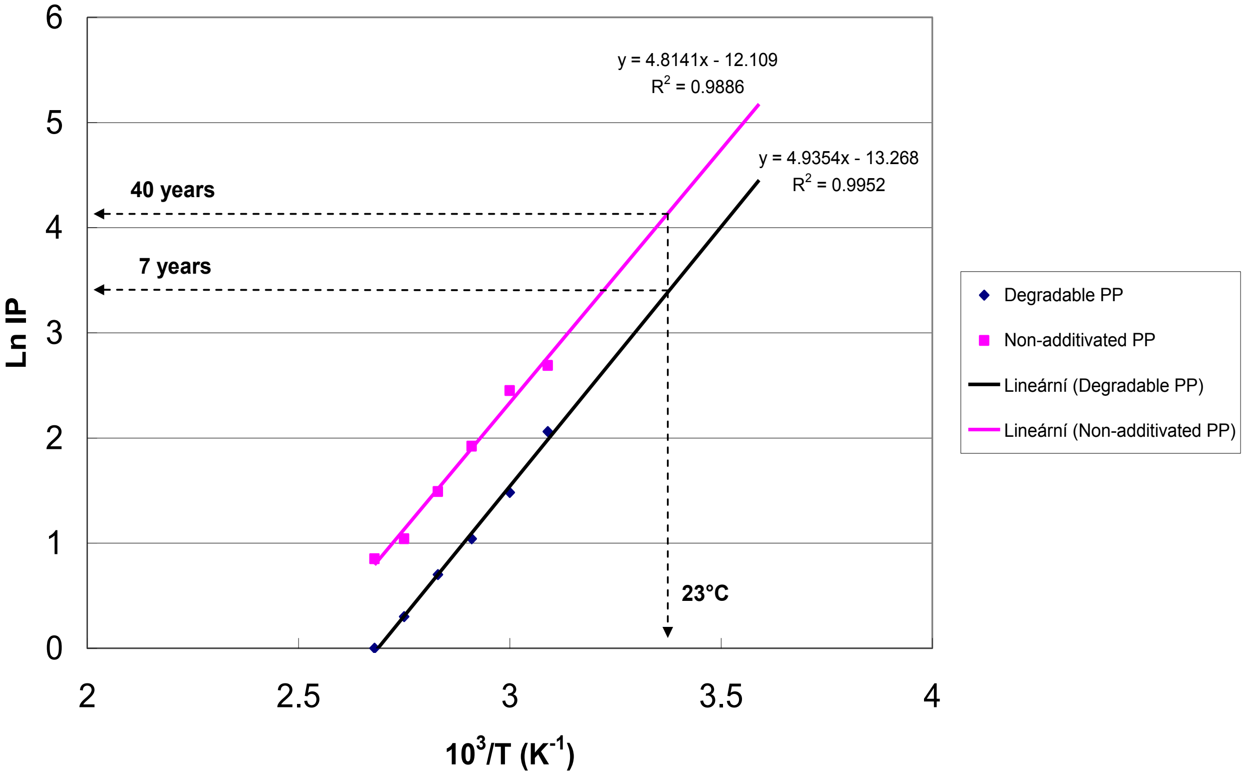


Figure 9 Polymer life-time prediction for thermo-oxidation exposure at 23 °C, in the absence of UV radiation; PP-homopolymer, with prodegradation additivation and additive-free reference; compression moulded films 0.5 mm; IP = induction period (days), T = temperature Degradation criterion = brittle failure

7. Processing Degradation Index (PDI) – a contribution to polymer testing methodology

Being long time involved in the research issues dealing with polypropylene processing, the author has observed that in contrast to other thermo-oxidation stability measurements, processing stability was not satisfactorily quantified.

Laboratory evaluation of PP processing stability has commonly been carried out using the so called “multiple extrusion”, during which polymer is several times consecutively extruded and after each extrusion MFR at 230 °C/2.16 kg is measured. MFR plotted against the number of extruder passes provides the so called “processing curve”. Its position is subjectively correlated with reference materials and/or the relative increase in MFR between the starting and end extrusion is calculated. Despite this approach has a certain value and has been used for at least three decades [T6,T7, 4,10,19,85-92], it does not reflect the position and shape of the processing curve properly. The subjective comparison of curves mutual positions is not exact and in some cases may be misleading.

Keeping this in mind, we have proposed and practically verified a new way of processing stability quantification stemming from the processing curve and defining a new parameter - Processing Degradation Index (PDI). PDI fairly reflects the shape and position of the processing curve and is defined as follows [T22, T23]:

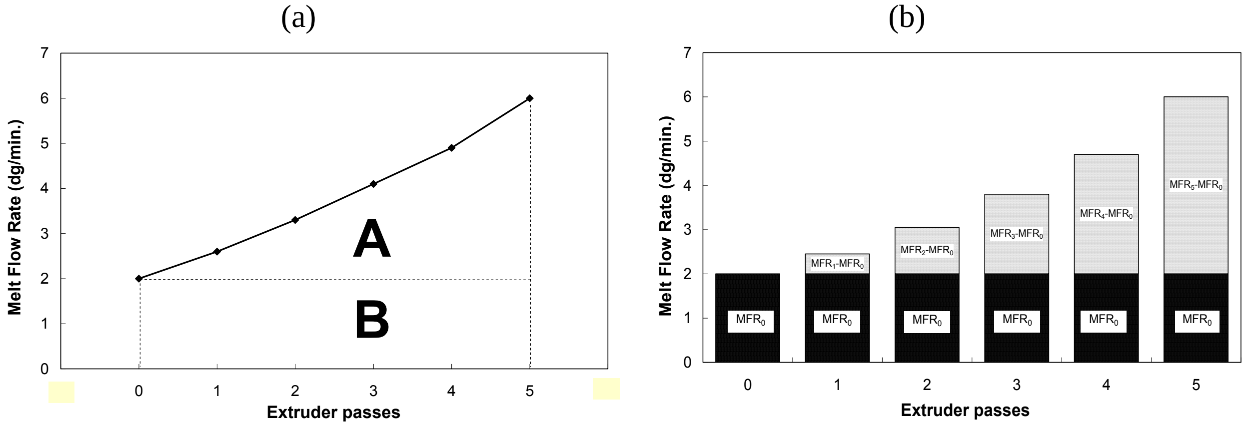


Figure 10 Definition of areas A and B under the processing curve (a) and calculation of differences in MFR between individual extrusions and the original state (b).

Then PDI may be calculated in two ways either according to eqn. (15) or eqn. (16), both ways provide identical results.

$$PDI = \frac{A}{B}\, x\, 100 \qquad (15)$$

PDI value is a positive, dimensionless number, ranging between 0 and a finite number.

If A=0 then PDI = 0 ideal polymer, non-degrading
If A>0 then PDI > 0 real polymers, measurably degrading

$$PDI = \frac{\left(MFR_1 + ... + MFR_n\right) - nMFR_0}{\left(n+1\right) MFR_0}\, x\, 100 \qquad (16)$$

Where n …….. number of “degradation” extrusions
MFR_0 …… melt flow index of the material after compounding extrusion
MFR_n …… melt flow index after n-th “degradation” extrusion

The value of PDI reflects the extent of mechano-chemical deterioration of the polymer matrix initiated by processing and being, thus, a single number, it can easily be plotted against other variables. Beside others, it was verified on a series of experiments carried out with isotactic PP homopolymer processed at different barrel temperatures. For each curve/temperature PDI was calculated and plotted against temperature reciprocal according to Arrhenius. A linear plot was obtained, Figure 11.

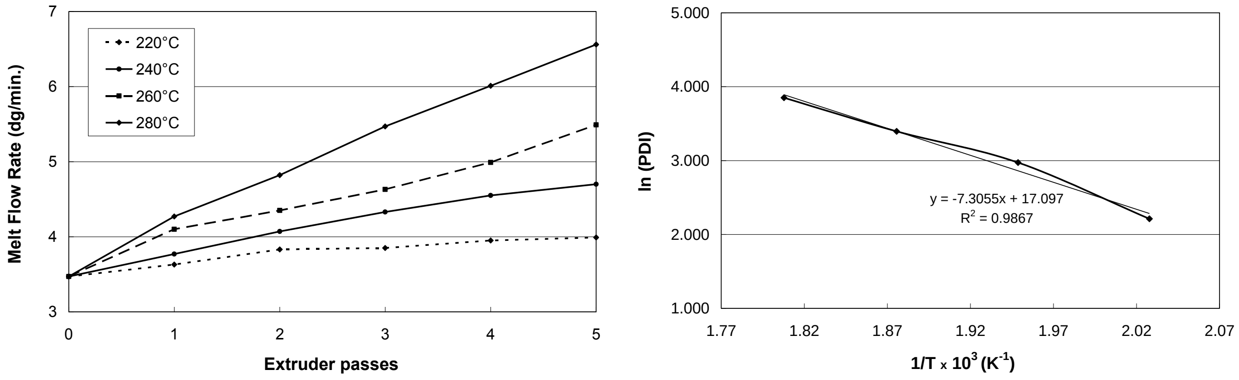

(a) (b)

Figure 11 Processing curves of 5-fold extrusion of PP isotactic homopolymer carried out at temperatures 220 to 280 °C on a 19mm single screw-extruder Brabender at 100 rpm (a), the logarithm of PDI calculated from the curves plotted against temperature reciprocal according to Arrhenius (b).

This was one of our latest works. We believe that PDI becomes a useful tool for the quantification of PP processing stability and will induce increased citation response. Generally, PDI calculation may be applied also for other polymers, where degradation induced by extrusions unambiguously lead to the decrease in melt viscosity and is not complicated by other phenomena, such as e.g. crosslinking.

8. Summary

The submitted thesis provides an overview of applicant´s scientific activity in the field of his professional specialization – degradation and stability of polymers, focused to the dominating group of commercially available plastics – polyolefins. The submitted and discussed topics are the examples of areas of specialized polymer research, in which the applicant was involved. The applicant spent in degradation and additivation of polymers the major part of his professional career and during this period he co-operated with all of the branches of plastics industry. Applied research, in which applicant was involved, was mostly on a contract base, so that the achieved findings were the property of the principal and nearly none of them were intended for publication.
The presented overview, thus, shows only the portion of applicant´s research findings, which were not parts of any research contract. They were supported by other sources and, hence, allowed to be released to the public.

Being long-time involved in the applied research of polymers, his specialization brought him to the close cooperation with other specialized research groups, such as those going in polymerization, degradation, analytics and materials research. Coming out from a good knowledge of polymer degradation mechanisms, applicant´s main activities consisted both in the investigation of phenomena diminishing the deteriorative environmental impacts and development of new, more efficient polymer protective systems. Modification of polymer physico-chemical characteristics and development of new polymer grades were only another features of his research scope, indivisibly connected with the polymer stability issues.

Development of new polymeric materials as well as their antioxidant protective systems, investigation of interactions among the components of the matrix, modification of physico-chemical properties, polymer processing, elucidation of causes of polymer failure, accelerated ageing and the prediction of polymer useful life may be considered as the principal fields of the applicant´s research activity in the branch.

The applicant was 28 years employed in Polymer Institute Brno (up to 1994 Výzkumný ústav makromolekulární chemie), in 2008 he joined Brno University of Technology, the Faculty of Chemistry, later on CEITEC, the employee of which is up to now. Due to his long-term systematic involvement in the issues of polymer degradation, he became a skilled in the field and presently ranks among only a few people in the Czech Republic, who are professionally concerned with the topic.

9. Papers included in the habilitation thesis

9.1 Author´s selected publications

T1. **Tocháček J**., Sedlář J., The Influence of Molecular Weight on Efficiency of Hindered Phenols as Stabilizers for Polypropylene, 13th International Conference on Advances in Stabilization and Degradation of Polymers, May 21-24, 1991, Luzern, Switzerland

T2. **Tocháček J.**, Sedlář J., The Influence of Molecular Weight on the Efficiency of Phenolic Antioxidants as Stabilizers for Polypropylene, Polym. Degrad. Stab. 24 (1989), 1-6

T3. **Tocháček J.**, Effect of secondary structure on physical behaviour and performance of hindered phenolic antioxidants in polypropylene, Polym. Degrad. Stab. 86 (2004) 385-389

T4. **Tocháček J.**, Sedlář J., Metal-Containing Phenolic Antioxidants - Physical Behaviour and Efficiency of Stabilization in Polypropylene, Polym. Degrad. Stab. 27 (1990), 297-307

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Abstract

The submitted thesis represents an overview of applicant´s scientific activity in the field of his professional specialization – degradation and stability of polymers, focused to the dominating group of commercially available plastics – polyolefins. The submitted and discussed topics are the examples of areas of specialized polymer research, in which the applicant was involved. The applicant spent in polymer degradation and additivation research the major part of his professional career and during this period he co-operated with all the branches of plastics industry. Applied research, in which the applicant was involved, was mostly on a contract base, so that the achieved findings were the property of the prinicpal and nearly none of them were intended for publication.

The presented overview, thus, shows only the portion of applicant´s research findings, which were not parts of any contract research. They were supported by other sources and, hence, allowed to be published in public journals.

Abstrakt

Předložená práce představuje průřez vědeckou činností uchazeče v oblasti jeho profesní specializace – degradace a stabilizace polymerů, s užším zaměřením na dominující skupinu komerčně dostupných plastů – polyolefinů. Předložená a diskutovaná témata jsou ukázkami oblastí specializovaného polymerního výzkumu, v nichž se uchazeč angažoval. Uchazeč strávil ve výzkumu degradace a aditivace polymerů většinu své profesní kariéry a při své činnosti spolupracoval se všemi oblastmi průmyslu plastů. Aplikovaný výzkum, ve kterém uchazeč dlouhodobě pracoval, měl povahu smluvní, výsledky v něm dosažené byly duševním majetkem zadavatele a téměř žádné z nich nebyly uvolněny k publikaci.

Presentovaný výběr aktivit proto ukazuje pouze tu část z prací uchazeče, která nebyla součástí výzkumných kontraktů, byla pořízena v rámci jiných zdrojů a může tak být doložena veřejně dostupnými publikacemi.