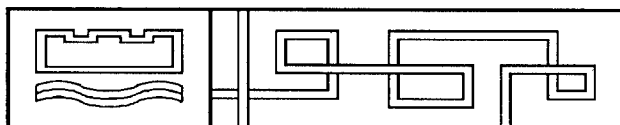


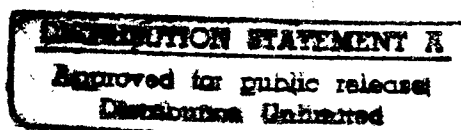
***11th Bratislava IUPAC/FECS International
Conference on Polymers***

**THERMAL AND PHOTO-INDUCED
OXIDATION OF POLYMERS AND ITS
INHIBITION IN THE UPCOMING 21ST
CENTURY**

P r o c e e d i n g s



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June 24-28, 1996
Hotel Academia, Stará Lesná, High Tatras,
Slovak Republic

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INTRODUCTION

This Proceedings cover the abstracts of contributions arranged as Main Lectures (ML), Contributed Lectures (CL) and Posters (P) with the numbers identical to those in the Programme of

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held in the Hotel Academia, Stará Lesná, High Tatras,
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The Organizers of the Conference welcome you in Stará Lesná with the hope that the Proceedings submitted will contribute to the stimulation of the discussion and to your further scientific work.

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ML-1

A SPREADING MODEL FOR THE OXIDATION OF POLYPROPYLENE

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One of the current dilemmas in the understanding and application of the oxidation kinetics of solid polyolefins is the apparent success of the homogeneous free radical kinetic scheme (typical of liquid phase hydrocarbon oxidation) in explaining the product distribution and concentration profiles with oxidation time, whereas evidence from microscopy and failure analysis of solid polymers is that the oxidation is very non uniform in nature and may occur to high extents in localized regions of the polymer. It is important in the field of lifetime prediction of polymers to be able to determine the extent of degradation corresponding to the failure of the solid polymer (e.g. embrittlement) and the rate of the chemical process leading to this failure.

In order to explore the link between the apparently homogeneous chemical kinetics on the one hand and the non-homogeneous failure initiation process (described by the growth of a flaw in the material to a critical size) we have focussed on the heterogeneous nature of the oxidation of solid polyolefins. In the heterogeneous model for the thermal oxidation of polypropylene, it is considered that there are highly reactive zones which, because of the presence of catalyst residues or impurities, are able to undergo a degenerately branched oxidation at a high rate. This soon leads to secondary oxidation involving *p*-, *s*- and *t*- alkylperoxy radicals resulting in the evolution of volatile oxidation products, the observation of chemiluminescence and significant molecular restructuring owing to chain scission and recrystallization at the oxidation temperature, resulting in microcracking. All of this can in principle occur within the time frame of the classical induction period obtained, for example, as the time period before the apparently 'linear' region of an oxygen uptake-time curve.

In the spreading model, the classical sigmoidal oxidation profile represents an increased fraction of the total polymer occupied by these oxidizing zones. This must involve a spreading of the oxidation from the 'infected' zones into the noninfected bulk of the polymer. The analysis of such infectious spreading through static or dynamic populations has been investigated in epidemiological and sociological research and is often found to obey a sigmoidal logistic function.

In the spreading model it is considered that at zero time there is a small fraction, p_0 , of the total volume of the polymer in which oxidation is occurring. Within these highly reactive zones the formation of volatile reaction products and free radicals occur which increase the instantaneous oxidizing fraction of the polymer from p_0 to some value p_i . At the same time the fraction of polymer which is unaffected will decrease from $1-p_0$ (≈ 1) to some value p_r .

$$-\frac{dp_r}{dt} = bp_r(1-p_r) \quad \dots(1)$$

where b is the rate coefficient for spreading. The end product of these spreading reactions will be oxidized material in which all free radical reactions have terminated. This is analogous to the fraction of the population which has succumbed to the infection or is 'dead'. The rate of formation of this 'dead' or oxidized fraction, p_d from the infectious fraction, p_i will be given by:

$$\frac{dp_d}{dt} = \alpha p_i \quad \dots(2)$$

where α is the rate coefficient for this process of removal of the oxidizing species.

The time dependence of the oxidizing or infectious fraction will then be given by

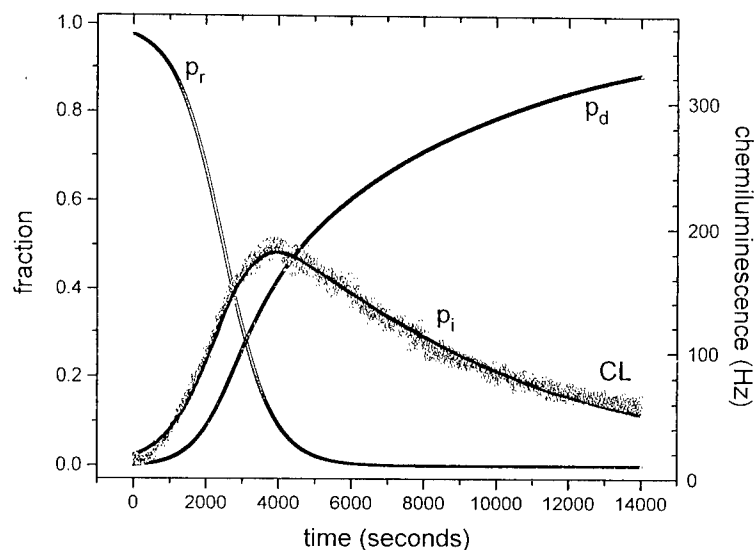
$$\frac{dp_i}{dt} = bp_i p_r - \alpha p_i \quad \dots(3)$$

Integration of equations (1), (2) and (3) allow the three populations to be determined at any time. For example, if p_o , the initial infectious fraction is small then it may be shown that the solution to (3) is:

$$p_i = p_o p_r e^{(b-\alpha)t} \quad \dots(4)$$

Values of the coefficients b and α , may be obtained from an analysis of chemiluminescence (CL) in the early stages of the oxidation (p_i).

Figure 1 shows the result of an analysis of the CL from single reactor particles of unstabilized polypropylene over the first 800s which enabled p_o , α and b to be calculated and then p_i simulated (solid curve) for comparison with the experimental CL data. The curves for the oxidized (p_d) and remaining (p_r) fraction were then simulated using these parameters. The similarity of the p_d vs time curve to a classical oxygen uptake or product distribution curve is apparent. The comparisons of the temperature dependence of these parameters as well as variations with spatial distributions of particles which enable inter- and intra-particle spreading parameters to be determined will be discussed along with the implications for polymer stabilization. A method for simultaneous CL-FT-IR emission for the determination of p_i and p_d will be described.



ML-2

ON THE AUTOACCELERATED CHARACTER OF THE BRANCHED OXIDATION OF POLYOLEFINS

J. VERDU

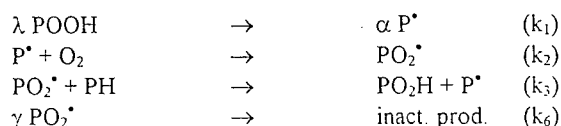
ENSAM 151 Bd de l'Hôpital, 75013 Paris, France

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The thermal oxidation of polyolefins, for instance polypropylene (PP) or polymethylpentene (PMP) at low to moderate temperatures (typically $T < 150^{\circ}\text{C}$), displays the following features :

- There is a steady state during which oxidation rate (oxygen absorption, carbonyl growth, chemiluminescence intensity ...) is constant or decreases slowly as a result of substrate consumption, secondary processes, etc...
- There is an initial « transient », often called « induction period », of duration t_i , during which oxidation rate increases in an autoaccelerated way until its steady state value.
- The steady state rate is independent of the factors influencing specifically the POOH decomposition, for instance presence of catalysts.
- For reasonably clean, non preoxidized samples, the duration of the « induction period » is independent of the sample source, morphology, processing, etc... It appears to be scaled only by the reciprocal of the rate constant of POOH decomposition.

It can be shown that the steady state properties (1) and (3) are general, and presumably exclusive, properties of « close loop » schemes in which the only source of radicals is the propagation product e.g. POOH :



NB : Terminations involving radicals $\text{P}^{\bullet}$ are not considered here.

The quasi universal character of « induction time » (property (4)) is an exclusive property of « close loop » schemes where POOH decomposition is unimolecular ($\lambda = 1$) and termination is bimolecular ($\gamma = 2$).

The set of differential equations expressing the rates of variation of $[\text{P}^{\bullet}]$, $[\text{PO}_2^{\bullet}]$ and $[\text{POOH}]$ can be numerically resolved in the general case (no hypothesis of stationary state on radical concentration). The model agrees well with the above listed characteristics provided that $k_1 \ll k_3 (\text{PH})$ and $k_2[\text{O}_2]$. However it is not easy to use in practice.

An analytical resolution of the system can be obtained making the hypothesis of stationary state. Rigorously speaking, this hypothesis is no physically valid but the structure of the system

of differential equations and the parameter values are such as this (wrong) analytical solution gives practically the same results as the (sound) previous numerical solution and appears as a suitable, easy to check, easy to use, kinetic model for thermal oxidation, displaying good predictive properties.

Kinetic analysis can be used to assess the spatial heterogeneity of the oxidation, provided that this heterogeneity can be expressed in terms of distributions of rate constants, homogeneity corresponding to the homodisperse case. It can be easily shown that sharp autoaccelerations and, more generally, fast changes of the kinetic regime, as observed for instance in gravimetric studies, cannot be consistent with a wide spreading of rate constants (or time constants derived from these latter) (Fig. 1).

The principles of a quantitative approach of heterogeneity / homogeneity based on the above idea are proposed. Gravimetric curves, which display a relatively sharp peak due to the simultaneous occurrence of mass gain due to O_2 incorporation and to mass loss due to elimination of water and short chain fragments, can be used in this modelling. It is easy to show that the peak width is directly linked to the polydispersity of the distribution of rate constants. If this latter is assumed to be Gaussian, then the kinetic model allows to establish a relationship between the standard deviation of the distribution and the gravimetric peak width. The preliminary results indicate that PP thermal oxidation displays the characteristics of an homogeneous reaction despite its well known heterogeneity at the morphological scale. This means that oxidation is presumably homogeneous within the (amorphous) domains.

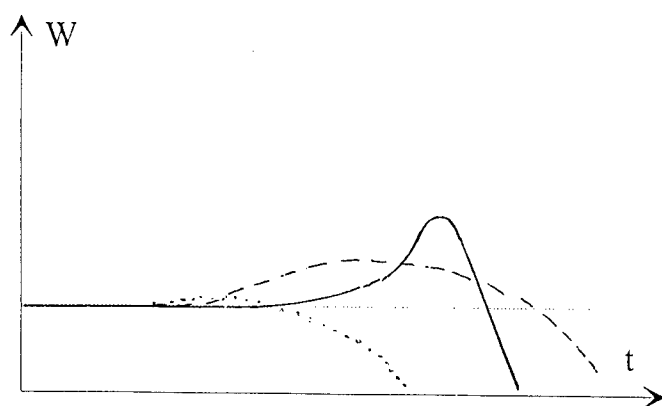


Fig. 1 : Expected shape of gravimetric curves in the case of distributions of initiation rate constants with low (—), medium (- - - -) and high (.....) polydispersities

ML-3

THE ROLE OF TRIPLET REPULSION IN ELEMENTARY STEPS OF CYCLIC CHAIN TERMINATION OF OXIDIZING POLYMERS AND OTHER COMPOUNDS

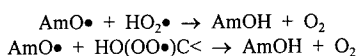
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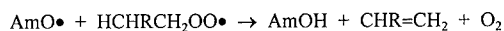
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The intensive study of cyclic chain termination in oxidizing polymers, alcohols, and hydrocarbons cleared up that there exist systems (oxidized substance $RH + O_2$ + inhibitor InH) where cyclic chain termination is going intensively. What are the grounds of such mechanistic selectivity? This problem was analyzed with using of parabolic model of transition state in application to free radical reactions with hydrogen atom abstraction. The main results are the following.

Nitroxyl radicals react very fast with $O-H$ -bond of $HO_2\bullet$ and hydroxyperoxyl radical:

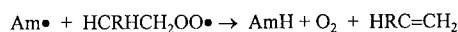


Calculation showed these reactions to flow without activation energy due to high exothermicity and absence of triplet repulsion in transition state. That is why nitroxyl radicals create cyclic chain termination in oxidizing polymers containing hydroperoxide groups, some olefins and alcohols. The similar reaction of $AmO\bullet$ with $RO_2\bullet$



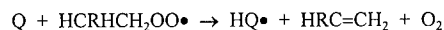
is going slowly due to sufficient activation energy. The last is the result of strong triplet repulsion in transition state of the type $O\cdots H\cdots C$. So that slow reaction can not compete with another fast reactions of nitroxyls disappearance. As the result there is no cyclic chain termination by nitroxyls in oxidizing hydrocarbons.

Aromatic aminyls $Am\bullet$ react very fast with $HO_2\bullet$ and $>C(OH)O_2\bullet$ with reduction into AmH . Calculation showed that these reactions are very fast due to weak triplet repulsion and attraction of N and O atoms in transition state as result of their different electron affinity. The similar reaction of aminyl radical with $C-H$ -bond of alkylperoxyl radical



should proceed slowly due to activation energy as result of triplet repulsion in transition state of the type $N\cdots H\cdots C$.

Benzoquinone Q is reduced by radicals $HO_2\bullet$ and $>C(OH)O_2\bullet$ into semiquinone radical rather fast. That is why quinones terminate the chains in oxidizing polymers and alcohols. However the reduction of benzoquinone by alkylperoxyl radical in reaction



is proceeding very slowly due to high activation energy. The last is the result of high endothermicity of reaction and strong triplet repulsion in transition state.

So in all cases where reduction of $Am\bullet$, $AmO\bullet$, and Q is the result of their reaction with $O-H$ -bond of peroxyl radical, reaction is going sufficiently fast for to create cyclic chain termination. Similar reaction of the same species with $C-H$ -bond of alkylperoxyl radical proceed very slowly. That is why the cyclic mechanism of chain termination with participation of peroxyl radicals in both stages is not observed in hydrocarbons. The main reason of such difference in reducing activity of peroxyl radicals is the intensive triplet repulsion in transition state of the type $C\cdots H\cdots O$ and $C\cdots H\cdots N$ and very weak triplet repulsion in transition state of the type $O\cdots H\cdots O$ and $O\cdots H\cdots N$.

ML-4

PHOTOOXIDATION OF COPOLYMERS OF FLUORINATED OLEFINS AND ALLYL OR VINYL ETHER

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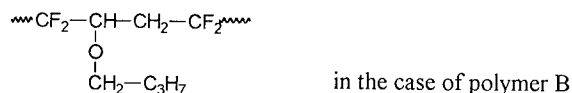
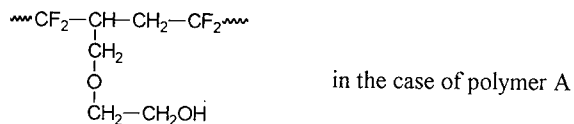
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ABSTRACT

This presentation reports on the photooxidation of two copolymers of fluorinated olefins and allyl or vinyl ethers. Because the ether groups that constitute the reactive part of both the polymers are located on short, branched chains, the oxidation produces notable quantities of low-molecular weight photoproducts that can migrate out of the solid polymeric matrix. For that reason, the classical techniques based on FTIR analysis of the solid polymeric matrix coupled with chemical derivatization methods, have been complemented by analysis of the gas phase during irradiation using mass spectroscopy. Coupling both analytical techniques has permitted the unambiguous identification of all the photoproducts. Unanticipated results were obtained, showing that the presence of fluorine strongly influenced the oxidation mechanisms and the kinetics. Comparison was made with non- fluorinated polyethers in order to elucidate the role played by the fluorine atoms in the chain on the primary hydrogen abstraction reactions.

EXPERIMENTAL

The two copolymers were based on the following units.



The non-fluorinated polymers studied were poly(vinylethylether) (PVE), poly(vinylisobutylether) (PVI) and poly(propyleneglycol) (PPG).

RESULTS

The polymeric samples were irradiated in the form of thin films in a SEPAP 12.24 unit ($\lambda \geq 300$ nm). The photooxidized samples were submitted to various chemical treatments including SF₄ and NH₃ derivatization. FTIR analysis were carried out before and after the chemical treatments.

The oxidation mechanisms proposed on the basis of the identification of the photoproducts showed that oxidation was initiated by radical attack on the groups in the α -position to the oxygen atoms of ether groups. In the case of the non fluorinated polymers, the hydrogen abstraction started at the tertiary carbon atom. In the case of polymer B, the site of oxidation was, surprisingly, the secondary carbon atom and not the tertiary. In the case of polymer A, the site of oxidation was the secondary carbon atom the farthest from the CF₂ groups.

These results were analysed considering the different factors that control the free radical reactions, on the basis of the role of orbital interactions.

In the case of polymer A, the secondary carbon atom nearest to the main chain is influenced by the electron withdrawing effect of the CF₂ substituents. The C-H bond presents then a weak reactivity towards hydrogen transfer. In contrast, the other secondary position is not deactivated and reacts more easily with incoming radicals. The behaviour of polymer B has to be analysed similarly. The tertiary carbon atom is adjacent to CF₂, which produces a strong polar effect. The result is that the rate of hydrogen abstraction is considerably reduced from the tertiary site. As a consequence the reaction takes place essentially at the secondary carbon atom.

The rate constants for hydrogen abstraction from the tertiary and the secondary carbon atoms on both sides of the oxygen atoms could be evaluated from the literature data in the case of polymer B and PVE. The literature values confirmed the experimental data obtained by analysis of the photooxidized polymers.

ML-5

PVC PHOTO-OXIDATIVE DEGRADATION: DETECTION OF VOLATILES AND THEIR IMPLICATIONS

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In recent years, considerable progress has been made in characterizing the complex array of products resulting from the oxidative degradation of commodity polymers. Often this work has depended upon infrared (IR) spectroscopy coupled with chemical derivatization. Specific focus has been on reactions leading to backbone scission and quantification of scission products. Techniques that can detect incipient degradation, during the "induction period" are particularly important to allow the prediction of the useful working lifetime of polymeric materials.

PVC photo-degradation is particularly difficult to characterize in many applications because of high pigment loadings. Also this results in PVC degrading by a surface erosion process. Detection of oxidative scission of the polymer backbone is an important objective, especially with high sensitivity to allow early measurement of PVC breakdown. Recently we have begun to apply gas chromatography to identify breakdown products evolved from weathered PVC. The use of mass spectrometry and highly sensitive, chlorine-specific, electron capture detectors allows the detection and identification of chlorinated volatiles. This information can be combined with IR, scanning electron microscopy and molecular weight determinations on surface material to detail the processes leading to erosion by PVC destruction and pigment loss. This information is particularly relevant to the extensive use of PVC in the construction of siding, eaves trough and window profiles (about 15% of PVC production in North America). In addition this information is pertinent to the increased use of PVC to consume the growing quantities of chlorine becoming available as traditional markets (solvents, pulp and paper, water purification, etc.) decline.

ML-6

THE PHOTOOXIDATIVE DEGRADATION AND STABILISATION OF WATER-BORNE ACRYLIC COATING SYSTEMS

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ABSTRACT

In recent years the tightening of world-wide environmental legislation, has forced coating industries to decrease levels of pollutant substances released to the atmosphere [1,2]. For this reason there is an increasing tendency to move away from conventional solvent borne coatings to those that utilise water as the fluid vehicle. In this regard one of the more important film forming pigment binders used in water borne coatings is that class of resins known as acrylics. These are, for the most part, the acrylate and methacrylate esters of lower alkanols, of which methanol and butanol have the widest application. The influence of manufacturing and processing parameters on the photooxidative stability of aqueous acrylic based latices is examined by FTIR and hydroperoxide analysis in this lecture. Here acrylic latices based on different formulations are chosen as homo-polymers and copolymers. The nature of impurities and oxidation products generated during their manufacture are characterised and inter-related to their influence on subsequent photooxidative degradation. This involves the use of reflectance FT-IR spectroscopy to show functional group changes together with colourmetric U.V. analysis to determine photochemical generation of hydroperoxides. The early chemical changes and their subsequent influence on the physical and chemical properties of the latices during the later stages of photooxidation are found to exhibit a close inter-relationship. To date the nature of the surfactant and the composition of the latex in terms of end group modification are important parameters. De-esterification and hydroperoxide formation are found to be important processes during latex photooxidation while the addition of low levels of co-monomer such as styrene to the emulsion, give latices with improved photostability. While co-reactive acrylated hindered piperidine stabilisers are found to be effective the incorporation of simple terminal dialkyl acrylamide/methacrylamide groups are equally as effective. Acrylamide itself is ineffective indicating that oxidation of alkyl groups adjacent to the nitrogen atom is important in the stabilising mechanism thus preventing the main chain from oxidation.

THE PARTICIPATION OF SINGLET OXYGEN IN THE DEGRADATION OF AN ELECTROLUMINESCENT POLYMER

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Singlet oxygen behavior in bulk polymers

Singlet oxygen is an important intermediate in the photooxidation of many organic compounds in liquid solution. In some cases, it may also play a role in the photooxidation of additives (e.g., dyes, stabilizers) contained in polymeric materials, or of the macromolecules themselves. Elucidating when or if singlet oxygen is involved in various polymer systems has proven difficult, and much controversy has been created on this issue. We began working several years ago to try to better understand the fundamental nature of how singlet oxygen behaves within bulk polymer matrices, particularly within glassy materials. We have gained a number of insights into this problem by monitoring the time-resolved phosphorescence signal (1270 nm) of singlet oxygen generated in a photosensitized process involving solid polymer samples containing dissolved oxygen and a sensitizer dye. We have found that the lifetime of singlet oxygen in both glassy and rubbery materials is very similar to lifetimes measured in liquid analogs, and depends primarily on the atomic composition of the polymer. The quantum yield for singlet oxygen formation in a bulk polymer was found to be only somewhat smaller compared with a liquid of comparable molecular structure. In addition to the photosensitized process, it was shown that singlet oxygen could be generated by irradiation of the oxygen-organic charge-transfer band which arises when oxygen dissolves in typical polymers. The deactivation (physical quenching) of singlet oxygen by additives contained within glassy polymer matrices has been examined, and it is found that very efficient quencher molecules operate with much lower efficiency than in liquid solutions, whereas inefficient quenchers operate with relatively similar efficiency in the two media. The reaction of singlet oxygen with small molecules dissolved in a polymer matrix ("reactive quenching") has been studied by time-resolved phosphorescence observations, by observation of oxygen depletion within the matrix and also by subsequent recovery of specific singlet-oxygen oxidation products by extraction from the matrix. As with physical quenching, highly reactive molecules have rate constants that are much lower in glassy materials versus a liquid solution, whereas compounds of low reactivity have reaction rate constants that are comparable in the two media. All of these observations support the conclusion that singlet oxygen is readily created within bulk polymers, and that its lifetime and mobility within a polymer matrix is sufficient that it can undergo chemical reaction, if suitable reaction sites are present in that matrix.

Singlet oxygen involvement in the oxidation of a PPV polymer for light-emitting diodes

The upcoming century will see polymeric materials used in an increasing array of "high-tech" applications, such as new electronic and electrooptic devices. Material stability will be a critical factor in these applications. For example, extensive work has been underway on developing a new type of flat panel display (for TV, computer monitors, etc.) based on an organic light emitting diode (LED), constructed by depositing an electroluminescent polymer film between two electrodes, one of which is optically transparent. A primary

limiting factor for commercialization of polymer-based LEDs has been the limited lifetimes of such devices. Literature evidence suggested that a major failure mechanism is the degradation of the polymer, and that the process involves oxygen. Operation of an LED device induces the electrically-stimulated formation of the singlet excited state of the electroluminescent polymer, which then emits light. We hypothesized that triplet states of the polymer, which could also be expected to be produced, might serve as sensitizers that induced the formation of singlet oxygen, which then attacked the polymer.

To test this idea, we have carried out studies of the excited state chemistry of an important class of electroluminescent polymer, polyphenylenevinylene (we used BCHA-PPV), in the presence of oxygen. In our studies, the excited states were conveniently produced by photolysis, to generate the BCHA-PPV singlet. By flash absorption experiments on BCHA-PPV, both in solution and in the form of cast films, we were able to monitor the appearance of a transient which could be assigned to the BCHA-PPV triplet state, indicating that the BCHA-PPV singlet indeed undergoes a significant amount of intersystem crossing. Upon admission of oxygen to the sample, the BCHA-PPV triplet lifetime was substantially reduced, indicating energy transfer to ground state oxygen. In solution phase experiments, we were able to observe the formation of singlet oxygen during the photolysis of BCHA-PPV by detecting its characteristic phosphorescence signal at 1270 nm. We could estimate the quantum yield for singlet oxygen formation from BCHA-PPV as ~ 0.025 (in CS_2 solution). By varying the concentration of BCHA-PPV in a liquid solution, we were able to show that BCHA-PPV quenches singlet oxygen with a rate constant of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Following irradiation of BCHA-PPV in the presence of oxygen, either in solution or as a solid film, we could observe a marked change in its absorption spectrum, and a dramatic decrease in its molecular weight as seen by GPC. These changes, indicative of extensive chain scission, did not occur in the absence of oxygen. When we incorporated the well-known physical quencher of singlet oxygen, DABCO, into either a solution or a film of BCHA-PPV, we observed a substantial decrease in the rate of photooxidative degradation of the material. By flash absorption experiments, we could show that the DABCO did not affect the BCHA-PPV triplet. When BCHA-PPV was cast into a matrix of: 1) polystyrene, and 2) perdeuteropolystyrene (in which the lifetime of singlet oxygen is $\sim 10 \times$ longer compared with the protonated polymer), it was found that the rate of BCHA-PPV photodegradation in the latter case was about $5 \times$ faster.

We conclude that singlet oxygen is the primary intermediate in the oxidative degradation that ensues when electronically excited states of BCHA-PPV are produced. We suggest that the attack of singlet oxygen on BCHA-PPV occurs via a 2+2 cycloaddition reaction involving the double bonds along the chain backbone, and that subsequent cleavage of this dioxetane product results in chain scission. We anticipate that singlet oxygen may be important in the stability of other organic materials which will be developed for use in future optical or electronic devices, if such applications involve the formation of excited states.

Acknowledgment

This work was supported by the U.S. Department of Energy under Contract DE-AC04-94DP8500 and by a grant from the National Science Foundation (CHE-9402145).

ML-8

KINETIC ANALYSIS OF THE PHOTODEGRADATION OF UV ABSORBERS

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All commercially-available classes of UV absorbers (UVA) photodegrade at rates that can limit the performance of articles that contain them. This has been extensively described in the literature for polyolefin matrices and more recently for coating applications. Although the loss of UV absorbers can be important when they are used as bulk additives, the photostability of the UV absorbers can be the dominant factor that determines the lifetime of coatings and other surface-treated polymer systems. As the demands for weatherable polymer systems increase in the next century, an understanding the degradation of UV absorbers is essential for the rapid design of high performance materials.

The loss of absorbance for a coating or polymer film containing a UVA appears first order in UVA when the absorbance is very low (less than 0.1) in the range of 300-350 nm. When the absorbance is very high (>1) the loss of absorbance appears zero order in UVA. Equation 1 describes the rate of loss of absorbance over the entire absorbance range where A is the absorbance, k is a rate constant (essentially the product of quantum yield and light intensity), and T is the transmission of the film or coating ($T = 10^{-A}$):

$$dA/dt = -k(1-T) \quad (\text{Eqn. 1})$$

Integration of Equation 1 gives an analytical solution for absorbance as a function of time as shown in Equation 2 where T_0 and A_0 are the initial transmission and absorbance respectively, k is the rate constant, and t is time or light exposure. This equation is expected to be valid when the more highly absorbed wavelengths of light are the ones mostly responsible for the photodegradation of the absorber. It has been verified experimentally for the benzophenone and benzotriazole classes of UV absorbers.

$$A = \log_{10}[(1-T_0)10^{(A_0-kt)} + 1] \quad (\text{Eqn. 2})$$

The rate constant, k , can be determined by exposing a polymer film or coating containing the UVA to light and plotting the loss of absorbance at some wavelength against time or light exposure. The slope of this curve is an observed rate, k_{obs} , and can be converted to the rate constant, k , by use of equation 3 where A_{obs} is the absorbance at the point where k_{obs} is determined.

$$k = k_{\text{obs}} / (1 - 10^{-A_{\text{obs}}}) \quad (\text{Eqn. 3})$$

In very thin sections or in sections with absorbance < 0.1 , first order kinetics apply as described by Equation 4. This often occurs near the surface of coatings or polymers containing UV absorbers. In this absorbance range, one can properly speak of a half-life as shown in Equation 5. The concept of half-life does not strictly apply to coatings or films when the absorbance is < 0.1 , because the kinetics are not first order. When the absorbance is > 1 , then essentially zero order kinetics are observed and the absorbance of a film or coating appears to decrease linearly with time (Equation 6).

$$\log_{10}(A/A_0) = -kt \quad (\text{Eqn. 4})$$

$$t_{1/2} = \log_{10}(2) / k = 0.301 / k \quad (\text{Eqn. 5})$$

$$A = A_0 - kt \quad (\text{Eqn. 6})$$

A number of factors control the degradation rate of a UV absorber with the structure of the absorber and the nature of the matrix being the dominant ones. Concentration of the UVA, the presence of hindered amine light stabilizers (HALS), and nature of the light source have little effect except if the latter two factors affect the rate of matrix degradation. UVA loss is increased if the matrix itself degrades to generate free radicals. In general, the rate of UVA loss must be determined experimentally for each absorber in each particular matrix.

HIGHLIGHTS AND PROSPECTS IN CHEMISTRY AND PHYSICS OF POLYMER STABILIZATION

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Polymers are degraded during their lifetime by a complex of chemical and physical agents. Proper exploitation of the knowledge of degradation mechanisms, chemical reactivity and physical interactions with stabilizing additives enables to improve processing stability of commodity and engineering polymers and prolong their lifetime during application in aggressive environments. Specific approaches have to be considered in protecting polymers for high-tech applications.

The contemporary approaches to the solution of polymer stability have been based on understanding of intricate mechanisms of stabilizers in polymeric systems arising from product studies and in-polymer tests. This includes chemistry and photochemistry of compounds generated during the sacrificial stabilization mechanism. The attention has been focussed on processes depleting stabilizers, influence of traces of inherent polymeric impurities, like residues of polymerization catalysts, content of polymer degradation products, interactions with fillers or introduced metallic impurities. This approach enables better understanding of the complex process and modifies some mechanistic conclusions arising from early formal kinetic elucidations.

Molecular architecture of stabilizers reflects expectations of the plastic, rubber and coatings industries. Relations between high inherent chemical efficiency and physical persistence have been balanced in optimum way in additives of different classes. Physical studies, including elucidation of morphological phenomena governing semicrystalline and multiphase structures, and search for detection of initial stages in the degradation/stabilization process involving energy concentration and transfer, participation of excited complexes, and detection of inhomogeneities of the process accounting for delocalization of defects offer new insight in effective stabilization.

The most considerable mechanistic development accounts for understanding of the degree of sterical hindrance in phenolic antioxidants and their architecture enabling a partial regeneration of consumed phenolic moiety, resistance against gas fading, high efficiency in synergistic combinations and incorporation of bifunctionality by structural modification. Aliphatic hydroxylamines, discoloration resistant aromatic and semihindered heterocyclic amines extend the family of chain-breaking antioxidants for plastics. Better understanding of mechanisms of hindered heterocyclic amines resulted in structural modifications imparting enhanced resistance to acidic impurities and bifunctionality. Efficient UV absorbers for surface protection and applicable in photo-cured coatings represent top development in light stabilization.

The solution of polymer stabilization remains open for development of new efficient, physically persistent and environmentally acceptable systems: scavengers of alkyl radicals, light stabilizers absorbing in the UV-B area, synergistic systems for polyolefins of new generations, bifunctional stabilizers and stabilizer/compatibilizer blends for recycled plastics are the examples of some topics.

ML-10

INTERACTIONS OF STABILIZERS DURING OXIDATION PROCESSES

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To protect organic polymers from deterioration during processing and long-term application, mixtures of stabilizers, in particular sterically hindered phenols, organic phosphites and hindered amines (HALS), are widely used. Compared to the behavior of the individual compounds, of which the action modes are rather clear with some restrictions concerning HALS, the interactions of stabilizers have been investigated far less and partly even with contradictory results. We studied the antioxidative action of mixtures of phenols, phosphites, HALS and partly also their transformation products in various compositions in the thermo- and photo-oxidation of hydrocarbons and polypropylene under different conditions.

In the AIBN-initiated oxidation of hydrocarbons at low temperatures ($< 80^{\circ}\text{C}$), only hindered phenols and hindered aryl phosphites act antioxidatively when used individually. Alkyl phosphites exhibit an prooxidative effect due to their chain propagating reactions with peroxy radicals. Secondary HALS do not show any induction periods but a certain retardation of the oxidation process after some reaction time. The nitroxyl derivatives of HALS, however, significantly inhibit the oxidation. The magnitude of their inhibiting efficiency cannot be explained completely by the currently accepted action mechanisms of HALS, and must therefore also be attributed to the reaction of the nitroxyls with alkylperoxy radicals.

In mixtures with hindered phenols, HALS have almost no influence on the rate of oxidation at low temperatures. Their nitroxyl derivatives, however, always exhibit synergism, most pronounced when both stabilizers are used in an equimolar ratio.

In the autoxidation of hydrocarbons and polyethers at higher temperatures ($\leq 100^{\circ}\text{C}$), all HALS and both aliphatic and aromatic phosphites studied act synergistically when used together and with phenols. This demonstrates that for acting as synergist for phenols, the hydrogen peroxide decomposing capability of the phosphites and not their chain breaking activity is crucial. HALS-phosphites and phosphonites, containing the amine and the phosphorus units in one molecule, are highly effective stabilizers, exhibiting lower critical antioxidant concentrations and longer induction periods than phosphites alone. They even exceed the efficiency of phenols in many cases.

The influence of mixtures of stabilizers on the oxidative stability of polypropylene is rather different and depends on the oxidation conditions, the structure and the ratio of the stabilizers. In this context we studied and compared the stabilizing efficiency of various stabilizer combinations (HALS, phosphites, HALS-phosphites and phenols) during thermo- and photo-oxidation and processing of polypropylene. Synergistic, not pronounced, but also antagonistic effects are observed. Details of the results obtained are represented and discussed.

ML-11

STABILIZATION BEYOND THE YEAR 2000

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Inhibition of oxidative degradation of polymers has been a key issue for the use of plastic materials in various applications. Without the development of stabilizers, which interfere at different stages of the autoxidative chain reaction, production and end-use of such materials would not have been possible.

Early studies involving natural rubber have shown that aromatic amines contribute efficiently to the stability of the polymer. Aromatic amines act as H-donors, breaking the chain of the autoxidation reaction through the formation of ROOH groups. However, the use of aromatic amines leads to severe discoloration of the substrates and is limited to applications which need no approvals for indirect food contact such as packaging materials, appliances, or toys. The discovery of sterically hindered phenols as equivalent in performance as H-donors led to an enormous progress in the stabilization of polymers against oxidative deterioration. Mechanistic studies of the inhibition reaction involving hindered phenols allowed the synthesis of a great number of commercial products. Besides the ability of phenols to act as H-donors, phenols with a suitable substitution pattern can also react as radical scavengers. Through the formation of an intermediate quinone methide, regeneration of the phenolic group in subsequent steps is possible, as shown in the case of p-propionic ester type phenols.

Hydroperoxide groups are relatively unstable when exposed to heat and light. They decompose into highly reactive alkoxy- and hydroxy radicals, RO[•] and [•]OH. These species initiate further autoxidation of the polymer.

Hydroperoxide decomposers, which are able to transform the hydroperoxides into an alcohol and an inert oxidation product, have led to a break-through in the art of stabilization, especially when used in combination with phenols.

Blends of hindered phenols with trivalent organo phosphorous compounds represent the state of the art of today's stabilization. The availability of a large number of different phosphites and phosphonites allows the selection of such blends for different applications, which can provide good compatibility with the substrates or suppression of color formation caused by traces of residual catalysts in various substrates. Due to the kinetics of the hydroperoxide decomposition involving trivalent organo-phosphorous derivatives, such blends do not largely contribute to the service lifetime of the polymeric article. Lifetime is only governed by the choice and the concentration of the hindered phenol, the phosphites protect the phenols from being consumed upon processing.

Thiosynergists such as dilauryl- and distearylthiodipropionate act also as hydroperoxide decomposers and contribute to a prolonged service lifetime especially when used in combination with phenols. An intermolecular co-operative effect of thiosynergists with hindered phenols is observed when the substituent in the 6-position of the phenol group is relatively small, e.g. a methyl instead of tert-butyl group.

Hindered phenols linked together via a thioether group are known to be powerful stabilizers, acting as H-donors and hydroperoxide decomposers at the same time. Recently, a new class of hindered phenols having a suitable thioether moiety in the 6-position of the phenol group have shown a large synergism. This effect is caused by an intramolecular co-operation involving the hydroperoxide, the phenol and the thioether group.

Scavenging alkyl radicals would immediately stop autoxidation. However, the reaction rate of molecular oxygen with alkyl radicals is so fast that it is hard for any alkyl radical scavenger to compete with this reaction. Aminoxyl radicals, $N-O^\bullet$, formed through the oxidation of hindered piperidine derivatives, HAS, are able to react with alkyl radicals, especially when the oxygen concentration is relatively low. HAS stabilizers were initially designed as light stabilizers and their discovery led to a revolution in the world of polyolefin stabilization against photooxidation. Today, they gain increasing importance as long-term thermal stabilizers. Since the aminoxyl radical is formed during exposure of the stabilized polymer to heat and light, addition of a process stabilizer is needed to protect the polymer during processing. Modern stabilizer systems contain HAS in combination with phosphorous hydroperoxide decomposers. Blends of HAS with different ancillary properties like low and high molar mass or with different kinetics of the aminoxyl radical formation show synergistic effects compared with the use of the single HAS at the same total concentration.

Very recently, process stabilizers like alkylhydroxylamine or benzofuranone derivatives, acting basically as C-radical scavengers, in combination with HAS have shown outstanding performance with regard to stabilization of polypropylene fibers. A new class of C-radical scavengers has been developed for the stabilization of rubbers during processing. Some rubber compounds are prone for crosslinking and gel-formation, the addition of a 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate efficiently scavenges C-radicals. In a first step the alkyl radical is trapped by the addition to the double bond of the acrylate moiety, followed by a intramolecular hydrogen transfer from the neighbouring phenol group.

As mentioned, HAS are excellent stabilizers, inhibiting oxidation of polymers. However, HAS in presence of compounds which can form acids upon irradiation or heat, like thiosynergists, halogenated flame retardants, and crop protection agents, salt formation occurs and a strong antagonistic effect is observed. HAS with very low inherent basicity like NOR-derivatives do not show such antagonism.

Most of the engineering thermoplastics like polyesters, polyamides, polycarbonate, or polyacetals need to be protected against photodegradation. UV-absorbers, e.g. benzophenones and 2-hydroxyphenylbenzotriazoles have been used for many years. Some of the UV-absorbers show inherent

instability when exposed to light. Recent developments of hydroxyphenyltriazines have shown that this class of UV-absorbers is photostable and gives outstanding performance, enabling the use of engineering thermoplastic parts over a prolonged period of service lifetime.

Knowledge of degradation of polymers upon processing and service lifetime is the basis for the selection of a stabilizer system to fulfill the requirements under given exposures to light and heat.

Expanded toxicological investigations are needed to obtain the approvals for indirect food contact applications.

Further, the re-use of plastic materials, e.g. mechanical recycling, will gain importance. Restabilization with specially designed stabilizer systems will lead to high value recycled plastic parts.

OXIDATION AND STABILISER PARTITIONING IN RUBBER-REINFORCED POLYPROPYLENE

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Although polymer blends are an increasingly important group of materials, relatively little work has been reported on their degradation and stabilisation. In particular rather little is known about the partitioning of stabilisers between phases in phase-separated blends and how it may affect stability.

Previously reported studies of ABS and of Polycarbonate/PVC blends have shown that stabilisers partition preferentially into the rubbery phase. However, in both of these cases the continuous phase is a glassy material, in which the additive migration rate is low, and the disperse phase is the unstable phase. Thus preferential stabilisation of the disperse phase is advantageous.

We have studied the partitioning of two commercial stabilisers, Irganox 1076 and Cyasorb UV531, between polypropylene and an ethylene/propylene rubber, typical components of rubber-toughened products. In this case the rubber forms the disperse phase, but is more stable than the PP matrix.

Solubility measurements show that both additives are highly soluble in both polymers, with the rubber being the better solvent. In particular, solubility in the rubber is highly non-ideal. We have measured partitioning between bulk samples of PP and rubber, initially containing the same concentration of additive. Although the partition coefficient favours the rubber, the non-ideality of solution means that the partition coefficient is concentration dependent and not equal to the ratio of overall solubilities. Based on these measurements it is predicted that the fraction of the total additive present in the rubber will increase with temperature, so that over 80% may be in the rubber phase at typical oven ageing temperatures; stabilisation studies at high temperature are consistent with this observation.

Ultra-violet microscopy of model polymer blends has confirmed the results of bulk measurements for the UV absorbing additive.

We will also report model and experimental studies of the migration of stabilising additives in a composite of two polymers and discuss their implication for studies of degradation and stabilisation of blends.

CL-1

A COMPARISON OF THE UV-DEGRADATION CHEMISTRY OF UNSTABILIZED AND HALS-STABILIZED POLYETHYLENE AND POLYPROPYLENE

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The UV-degradation of unstabilized and HALS-stabilized polyethylene (PE) and polypropylene (PP) is studied. The degradations are characterized by measuring the oxygen uptake, the formation of CO and CO₂, the FT-IR spectra, the mechanical properties and the oxygen content of the films.

In the case of unstabilized PP and PE the oxygen uptake led to expected changes, but this is not the case for the HALS stabilized polymers. At the same oxygen uptake the IR absorptions increased more for the unstabilized than for the HALS-stabilized polymers.

The results can be explained assuming two different oxygen uptake mechanisms:

- The free radical chain oxidation mechanism, converting oxygen in the expected oxidation products.
- Oxygen uptake through CTCs of oxygen and the polymer leading to alkyl radicals and water.

For the unstabilized polymers the radicals formed by the CTCs initiate the normal free radical chain oxidation mechanism, causing that the oxygen is consumed through both mechanisms. For the HALS-stabilized polymers the oxidation is also initiated by the CTCs, but in this case the radicals formed are trapped by the stabilizer, causing that the oxygen is mainly converted via the CTC-mechanism into water.

For the HALS-stabilized PP the increase of the IR absorptions are larger than for the HALS-stabilized PE (at the same oxygen uptake). This is probably due to the higher susceptibility of PP to free radical chain oxidation, causing that radicals formed from the CTC will give more free radical chain oxidation before they are trapped by the stabilizer.

THE CORRELATION BETWEEN CHEMILUMINESCENCE AND PEROXIDES IN OXIDISED POLYPROPYLENE AND THE EFFECTS OF DIMETHYLSULFIDE EXPOSURE

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Oxidative degradation of polypropylene (PP) has been investigated by chemiluminescence (CL) measurements. The chemiluminescence has been measured during heating of preoxidised PP powder in an inert atmosphere, and proportional relationships were found when the integrated emission was plotted against peroxide concentration (measured iodometrically) for all studied sets of parameters (Figure 1)¹.

Dimethylsulfide (DMS) has previously been presented as a tool to distinguish between different types of PP peroxides². Preoxidised PP has been exposed to DMS for different periods of time with subsequent measurements of TLI and peroxide concentration. Both the peroxide concentration and the TLI exhibited a two-stage decay, indicating two fractions of peroxides with different reactivity towards DMS (Figure 2)¹. The unreactive peroxides exhibited a higher thermal stability than their more reactive analogues. Thus, the fraction of unreactive peroxides was found to increase with increasing aging time. Furthermore, the oxidative stability, measured by CL induction times in oxygen, was found to increase when samples were exposed to DMS.

A catalytic effect of protic species on the reaction between peroxides and DMS has been found. The reactivity of peroxides towards DMS is proposed to be governed by the presence of surrounding peroxides. The higher DMS reactivity of adjacent peroxides would then correspond to the lower thermal stability reported by Chien and Jabloner³. The amount of DMS resistant was found to be correlated to the melting temperature and glass-transition temperature. This lead to the conclusion that the reactivity of peroxides towards DMS was governed by the segmental mobility in the polymer, as a consequence of the catalytic effect of an adjacent protic species.

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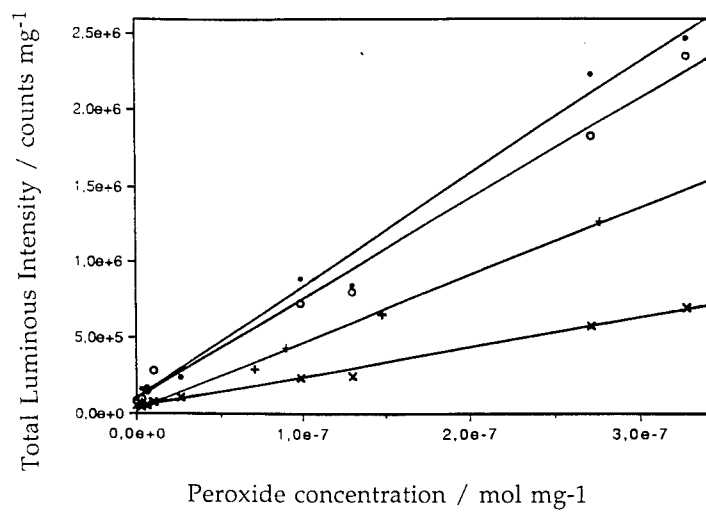


Figure 1: Integrated CL emission (TLI) versus peroxide concentration;
 (o) PP aged at 70°, TLI measured at 120°C; (•) PP aged at 70°, TLI measured
 at 150°C; (+) PP aged at 120°, TLI measured at 120°C; (x) PP aged at 70°,
 TLI measured at 150°C in a different CL-detector.

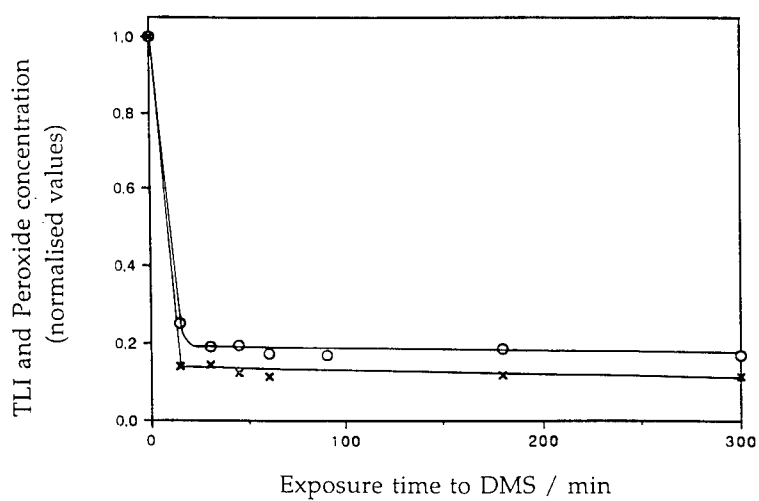


Figure 2: Relative concentration of peroxides and relative TLI of PP powder,
 aged 1420 hours at 70°C in air, for different exposure times to DMS.

CL-3

POLYOLEFINS - STATE OF THE ART AND OUTLOOK TO THE YEAR 2000

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Polyolefins account today for about 60% of the commercially important high-tonnage thermoplastic polymers, and their share is predicted to increase even more in the future. Polyethylene is the major tonnage plastics material world-wide and polypropylene is growing the most strongly. The emerging catalysts and technologies extend the properties and application limits of polyolefins beyond those traditionally accepted for these resins.

Stabilisers and stabilisation technology paralleled the growth of the polyolefin industry. Most of today's highly efficient antioxidants and light stabilisers are the result of the research efforts made since 1950s, when polyolefins via transition metal catalysts appeared on the market. Polyolefins dominate the world thermoplastic market in terms of both antioxidants and light stabilisers consumption. About 60% of the antioxidants and 75% of the light stabilisers produced world-wide for thermoplastics are consumed by the polyolefin industry.

The large number of polyolefin grades available on the market for the most different applications may be regarded as:

A. Physically functional materials, where tailoring of polymer structure and properties is performed during polymerisation;

B. Chemically functional materials, by in- or post-reactor modification making use of different functional monomers and chemical reactions.

Both approaches allow to enhance some useful properties of the polyolefins or to provide them with new properties which extend their application. Whereas the vast majority of the physically functional polyolefin grades are cheap commodity resins with large markets, most of the chemically modified polyolefins are speciality resins, more expensive, or even "exotic" resins, often tailored for very specific end uses and niche markets.

The followings may be regarded as the major driving forces in the development of the polyolefin industry:

1. Developments in catalysts: increased productivity, controlled morphology of the polymer powders, copolymerisation capability, tailored stereoregularity.

2. Developments in the engineering of the polymerisation processes: reactor design, increasing of the reactor capacity, e.g. the condensing and supercondensing mode for gas phase reactors, cascade arrangements of reactors for bimodal molecular weight distribution polymers.

3. Understanding of polymerisation kinetics and polymer microstructure.

4. Developments in additive packages: enhancement of the useful properties of polyolefins.

These developments are presented for the main technologies of polyolefin production: bulk, solution, slurry and gas phase polymerisation processes.

The polyolefin industry is also characterized by a strong and often wild competition concerning catalysts, polymerisation processes and polymer grades. Thus, polyolefins compete not only among themselves, e.g. LLDPE will overtake HDPE in 1996 and LDPE in 1998 whereas PP increasingly captures some PE markets, but also with other commodity thermoplastics, elastomers and engineering resins.

Metallocene catalysts opened a new era in the polyolefin industry. For a long time the metallocenes were quite unable to compete with the Ziegler-Natta catalysts although both were discovered during the 50's. Today metallocenes are making a vital step towards the industrial-scale production of polyolefins. The power of metallocenes mainly lies in the followings: extremely high productivity, unusual copolymerisation capability, precisely controllable polymer microstructure (comonomer distribution, stereoregularity). The development of metallocenes is far from over, and for individual processes such as the production of polyethylenes, polypropylenes and cycloolefin copolymers, only the first successes have been achieved.

There is no other family of polymers where such important developments occurred since their appearance on the market. The new polyolefin grades will certainly affect to some degree the field of stabilisers and stabilisation technology. Researchers involved in this field should be therefore prepared for the actual and future development of polyolefins.

STRUCTURAL EFFECTS ON HYDROGEN ATOM ABSTRACTION FROM AMIDES BY EXCITED STATE KETONES: INITIATION OF AMIDE OXIDATION

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Our interest in polyamide photochemistry led us to investigate amide oxidation. It is accepted that one of the important steps in the initiation of amide oxidation is hydrogen abstraction^{i,ii}. We have used the technique of laser flash photolysis to investigate the quenching of triplet excited state ketones by a series of 17 aliphatic amides. The decrease in the triplet-triplet absorption of the ketones was monitored in the nanosecond time domain as a function of added amide

Rate constants were obtained in this manner for the quenching of the triplet excited state xanthone with 17 amides (Table I). The rate constants for quenching of a series of $\pi-\pi^*$ triplet excited state ketones with N-propylbutanamide were also obtained (Table II).

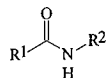


Table I. Rate Constants for the Quenching of the Triplet Excited State Xanthone by Model Amides in Acetonitrile Solution

R ¹	R ²	k _Q (M ⁻¹ s ⁻¹) ^a	k _Q /H (M ⁻¹ s ⁻¹) ^b
CH ₃ CH ₂ CH ₂	C(CH ₃) ₃	<2.4 ^c	
CH ₃ CH ₂ CH ₂	C(CH ₃) ₂ CH ₂ CH ₃	- ^d	
(CH ₃) ₃ C	C(CH ₃) ₃	- ^d	
CH ₃ CH ₂ CH ₂	CH(CH ₃) ₂	<2.4 ^c	<2.4 ^c
CH ₃ CH ₂ CH ₂	CH ₃	14.8	4.9
CH ₃ CH ₂ CH ₂	CH ₂ CH ₃	14.3	7.2
CH ₃ CH ₂ CH ₂	CH ₂ CH ₂ CH ₃	59.2	29.6
CH ₃ CH ₂	CH ₂ CH ₂ CH ₃	102.0	51.0
(CH ₃) ₃ C	CH ₂ CH ₂ CH ₃	15.7	7.9
CH ₃ CH ₂ CH ₂ ^e	CH ₂ CH ₂ CH ₂ CH ₃	112.0	56.0
CH ₃ CH ₂ CH ₂	CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	114.0	57.0
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	30.7	15.4
CH ₃ CH ₂ CH ₂	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	36.5	18.3
CH ₃ CH ₂ CH ₂	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	30.3	15.2
CH ₃ CH ₂ CH ₂	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	21.5	10.8
Pyrrolidinone	-	45.0	22.5
Caprolactam	-	21.0	10.5

^aRate x 10⁵. ^bk_Q/H = k_Q/# of hydrogens on the carbon α to the NH, value x 10⁵. ^cQuenching observed, reported rate constant is an upper limit. ^dNo quenching observed. ^eRate constant for amide concentrations 0.8M and lower.

Table II. Rate Constants for the Quenching of $\pi-\pi^*$ Triplet Excited States Ketone by N-Propylbutanamide in Acetonitrile Solution

Ketone	Triplet Energy (kcal M ⁻¹) ⁱⁱⁱ	k _Q (M ⁻¹ s ⁻¹) ^a
Xanthone	74.0	53.0
Benzophenone	68.6	33.0
Benzil	53.3	- ^b

^aRate x 10⁵. ^bNo quenching observed.

As the data of Table I shows, substitution of the hydrogens on the carbon α to the NH with methyl groups led essentially to an elimination of observable quenching. Blocking the position α to the carbonyl group as a *tert*-butyl substituent, however, led to only a moderate inhibition of the quenching

rate constant. The rate constants for quenching of the triplet excited state of xanthone by N-alkylbutanamides increase with alkyl chain lengths from C₁-C₄, but they fall off dramatically with chains longer than C₅. The control experiments show that random abstraction from an alkyl chain is slow (no observed quenching by pentane) and that potential impurities, such as water and butyric acid, do not contribute to the quenching. Table II shows that the quenching rate constant clearly increases with increasing triplet state energy.

An interesting concentration dependance of the absolute quenching rate was observed for N-butylbutanamide (figure 1). The rate constant for quenching of the triplet excited state of xanthone decreased at amide concentrations above 0.8M.

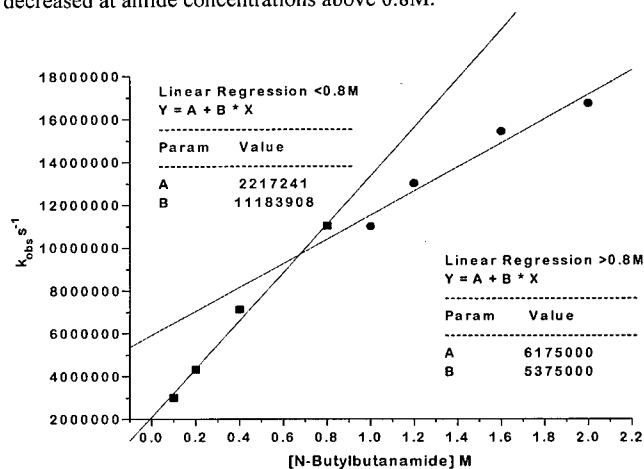


Figure 1. Plot of the quenching of triplet excited state xanthone with N-butylbutanamide in acetonitrile solution.

Explanations of the observed quenching behavior have been postulated and will be presented.

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WAVELENGTH SENSITIVITY OF THE PHOTODEGRADATION OF POLYMER MATERIALS

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INTRODUCTION

Many kinds of polymer materials for industrial purposes have been developed recently and such polymers are used under the influence of terrestrial sunlight or artificial light. Efficiency of light-induced degradation of a polymer material expressed as a function of the wavelength of incident radiation gives a crucial information on spectral sensitivity of the material. Such information is useful to identify the spectral region which causes damage to the material.

We have been investigating the wavelength effect of photodegradation on polymer materials such as vinyl polymer, polycarbonate and chitosan to determine the effective wavelengths for degradation. Such studies are possible using a large spectrograph built at the National Institute for Basic Biology(NIBB) at Okazaki Japan(OLS). **Table I Quantum Yields of Main-Chain Scission (Φ_{cs}) at Specified Irradiation Wavelengths in Air and In Vacuo**

$\Phi_{cs} \times 10^4$	Wavelength (nm)		
	260	280	300
In air*	2.07	2.34	4.31
In vacuo	0.84	1.06	4.21

EXPERIMENTAL

PMMA was purified by reprecipitation from methanol. Benzophenone(BP) was used after recrystallization from methanol. PMMA and PMMA-BP films were cast from acetone solutions on flat glass dishes. Samples were irradiated with monochromatic radiation using OLS. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. UV-, FTIR and ESR spectra of photoirradiated samples were measured to clarify the reaction scheme of these systems. Number of main chain scission was estimated from the results of viscosity and GPC measurements. Gel measurement was also carried out.

RESULTS AND DISCUSSION

PMMA: Wavelength dependence of the quantum yields of main chain scission(Φ_{cs}) of PMMA irradiated in air and in vacuum are listed in Table I. Φ_{cs} shows higher value in air when the irradiation was carried out

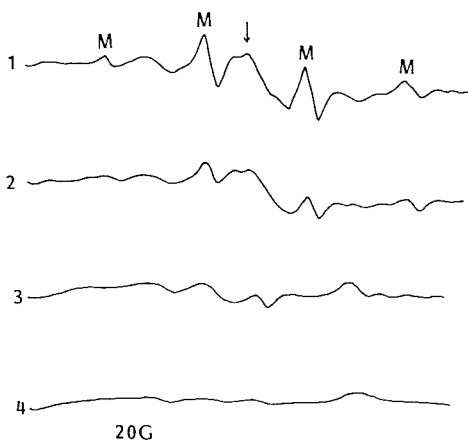


Figure 1 ESR spectra of photoirradiated PMMA at 77 K in vacuum. Irradiation wavelength: (1) 260 nm; (2) 280 nm; (3) 300 nm; (4) 320 nm. Total photon fluence: (1) 9.8×10^{19} photons/cm²; (2) 2.6×10^{20} photons/cm²; (3) 2.8×10^{20} photons/cm²; (4) 3.4×10^{20} photons/cm².

at 260 and 280nm. This fact means that some different process is concerned in main chain scission of PMMA at these wavelengths.

Fig.1 shows ESR spectra obtained at 77K in vacuum. Radicals due to the ester side chain scission were observed in case of the irradiation at 260 and 280nm. Only the scission type radical of PMMA was found by irradiating at 300nm. No radical was found with the irradiation longer wavelength than 320nm.

No change was observed in UV- and FTIR spectra when irradiated at longer wavelength than 320nm.

From these results, the threshold wavelength of photodegradation of PMMA was found to be around 320nm.

Ester side chain scission followed by main chain scission is the main process for the photodegradation of PMMA when the irradiations were carried out with 260 and 280nm radiation.

PMMA-BP:BP has its absorption bands at $\lambda_{\max}=253, 280, 340\text{nm}$. On photoirradiation of PMMA-BP film, the absorbance around 280nm decreased. The decreasing behavior is parallel to the absorption spectrum of BP in 320–400nm region. This decrease is dependent on the concentration of BP in PMMA.

The decrease in the intensity of 1700cm^{-1} ($\nu \text{ C=O}$) and 1100cm^{-1} ($\nu \text{ C-O-C}$) region were observed in FTIR measurement. These decreases are responsible for the consumption of PMMA.

The insoluble fraction in THF was produced in photoirradiated BP-PMMA with the irradiation of 260–360nm radiation. After filtering out the insoluble fraction, the number of main chain scission was calculated from the number average molecular weight ($\bar{M}_n$). In pure PMMA sample, number of main chain scission is 0 when the irradiations are carried out with the radiation longer wavelength than 320nm.

On addition of BP to PMMA, the degradation of PMMA is accelerated and this acceleration is dependent on additive concentration as shown in Fig.2.

Gel contents were also measured after extracted the soluble fraction with tetrahydrofuran. Gel content also increases with the increase of BP concentration in PMMA.

Main chain scission and the formation of gel with respect to the irradiation wavelength parallel to the absorption spectrum of BP.

From the experimental results, a possible mechanism for photosensitized reaction is proposed.

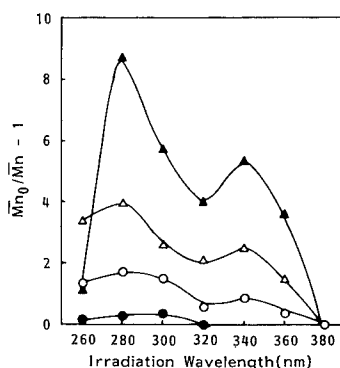


Figure 2 Changes in the number of main-chain scission of photoirradiated BP-PMMA films with irradiation wavelength. Concentration of BP: (●) 0 mol %, (○) 0.3 mol %, (△) 0.5 mol %, (▲) 1.0 mol %.

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CHARACTERISATION OF Si-AL-P CATALYTIC SPECIES IN INTUMESCENT SHIELDS

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Polyethylenic polymers are applied in many fields. Due to their chemical constitutions, they are easily inflammable and to reduce their flammability, flame retardants (FR) are added. The Laboratory develops intumescent FR systems using new carbonisation synergistic (zeolites [1]) agents.

The adduct of zeolites, in particular zeolite 4A [2], in intumescent formulations of thermoplastic polymers (additives : ammonium polyphosphate (APP) and pentaerythritol (PER)) leads to a very high degree of improvement of the fire-proofing performance. However the « efficiency » of the zeolite depends strongly on the polymer and an important polymeric matrix effect has been previously shown [3]. The presented results deal with Ethylene-Butylacrylate-Maleic anhydride (LRAM3.5)-based formulations because using this terpolymer the effect of the zeolite is the most important (fig. 1).

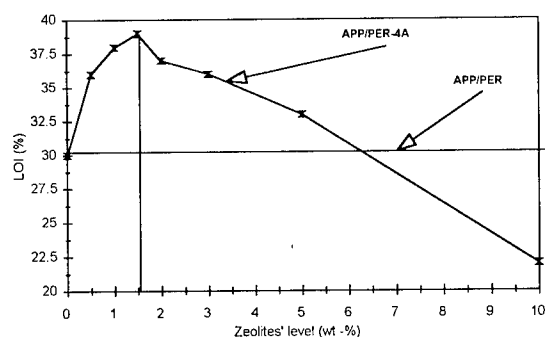


Figure 1 : Normalised fire testing values (Limiting Oxygen Index (LOI)) versus zeolites' level in an technical ethylenic terpolymer (ethylene-butylacrylate-maleic anhydride, Lotader P3200 from Elf-Atochem). The additives' level is kept constant equalling 30 wt.-% and the synergistic effect exhibits a maximum at 1.5 wt.-% 4A zeolite level.

TG analyses reveal that the zeolite may act as a catalyst for the development of the intumescent carbonaceous material and stabilise the carbonaceous residue resulting from the degradation of the intumescent shield.

In order to understand the part played by the zeolite in the protective material, the solid state NMR ^{13}C , ^{31}P , ^{27}Al and ^{29}Si are powerful tools. The spectrochemical study is led to the heat treated LRAM3.5-APP/PER and LRAM3.5-APP/PER-4A systems at four characteristic temperatures which correspond to the beginning of the formation of the intumescent material (280°C), the maximum of intumescence (350°C), the carbonaceous residue (430°C) and the high temperature residue (560°C) [4].

This shows that the presence of the zeolite hinders the complete thermooxidative degradation of the protective coating [5] and of the polyethylenic chains of the polymer. So, the stabilisation of the polymer links in the carbonaceous shield prevents the formation of small flammable molecules and as a matter of fact the fuel degradation rate feeding the flame. More, it is proposed that the stabilised polymer links bridging the polyaromatic network may provide the mechanical properties of interest.

Characterised by MAS-NMR ^{27}Al and ^{29}Si , it is finally proposed that alumino- and silicophosphate species formed, are catalysts active for the synthesis of a very efficient protective carbon-based material.

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PROBLEMS OF THE RIGID-CHAIN HETEROCYCLIC POLYMERS DEGRADATION IN CONCENTRATED SULFURIC ACID

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Many films and fibers with excellent mechanical properties are available from heterocyclic polymers. However, pronounced time changes of such important characteristics of the films as elastic modulus, relative elongation at break, and tensile strength may occur. These changes may be attributed to polymer degradation more often than to supermolecular time superposition only. Mechanism of the polymer ageing effect may be detailed by molecular characterization of the polymer sample and by checking of the time changes in polymer properties.

The purpose of this work is to analyze the influence of chemical structure of the macromolecule on thermal hydrolytical stability of the polymer in solution in relation to the polymer thermal stability in bulk.

The thermal degradation of different heterocyclic polymer molecules in conc. sulfuric acid has been studied by methods of molecular hydrodynamics and optics. The degradation rate was characterized by the time variation of molecular weight of the polymer degradation products. For this, translational diffusion of the macromolecules was studied, and the intrinsic viscosity of the polymer at various stages of thermal degradation in the solution was measured. The activation energy of the process was calculated from the temperature dependence of the degradation rate constant and related to the polymer chemical structure.

The following polymers will be under discussion:

- Poly(benzimidazole phenantroline);
- Poly(cyclohexane amide);
- Poly(*p*-phenylene oxadiazole);
- Poly(caproamide);

- Poly(*p*-phenylene terephthalamide);
- Poly(amide benzimidazole);
- Poly(naphthoylene imidobenzimidazole);
- Poly(*N,N'*-dimethyl-*p*-phenylene terephthalamide);
- Poly(tetraphenylmethane terephthalamide);
- Poly(*m*-phenylene isophthalamide);
- Poly(*p*-benzamide);
- Poly(*p*-amide hydrazide).

The thermal degradation of the fiber- and film-forming polyamides and heterocyclic polymers in conc. sulfuric acid is shown to be irreversible process which limits the possibilities of enhancing of temperature and acid concentration to increase the solubility capacity of a solvent. The features of the chemical structure of polymers resulting in a decrease of their thermal stability in sulfuric acid solutions are analysed. The examples of the usage of thermal degradation of the polymers in sulfuric acid as a method of controlled decrease of the macromolecule length (for analytical purposes) proceeding without degradation of elements of chemical structure responsible for the short-range interactions in the macromolecule will be presented for some of the polymers.

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IRRADIATION AND HEAT TREATMENT - INDUCED SPECTRAL CHANGES OF CR-39

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CR-39 is an important solid state nuclear track detector. It has an amorphous cross-linked structure which is very sensitive to heavy ion damage. In this study, this structure is investigated under the effect of either gamma irradiation or thermal treatment. Samples were irradiated with γ -doses up to 100 KGy in air while heat treatment was carried out by holding the samples at temperatures up to 180°C in an air oven for one hour. Optical absorption spectra in the UV-VIS range were obtained using a Perkin-Elmer Lambda 4B spectrophotometer at room temperature.

The spectrum of the untreated sample shows a weak absorption band at about 385 nm which can be attributed to an $n \rightarrow n^*$ transition of a nonbonding electron on oxygen. Spectra of the samples before and after gamma exposure and heat treatment are analysed by the direct - allowed transitions suggested by Mott & Davis.

The optical energy gap values were calculated for the irradiated samples and are found to decrease from 3.63 eV to 3.2 eV by gamma irradiation of 100 KGy, suggesting a degradation process to take place at these doses. Consequently, a disorder increase is expected in the polymer structure.

On the other hand, the calculated optical energy gap values for heat-treated samples are found to hardly decrease from 3.63 eV to 3.56 eV by heat-treatment up to 160°C which is attributed to the temperature coefficient of a gap evaluated as $1 \times 10^{-3} \text{ eV K}^{-1}$. Heating the samples to 180°C, the calculated optical energy gap value begins to increase (3.51 eV) accompanied by an abrupt change in the uv spectrum. This variation is suggested to be due to a phase transition in the cross linked amorphous structure of the polymer.

In both cases, plotting the induced optical absorption vs. wavelength indicated the formation of a colour center band at about 340 and 364 nm for irradiated and heat-treated samples respectively.

CHEMILUMINESCENCE FROM THE ISOTHERMAL OXIDATION OF SBR AND NBR ELASTOMERS

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INTRODUCTION

Chemiluminescence method has been widely applied for the evaluation of the stability of polymers and effect of additives on the polymer degradation. In this study CL emission from the isothermal oxidation of styrene-butadiene copolymers (SBR) and acrylonitrile-butadiene copolymers (NBR) was measured and the obtained CL data were compared with that of FT-IR and x-ray photoelectron spectrometry (XPS).

EXPERIMENTAL

Materials : SBR containing ST component of 0, 23.5, 46.0, 100 % and NBR containing AN component of 0, 18.0, 29.0, 40.5, 100 % were purified by reprecipitation method. Each solution of 2 wt % was cast on an aluminum foil to obtain sample films of 100 μ m thickness.

Measurements : The CL emission from the isothermal oxidation of the elastomer films was recorded on a CL analyzer at 100°C under oxygen flow of 50 ~ 60 ml/min. The size of the sample films was 10 mm x 25 mm for SBR and 10 mm x 10 mm for NBR. FT-IR (ATR) spectra of the sample films before and after oxidation were recorded using internal reflectance (IRE), KRS-5 at 45° and XPS spectra were measured with MgK α X-ray source at 14 kV, 300W, and take off angle at 45°.

RESULTS AND DISCUSSION

CL signals from the isothermal oxidation of SBR and NBR are shown in Figs.1 and 2, respectively. It is apparent that CL signals of NBR are extremely higher than that of SBR and the time to attain CL_{max} (maximum CL intensity) becomes shorter with an increase in the BD component in the elastomers. This is apparently ascribed to the easily oxidizable BD component in the elastomers. However, CL_{max} of the copolymers of the both elastomers were higher than that of each homopolymer, PBD, PST, and PAN, especially for NBR elastomers. The fact apparently suggests that the initial oxidation of BD component affects successive CL emission from the copolymer elastomers. Integrated CL emission from SBR

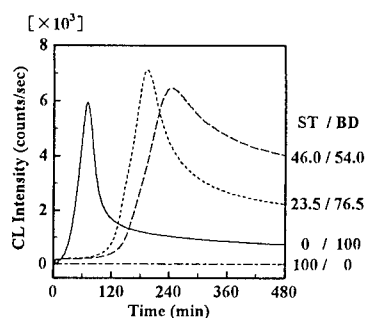


Fig.1 CL spectra of SBR at 100°C under oxygen.

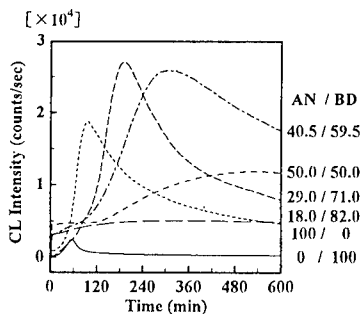


Fig.2 CL spectra of NBR at 100°C under oxygen.

shown in Fig.3 also indicates that the component ratio in the elastomers is a very important factor. Similar results were also obtained in NBR.

Changes in relative absorbance of carbonyl group at 1717 cm^{-1} and hydroxyl group at 3450 cm^{-1} observed in SBR are shown in Fig.4. Similar phenomena were observed in the NBR. It is quite obvious that PBD homopolymer oxidizes easily and forms oxygenated groups, and the formation of these groups in the elastomers increases with an increase in the BD component. Almost similar results were obtained in the XPS analysis.

The results obtained by IR and XPS data were quite different from that of CL data. This discrepancy between the formation of the oxygenated groups such as $>\text{C}=\text{O}$ and $-\text{OH}$ groups in the elastomers and CL signals from their isothermal oxidation suggests that there are certain factors to increase the CL emission through the effective energy transfer from the excited states $>\text{C}=\text{O}^*$ formed in the BD sites to the other component sites.

In this connection, Billingham* already pointed out that the CL intensity is dependent on various factors such as the rate of the luminescent reaction, a geometric factor and quantum yield of photons.

Taking account of his suggestion, the discrepancy between the CL intensity and formation of the oxygenated groups may be ascribed to the presence of flexible moiety which is susceptible to the oxidation in the elastomers. Glass transition temperature (T_g) of PBD is as low as $-95\sim-110^\circ\text{C}$ while that of PST is 100°C and PAN is 97°C . Thus, the mobility of BD component is restricted by the hard ST or AN segments in the elastomers, and decaying through a radiationless transition is retarded to emit light effectively.

This seems to be probable for the higher CL signals observed in the copolymer elastomers. However, difference in CL intensity between SBR and NBR can not be explained at present although AN sequence may be responsible for the higher CL intensity in NBR.

*: 206th ACS meeting in Chicago (1993)

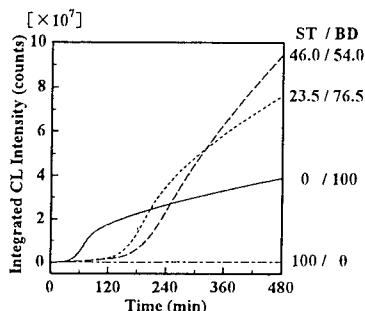


Fig.3 Integrated CL intensity of SBR at 100°C under oxygen.

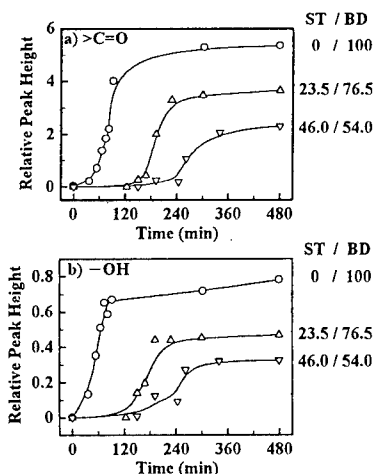


Fig.4 Relationship between relative peak height (internal reference: $\text{C}-\text{H}$, 2930 cm^{-1}) and oxidation time of SBR samples at 100°C under O_2 .

CHEMILUMINESCENCE AND OXIDATION OF POLYMERS, AN OVERVIEW OF POSSIBLE APPLICATIONS

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The chemiluminescence accompanying the oxidation of polymers at elevated temperatures was referred to as early as in 1961 by *Ashby* [1] and later by *Schard* and *Russel* [2] following the extensive work of Russian school of *Vassilev*, *Shlypintokh* and *Karpukhin* on chemiluminescence at oxidation of low molecular hydrocarbon models [3]. However, up to now when sophisticated imaging [4] and extremely sensitive photon counting technique are being successfully used, no uniform mechanism explaining the origin of the light emission when examining various polymers has been put forward. According to the shape of kinetic curves of chemiluminescence appearance and decay in time during oxidation of a polymer we distinguish the polymers performing:

1. autocatalytic increase of light emission with a distinct induction time and maximum value after which luminescence starts to decrease. At this instant, however, the oxidation is so advanced that use properties of the polymer are lost. The group of the polymers is represented by polyolefins, some polyamides, ABS copolymers, etc., the most chemiluminescence studies being devoted to polypropylene.

2. steady decay of chemiluminescence from some initial value to the threshold sensitivity of the spectrometer observed e.g. for poly(2,6-dimethyl p-phenylene oxide), epoxides, poly(ethylene terephthalate), i.e. with polymers having either high T_g temperature or heteroatoms incorporated in the chain and considerably lower length of oxidation chains.

3. extremely weak chemiluminescence that the method does not appear suitable for correlation with oxidation experiments. This is e.g. the case of polystyrene, poly(methyl methacrylate) or other polymers degrading by unzipping mechanism. In fact, the chemiluminescence from the oxidation of such polymers was not studied, at all.

More systematic study of the phenomenon is required with an particular focus on:

- a) nature of the emitter (isolated carbonyl groups, C=C unsaturated carbonyls, dicarbonyls, singlet oxygen, etc.)

- b) how the significant quenching of e.g. carbonyl excited triplets affects the kinetics of chemiluminescence? The research of the oxidation and chemiluminescence of polymers with activators or light sensitizers is lacking.

- c) why some inhibitors (nitroxide radicals, HALSes, etc.) in particular polymers as, e.g. aliphatic polyethers increase the chemiluminescence intensity when compared with unstabilized samples [5].

Taking into account more than 30 years experience with the method in polymers oxidation, the lecture will bring an overview of the present state with a particular emphasis on our latest results.

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OXIDATION THICKNESS PROFILES DURING THE PHOTOOXIDATION OF NON PHOTOSTABILIZED POLYPROPYLENE

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Summary

Bulk polypropylene(PP) samples, free of photostabilizers, were exposed in different accelerated ageing devices: Actinic Fluorescent Lamp Reactors (AFL), UV Cond, Xenotest 150 (XT 150), Xenotest 1200 (XT 1200) and Wheater-O-Meter XR 35 (WOM). The sample temperature was from 40 to 70°C. The UV intensity was determined by polycarbonate actinometry and it ranged from $7 \cdot 10^{18}$ to $200 \cdot 10^{18}$ photon $\text{cm}^{-2} \text{h}^{-1}$. The thickness profiles of carbonyl index were determined by FTIR spectrophotometry on microtome slices of 20 μm thickness.

In all photochemical reactors under study the carbonyl index profiles of 50 to 300 μm thickness appeared at the end of an induction period and after relatively short time they were accompanied by surface cracking. They have generally a pseudo hyperbolic shape (Fig. 1) without a superficial horizontal plateau observed in the case of radio or photooxidation of polyethylene. The thickness of oxidized layer (TOL) increases with the irradiation time in all cases. Determinations just before cracks appearance shown that the "by cracks non perturbed" TOL increases with exposure temperature and is practically independent of the light intensity.

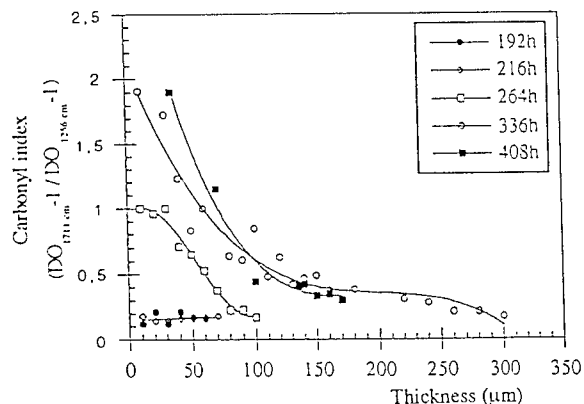


Fig. 1. Thickness profiles of carbonyl index obtained during the photochemical ageing of polypropylene samples in Xenotest 150S

The continuous increase of the TOL with exposure time can be attributed to autoceleration effects in the pseudo induction period and to the sample cracking shortly after the end of this pseudo induction period. An attempt is made to explain this peculiar behaviour of bulk polypropylene samples on the basis of an oxygen diffusion controlled photooxidation kinetics.

HYDROPEROXIDATION AND GRAFTING OF UNSATURATED RUBBERS

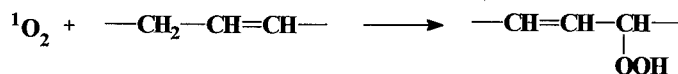
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The reaction of singlet oxygen with the carbon-carbon double bond to form allylhydroperoxide, the so called "ene" reaction is well known.



The presence of an isolated pendant double bonds in the terpolymer ethylene/propylene/5-ethylidene-2-norbornene (Vistalon VIST) and double bonds situated in the main chain in polyoctenamer (Vestenamer VES) has been used for earlier mentioned hydroperoxidation. Anthracene was used as a sensitizer for production of singlet oxygen under 365 nm irradiation. Secondary hydroperoxides are produced in both cases. Well distinguished isolated and associated hydroperoxides (VIST-OOH) are produced from VIST, while mainly associated ones (VES-OOH) are produced from VES at the hydroperoxidation in the solid phase. Anthracene reacts with singlet oxygen too and 9,10-anthracene endoperoxide is produced. Production of VIST-OOH in the film stops after the conversion of anthracene while in the case of VES-OOH the hydroperoxidation continues without any change of the reaction rate. The reason for this difference will be discussed.

Reactivity of VIST-OOH was tested by reaction with dimethyl sulfide (DMS). DMS reacts with hydroperoxides and corresponding alcohols are produced. Both the isolated and associated hydroperoxides react with DMS by dual fast and slow processes. Fast process is more significant in the isolated hydroperoxides. Their concentration dropped after DMS reaction to ca 10% of the initial value, whereas the concentration of associated hydroperoxides represented ca 40% of the initial one after the same reaction time.

Irradiation of hydroperoxidized rubber with the light $\lambda > 300$ nm in the presence of monomers or stable free radicals grafted these species onto the rubbers. Volatile monomers (methyl methacrylate, styrene, 1,2,2,6,6-penta-methyl-4-piperidyl acrylate = PPA) can be easily grafted on VIST-OOH film by irradiation in their vapour. Nonvolatile monomers as well as volatile ones and some stable nitroxyl radicals were grafted onto VIST-OOH films in methanol solution of monomers and stable nitroxyl radicals. Concentration of grafted monomers depends on the starting hydroperoxides concentration. Hydroperoxidation as well as grafting in the solid state occurs in the film, it is not only surface process.

Grafting on polyoctenamer was performed by irradiation of toluene solution of VES-OOH in the presence of monomers (2,2,6,6-tetramethyl-4-piperidyl acrylate = TPA and PPA) or stable nitroxyl radical (stearoyloxy-2,2,6,6-tetramethyl-4-piperidyl-N-oxyl = St-NO $\cdot$). PPA, TPA and St-NO $\cdot$ represent hindered amine stabilizers (HAS). Light stabilizing efficiency of grafted and low molecular HAS was tested in the polyoctenamer films.

THERMAL AND THERMO-OXIDATIVE STABILITY OF POLYETHER-BASED ELECTROLYTES

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The properties of solutions of inorganic salts (such as LiClO₄, NaCNS, etc.) in polyethers such as poly(ethylene oxide), PEO, poly(propylene oxide), PPO and their copolymers, are strongly dependent on the interaction between the backbone oxygen atoms of the polymer and the cation. The strong complexation of the cation is revealed in the conduction mechanism which involves predominantly anion migration. Complexation results in chain stiffening which leads to an increase in T_g with increasing salt concentration and also influences the thermal and oxidative stability of the polyether.

Generally, salts dissolved in, for example, PEO reduce the thermal stability in an inert atmosphere. The destabilising effect increases with increasing strength of the oxygen-cation interaction, which depends directly on the charge density on the cation. The stronger the O-M⁺ interaction, the weaker become the adjacent C—O bonds relative to those analogues in pure PEO. Salt complexation in PEO therefore changes the proportions of the various radical intermediates produced during the thermal degradation; these in turn influence the nature of the volatile products of degradation. Thus, complexes produce substantial amounts of CH₄, CO₂ and ethylene, which are produced only in trace amounts from pure PEO. The anion X⁻ of the complexed salt also influences the course of the degradation by screening the cation and in some cases through chemical involvement.

Oxygen renders PEO less thermally stable and changes the degradation chemistry as shown, for example, in different volatile products. However, in the presence of oxygen dissolved salts exert a stabilising influence, partly at least, by retarding thermal oxidation. The stabilising influence of the cations against thermal oxidation is approximately in the same order as their destabilising influence on thermal degradation in an inert atmosphere.

Other polyethers, such as PPO and poly(tetrahydrofuran), behave in a broadly similar manner to PEO, though they are generally poorer solvents for inorganic salts and are thermally less stable.

CHEMICAL REACTIONS DURING THE PROCESSING OF STABILIZED PE AND THEIR CONSEQUENCE ON PRODUCT PROPERTIES

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Polyethylenes are stabilized against the most diverse external effects according to the application conditions of the products produced from them. Processing stabilization, however, is almost always necessary and hindered phenolic antioxidants, as well as secondary stabilizers, usually phosphates, phosphonites or sulfides are used for this purpose. The primary and secondary stabilizers are often interact with each other, frequently antagonistic, or synergistic effects occur. Optimization of a stabilizer package is of utmost importance for any producer both from the technical and the economical point of view. Such an optimization procedure was carried out for the development of a recipe for blown films. During the study interesting correlations were observed among the quantities measured, close correlations were found among the colour, rheological characteristics of the granulates and the mechanical properties of the films produced from them. Such a correlation is shown in Fig. 1.

The recipes contained two different antioxidants in various amounts and a phosphonite co-stabilizer as well. After a first homogenization extrusion, 5 degradative extrusion were carried out on all recipes. Colour and MFI of the granulates were routinely measured, while additional characteristics, like OIT, tear strength both in the parallel and perpendicular direction of the extrusion, and dart drop impact strength were determined on selected samples. Additional analytical techniques (FTIR, UV, HPLC, GPC) were also used for the determination of the possible changes taking place during the extrusion of the material.

A detailed analysis of the experimental results have shown that chemical reactions take place during the extrusion of the polymer. Both the stabilizer and the polymer take part in these reaction. Stabilizer consumption leads to decreased product stability (OIT) and some of the reaction products result in colour formation. Reactions of the polymer change the number of

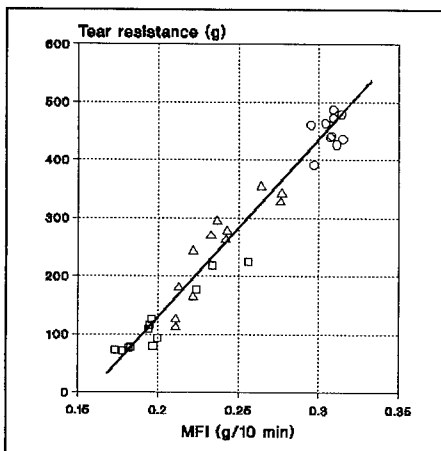


Fig. 1 Correlation of MFI of the granulates and tear strength of the PE film produced from them

functional groups (methyl, vinyl, vinylidene) on the chain, but must change also molecular weight, its distribution and branching as well, since rheological properties (MFI) are influenced significantly. A literature survey pointed out that numerous reactions may take place in the polymer during processing and the number of intermediate and end products of these reactions is also large [1-3].

As a consequence it was very surprising for us that both discolouration and the change in stability can be described quantitatively by a simple first order overall reaction kinetics. An example is shown in Fig. 2, where colour number of a recipe is plotted against the number of extrusions, a variable which takes the place of time in the kinetic treatment. A similarly excellent fit was obtained in all investigated cases and oxidative stability of granulate could be predicted from their colour.

Both colour and stability are related to the chemical reactions of the stabilizer. Those of the polymer were in unambiguous correlation with the changes in its properties. Moreover, close correlation between colour and MFI were obtained, while this latter quantity determined the mechanical properties of the blown films prepared from the granulates (see Fig. 1).

These correlations prove that the both the stabilizer and the polymer are involved in the chemical reactions taking place during the processing of a PE polymer. Small changes in the chain structure lead to profound differences in the properties of the end product. Since the composition of a stabilizer package used in practice and also in our present experiments is complicated, experiments are carried out with a polymer containing only one single component. Some of the new results are also reported in the conference in the form of a poster presentation.

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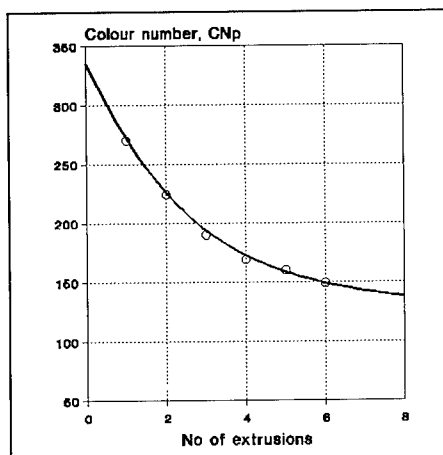


Fig. 2 Discolouration of a PE sample during multiple extrusion. (o) measured values, — fit of kinetic equation

STABILIZATION OF POLYMER BLENDS

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The thermooxidative stability of compatibilized and noncompatibilized polymer blends (such as for instance polystyrene/polyolefine, high-impact polystyrene/polyolefine, polycarbonate/ABS etc) was evaluated and compared with the stability of original component homopolymers.

Since the degradation mechanism of polymers highly depends on the experimental conditions and test methods used, a combination of methods was applied in the degradation study of polymer blends. Oxidative DSC studies combined with oxygen uptake measurements, IR spectroscopy data, and embrittlement tests proved to be sufficiently sensitive to detect differences in the stability of the above mentioned samples.

The chemical changes accompanying the degradation of selected polymer blends during the long-term oven aging experiments at temperatures 90 and 100°C, or during photooxidation, were monitored by means of IR spectroscopy and by changes in DSC curves.

In most cases, the evaluated blend stability was found between the stabilities of the original component polymers, showing that blending resulted in a less stable combination with respect to the more resistant component. The possible reasons for such behavior are considered and discussed.

A pronounced deterioration in the thermooxidative stability was also observed when two polymer components, one being effectively stabilized and the other unstabilized or not sufficiently stabilized, were blended. A relative drop of the antioxidant concentration is to be taken into account here. The antioxidant is (due to its migration ability and comparable solubility in both components) homogeneously distributed in the entire volume of the polymer blend at a relatively lower concentration, which is not sufficient to effectively inhibit the degradation processes in the blend. The resulting poor thermooxidation stability in such cases could, however, be improved by additional application of antioxidants.

It was also found that the nature of the compatibilizer, as well as its oxidative stability, has important impact on the thermooxidative behavior of compatibilized polymer blends. Moreover, DSC studies indicate that besides the chemical mechanisms, also the phase structure and morphology represent additional factors contributing to the overall stability of the blend.

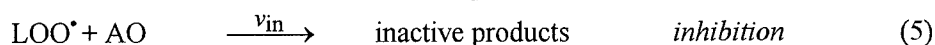
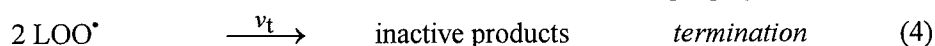
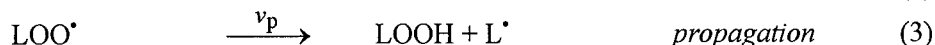
REACTION OF ANTIOXIDANTS WITH PEROXY RADICALS OF 6-HEXANELACTAM

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The most efficient organic antioxidants (AO) of polyamides (PA) are secondary aromatic amines. Phenols are inefficient in PA probably due to their reactions occurring in PA melts at high temperatures required for polymerization or processing (above 240°C). The antioxidation effect of HAS (hindered amine stabilizers) shows an induction period during which the NH group of piperidine is first oxidized to N-oxyl capable of reacting with the peroxy radical of PA.

The effect of AO in the thermooxidation of PA in solid phase is similar to that in the oxidation of 6-hexanelactam (HL) in the melt, with respect to both the kinetics of oxygen consumption and the mechanism of reactions, as can be judged from the composition of oxidation products. In the following scheme



the values k_p and k_t are known.^{1,2} The termination of $\text{LOO}^\bullet$ formed in the oxidation of HL at a defined initiation rate v_i was studied under the conditions when the reaction rate is not controlled by diffusion of oxygen and in the presence of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (MPO[•]), 4,4'-dimethoxydiphenylamine (MPA), diphenylamine (DPA) and 2,6-di-*tert*-butyl-4-methylphenol (BMP).

For the steady state in the inhibited HL oxidation it generally holds

$$v_p = k_p [\text{HL}] v_i (n k_{in} [\text{AO}])^{-1} \quad (6)$$

where n is the number of radicals $\text{LOO}^\bullet$ reacting with a molecule of AO.

The propagation reaction of the chain oxidation of HL does not proceed in the presence of AO if

$$k_p [\text{HL}] \ll n k_{in} [\text{AO}] \quad (7)$$

From this equation, the concentration of AO ($[AO]_{crit}$) which is necessary to suppress the propagation reaction of HL oxidation can be calculated.

For the given AO, k_{in} (Eq. 5), n (Eq. 6), and $[AO]_{crit}$ (Eq. 7) were determined and the oxidation products of HL were identified.

In contrast to the course of bimolecular termination (Eq. 4), the termination of $LOO^{\bullet}$ in the presence of AO was of the first-order. It was found that also the products formed in the reaction 5 from $MPO^{\bullet}$, MPA, or DPA are able to react with $LOO^{\bullet}$ and further inhibit the HL oxidation. After the first steady state, the oxidation rate increases gradually up to the second steady state and then up to the rate of the initiated oxidation of neat HL (see the Table).

Table

Critical concentrations $[AO]_{crit}$ (mmol.kg⁻¹) necessary to suppress the propagation reaction, rate constants $k_{in} \times 10^{-4}$ (kg.mol⁻¹ s⁻¹) and numbers n of $LOO^{\bullet}$ reacting with a molecule of AO in the first ($^1k_{in}$, ^1n) and the second ($^2k_{in}$, ^2n) stages of the initiated oxidation of HL at temperature T (°C)

AO	T	$[AO]_{crit}$	$^1k_{in}$	^1n	$^2k_{in}$	^2n
MPO	98	24	0.60	1	0.25	2
MPA	98	4	1.00	4	0.60	6
DPA	98	4	1.00	4	0.60	6
BMP	80	6	0.50 ^a	2	0	0
BMP	90	6	0.90	2	0	0
BMP	98	6	1.2	2	0	0
BMP	110	6	2.2	2	0	0
BMP	120	6	4.3	2	0	0

^aArrhenius parameters: preexponential factor 8×10^{12} ,
activation energy 62 kJ.mol⁻¹

Under the given conditions, one molecule of phenol, piperidine N-oxyl, or secondary aromatic amine are able to break two, three and ten oxidation chains of 6-hexanelactam, respectively.

The author is indebted to the Grant Agency of the Academy of Sciences of the Czech Republic for financial support of this work (Grant No. 450417).

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CL-17

EFFECT OF CARBON BLACK VARIABLES ON ITS UV-STABILIZING PROPERTIES IN POLYOLEFINS

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Carbon black is unique among pigments in its ability to stabilize polyolefins against UV light. Stabilizing efficiency is usually related to the fundamental pigment particle diameter in an inverse manner. However, other features of carbon black such as the structure of particle aggregates and chemical nature of particle surface have received little attention. This paper discusses the results of an investigation which attempts to correlate all major carbon black variables with their effect (if any) on pigment UV-stabilizing properties. Linear Low Density Polyethylene (LLDPE) 75 μ m films containing a variety of carbon black with known properties were exposed to two accelerated artificial weathering devices, a xenon arc source, *e.g.* Xenotest 150S and a fluorescent tube source, *e.g.* QUV/se with UV-B lamps, under controlled temperature and humidity. The changes in physicochemical properties during exposure were studied using tensile testing, Fourier transform infrared (FTIR) spectroscopic and differential scanning calorimetric (DSC) methods.

The time-dependent elongation-at-break of pure LLDPE film under the exposure to xenon arc irradiation (Xenotest 150S), which simulated outdoor sunlight at temperature 50°C and 65% humidity showed a relative slow decrease compared to the same film exposed to fluorescent tube irradiation from the QUV, UVB device at 60°C. There is a respective photodegrading intensity ration of 6:1 between the two weathering testers under such conditions.

Presence of each carbon black showed significant improvement in UV stabilization compared to clear films, especially for those with small particle sizes, as expected (see Fig. 1). There was no consistent effect of carbon black structure on UV stabilization for various particle size carbon blacks. However, the higher structured carbon black in medium (24-27nm) and large (40-60nm) particle sizes gave better UV durability. The increase in carbon black concentration from 1.5 to 3.5% w/w also responded UV stabilization.

Changes in tensile properties, and in particular, the elongation-at-break with exposure time were accompanied by the sensitive changes in hydroperoxides and carbonyl groups. Fig.2 shows the effect of UVB exposure time and particle size on the generator of hydroperoxide and carbonyl group. The hydroperoxide at 3431cm⁻¹ and carbonyl group at 1712cm⁻¹ show rapid increases with the increase in exposure time. The formation of carbonyl groups is closely connected with the involvement of hydroperoxides in the photooxidation reaction. The carbonyl absorbance index increase at 1712cm⁻¹ for the filled films is not accompanied by significant changes in vinyl group, absorption at 908cm⁻¹ and hence Norrish II scissions are absent i.e the presence of carbon black may suppress the latter to a greater degree than the former. This suggests that the UV-stabilising mechanism of carbon black has a chemical component which differs from that of commercial organic UV stabilizers.

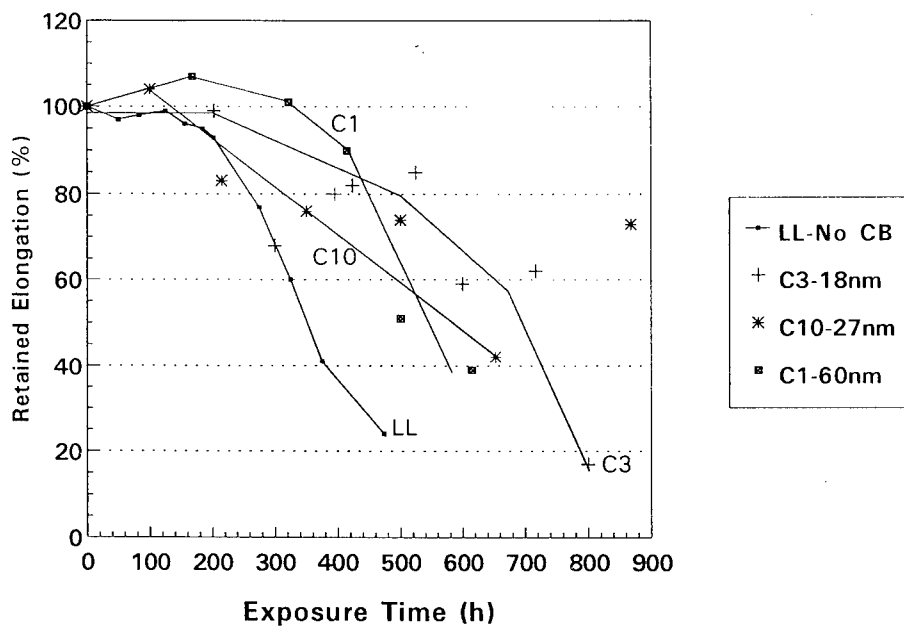


Fig.1: Effect of Particle Size on UV Stability of Xenon Arc-irradiation LLDPE Films; LL-No CB, C3-18nm, C10-27nm, C1-60nm Diameter

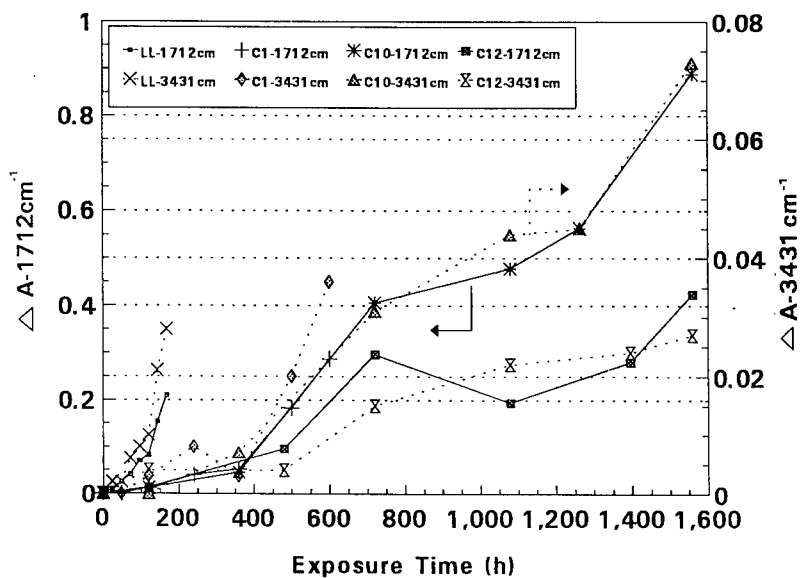


Fig.2: Effect of QUV UVB Exposure Time on Carbonyl and Hydroperoxide Group Formation; LL-No CB, C12-20nm, C10-27nm, C1-60nm Diameter

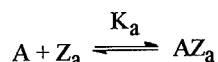
ANTIOXIDANT EFFICACY IN POLYOLEFINS. ROLE OF POLYMER DISORDER

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Polymers have a complex structure with properties depending not only on the chemical composition and length of the macromolecules but also on the character of their arrangement. A molecule of antioxidant present in polymer does not influence the surroundings very much and it is dissolved only in certain zones around chain entanglements where there is free volume to hold the molecule. Such zones have either a relaxed [1] or topological [2] structure. The latter are relatively stable and can exist for a long time even in the polymer melt. The dissolution of additive A in the polymer may be considered as a reversible interaction with centers of Z_a containing chain entanglements, with formation of the immobile complex AZ_a :



The total concentration of A in the polymer is $[A]_p = [A] + [AZ_a]$, where $[A]$ and $[AZ_a]$ are the concentrations of true dissolved (mobile) and immobile molecules. If $[A] \ll [AZ_a]$,

$$[A] = [A]_p / [K_a([Z_a] - [A]_p)] \quad (1)$$

Retardation of polymer oxidation is based on the reaction between virtually immobile macroradicals $RO_2 \cdot$ and mobile antioxidant molecules. The rate of this reaction is directly proportional to the concentration of mobile A molecules

$$W_t = k_t [RO_2 \cdot][A] = k_{ta} [RO_2 \cdot][A]_p \quad (2)$$

where k_{ta} is the apparent rate constant of chain termination by the antioxidant, related to the real constant by the expression: $k_{ta} = k_t / [K_a([Z_a] - [A]_p)]$ or at a small concentration of antioxidant

$$k_{ta} \cong k_t / (K_a[Z_a]) \quad (3)$$

According to (3) the efficiency of an antioxidant depends on the sorption properties of the polymer ($[Z_a]$, K_a) which can be changed either during polymerization, where the main part of entanglements are formed, or on the polymer. In the latter case, the concentration of mobile antioxidant can be increased: (a) by addition of inert compounds which do not participate in polymer oxidation and which can partially substitute the antioxidant molecules in the sorption centers [3], (b) by multiple repeats a melting and crystallization of the polymer [2], (c) by orientation drawing followed by polymer melting [4], (d) by varying the conditions of polymer precipitation from solutions. During the precipitation, macromolecules have to overcome the interaction with molecules of the solvent which is more difficult in case of a "good" solvent with the consequence that the concentration of Z_a formed depends on the solvent used. The number of

collisions between the molecules in solution and, consequently, the probability of entanglements formation, is directly proportional to the polymer concentration. On the other hand, the sedimentation of the polymer during slow cooling can produce less entanglements than those during rapid cooling.

In this work we studied the inhibited oxidation of PE samples in the melt obtained by precipitation from decane and chlorobenzene using various concentrations of the polymer in solution and different rates of polymer sedimentation.

The induction period of PE oxidation at 180°C and $PO_2=300$ Torr in the presence of Irganox 1010 (0.15%)

<i>Solvent</i>	<i>PE concentration in solution, %</i>	<i>Induction period, min</i>
Chlorobenzene (fast cooling, 50°/min)	1.0	150
	0.5	215
	0.25	490
Decane (fast cooling, 50°/min)	1.0	60
	0.5	150
	0.25	220
Decane (slow cooling, 2°/min)	1.0	110

The results obtained show that the efficiency of Irganox 1010 (induction periods and critical antioxidant concentrations) is higher in the samples precipitated from chlorobenzene than in those precipitated from decane; the efficiency of the antioxidant increases with decreasing of the polymer concentration in solution during precipitation and with decreasing of the rate of sedimentation. To verify the changes of polymer structure after precipitation, the sorption of 2,6-di-*tert*-butyl-4-methylphenol by the PE at 180°C was also studied. It was shown that the concentration of sorption centers is higher in the polymer samples prepared by sedimentation from decane than in samples from chlorobenzene and this also depends on the polymer concentration in solution. Thus, the topological structure of a polymer melt depends on the conditions of precipitation and this affects the antioxidant efficiency during polymer oxidation.

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PHOTO-INDUCED AGEING OF TINTED HORTICULTURE POLYMER FILMS AND COATINGS UNDER ENVIRONMENT

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Certain colors in the spectrum provide more efficient photosynthesis than others. Significant yield increases have been achieved with certain crops using special luminescence dyes when implanted in plastic sheeting.

This contribution contains results on photo-induced ageing of red luminescent dye (ROT-300) incorporated into LDPE multilayer films and polymeric glass coatings used in greenhouses. Israel is known to be a country with very high level of solar incident energy which is about 180 kLy/y. (For Western Europe annual solar incident energy is 80-100 kLy/y). The latter results in very fast polymeric photo-degradation and fading of dyes. High temperature background in particular in summer season (35-40°C) also accelerates strongly photo-induced reactions.

In the case of polymer films made of LDPE dye's discoloration is brought about by both direct action of light and interaction with intermediates results from polymer photo-induced oxidation (for example RO₂• and RO• radicals).

Conventional methods of polymer and dye photo-stabilization involve incorporation of UV-screens, Ni-quenchers and HALSes. The application of high UV-absorber concentrations (0.4-0.5%) and HALSes (0.9-1%) in thick LDPE film (200 μm) allows to stabilize tensile properties of film for 24 months life time (2 summers). But mentioned stabilizing system is not able to provide fastness of luminescent dyes during two working seasons of greenhouses. The increase of concentration of stabilizers is limited by their low compatibility with polyolefins.

The application of three layer film with inner layer doped with luminescent dye allows to increase the life time of product. But the concentration gradient results in dye migration onto film surface followed by photo-degradation of dye.

Our contribution presents results on red luminescent dye photo-ageing depending on layer thickness of multilayer film, and concentrations of dye and stabilizers. Results obtained in our experiments permitted to increase lifetime of tinted polyethylene films for greenhouses twofold compared to conventional systems in the case of areas with high level of solar irradiation.

Red luminescent dye ROT-300 was also used as an additive into polymer coatings onto glass greenhouses. This coating mainly consists of acrylic based resins which are known to be very stable for UV-irradiation. In this contribution we present results on photo-degradation of luminescent dye in ELVACITE acrylic coatings (Du Pont) containing also UV-screens as dye protectors.

It was revealed the concentration of benzophenone UV-screener has to be five times more in acrylic polymer compared to LDPE in order to provide light stabilization of red dye during expected life period of coating (about 10 years). The reasons of this fact are discussed.

The contribution will also contain experimental data and consideration for photo-induced degradation of multi-layer coatings containing interactive dyes. These are multilayer coatings developed by Opticplast, Ltd. and comprising luminescent dyes in one layer and their quenchers in other layers which used as heat absorbing system for conditioning of greenhouses.

PHOTO-OXIDATION OF SOFT SBR LATEXES. EFFECT ON PARTICLE SIZE MEASUREMENTS

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Introduction

Even though a relatively large number of publications dealing with photo-oxidation and photo-crosslinking of bulk rubbers have appeared (e.g., Bair et al., 1980; Pappas, 1992; Le Xuan and Decker, 1993); only a few works (Corio et al., 1962; Wilkins, 1968; and Eliçabe, 1990) have considered the effects of photo-oxidation on polymer latex measurements. As far as the authors are aware, this is the first work where the effect of UV irradiation on a soft polymer latex in relation to UV-Vis Turbidimetry measurements is thoroughly investigated.

Electron microscopy (EM) is the main (reference) technique for observing and measuring polymer latex particles. But when such particles are soft (i.e., the polymer is a rubber); then, prior to observation, particles must be hardened in the latex itself. This is to avoid particle shape distortion when dried onto the EM sample-holder. The hardening procedure is complicated, and can involve a molecular cross-linking by UV irradiation. But UV irradiation also promotes undesirable reactions of oxidation and degradation, however. Furthermore, the complete sample pretreatment (that involves at least hardening, drying, and tanning of the polymer particles), will in principle alter particle size with respect to their original values in the latex. After having obtained the electron-micrographs, an adequate data processing allows to obtain a particle size distribution histogram. From such distribution, the number-average particle diameter may be calculated.

Even though its use is little extended, UV-Vis Turbidimetry together with Mie's theory (Mie, 1908) is an experimentally simple technique for particle size determinations (Kourti et al., 1991; Llorent et al., 1996). To obtain the "turbidimetric" average particle diameter, a least squares procedure that fits the predicted spectrum to the experimental spectrum, can be applied. In any case, the refractive index functions corresponding to the media and to the polymer are always required. While refractive index functions for pure water are well established (Kerker, 1969), polymer refractive index functions are only scarcely known. For this reason, Eliçabe (1990) proposed a data treatment that simultaneously estimates the average diameter and a coefficient of an empirical expression that adjusts the refractive index data. The polymer refractive index function is clearly modified by oxidation. Thus, a variable refractive index function ought to be applied in turbidity data treatment, when such optical property is suspected to vary.

Dynamic Light Scattering (DLS) is another quick method for measuring latex particle size, and it can be shown that (at least for particles smaller than 200 nm), the technique is in principle independent on the polymer optical properties. Thus, DLS may be taken as a reference technique when evaluating particle size with unknown degrees of photo-oxidation. DLS provides an average diameter based on the scattered light distribution, that in theory is somewhat larger than the other two previously-mentioned averages. However, for sufficiently narrow particle size distributions, all of the three averages should in practice coincide.

Experimental Work and Turbidimetry Data Treatment

An industrial SBR latex was photo-oxidized and photo-cross-linked between 0 and 12 hrs with UV light; and the effect of such process was evaluated by Differential Scanning Calorimetry (DSC), Scanning EM (SEM), UV-Vis Turbidimetry, and DLS.

For the irradiation, a 450W Hanovia UV-lamp and a special elliptic mirror was utilized, with the (diluted) latex sample placed in a cylindrical quartz cell. Along irradiation and from the obtained bulk polymer samples, a Mettler TA3000 DSC allowed to follow the evolution of the glass transition temperature. For the SEM and Turbidity measurements, a Jeol JSM 35C instrument and a Waters 990 UV-Vis spectrophotometer were respectively applied.

The proposed turbidity data treatment allowed for simultaneous variations in the particle sizes and in the polymer optical properties; and also for errors in the (very dilute, and therefore highly inaccurate) latex concentration. To this effect, the least squares procedure simultaneously estimated: i) the average (turbidity) particle diameter; ii) one of the coefficients of the refractive index function corresponding to Cauchy's formula (Morgan, 1953); and iii) the dimensionless concentration, defined as the ratio between the polymer mass concentration in the latex and the bulk polymer density. For simplicity, light absorption was assumed negligible.

Results and Conclusions

- a) After irradiation, the originally white latex changed into a brownish colour. The UV-Vis turbidity spectrum also changed, particularly for wavelengths smaller than 450 nm.
- b) At least 2 hrs. irradiation were required to observe non-deformed (spherical) particles by SEM. Not only crosslinking but also photo-oxidation possibly contributed towards particle hardening. Such hardening was confirmed by the increase in the glass transition temperature, from -60°C without irradiation to around 10°C after 2.5 hrs. irradiation. Simultaneously, a reduction in the specific heat capacity from 0.43 to 0.15 J/g °K was observed.
- c) The average particle size remained practically unaltered along irradiation. The predicted average diameters according to SEM, Turbidimetry, and DLS varied very little around 60, 66, and 70 nm, respectively; without any clear tendency to increasing or decreasing. The lower SEM estimates were to be expected, considering the particle shrinkage caused by the drying treatment.
- d) Along irradiation, Turbidimetry predicts an essentially constant particle size and a constant dimensionless concentration, but a variable optical coefficient. Thus, the changes in the turbidity spectrum should be only attributable to changes in the optical properties, rather than to changes in particle size. Turbidity predictions may be subject to errors introduced by numerical artifacts, as a consequence of solution multiplicity and/or correlation between the adjustable parameters. However, the independent confirmation by DLS that the average diameter remains unmodified along irradiation provides a strong support to the Turbidimetry results.

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LIGHT STABILIZERS WITH REGULATED MOLECULAR MASS*Š. CHMELA AND P. HRDLOVIČ*

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The optimum efficiency of stabilizing additives to polymers is usually a compromise of the opposite requirements. Besides suitable chemical structure for proper functioning, the additive must fulfil several additional parameters. It must exhibit good processing stability, that means, the ability to stay in polymer and preserve high activity after thermal processing. At the same time the long term stability is required as well. This means the ability to remain in given polymer for a long time. On the other hand, the mobility is necessary for proper functioning, too. As a result the additive fulfils different functions during its life time. During product preparation the additive for long term stabilization should have similar properties as the polymer to be protected. Consequently, the higher molecular mass additive would be of some advantage. Contrary to it, the additive should have exhibit the high mobility during the service life time (1). In oligomeric region the stabilizing efficiency of the additive might be optimized with respect to molecular mass (2). In polymeric region the stabilizing efficiency of the additive decreases with increasing molecular mass (3).

These considerations form a background for a new class of photoreactive oligomeric long term stabilizers. The new polymeric stabilizers are terpolymers containing a weak link in its structure. The light sensitive 1-phenyl-2-propenone (VPK) is used as the weak link (4). To secure the stabilizing action the following monomers were chosen: 2,2,6,6-tetramethyl-4-piperidylacrylate (TMA) or 2-hydroxy-4-acryloxy ethoxy)benzophenone (2HAB). The third comonomer was n-octadecylacrylate (ODA). TMA contains a sterically hindered amine, as the light stabilizing unit (5-6) and 2HAB is a UV absorber (7). ODA improves the compatibility of oligomeric additives with non polar isotactic polypropylene (8). Photolysis of terpolymers TMA/ODA/PVK in solution revealed that terpolymers containing TMA structural units exhibit extensive degradation due to the Norrish Type II Reaction (4). The rate of the molecular mass decrease and final molecular mass of the fragment depend on the PVK content. The higher content of PVK the higher rates of degradation and the smaller fragments result. Contrary to it, no change was observed during photolysis of terpolymers containing UV absorber 2HAB instead of TMA. For terpolymers TMA/ODA/PVK with similar molecular

mass, the stabilizing efficiency in isotactic polypropylene (PP) depends on the VPK content. The higher stabilizing efficiency is observed for terpolymers with higher VPK content in the concentration range up to 15 mass % of VPK.. It means that the small fragments are more effective as stabilizers in comparison with the longer ones. For terpolymers 2HAB-ODA-VPK this relationship is not observed and the efficiency is extremely low.

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STUDY OF THE EFFECTS INFLUENCING STABILIZING EFFICIENCY OF PRIMARY ANTIOXIDANTS IN PBD

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Introduction

Polybutadiene (PBD) is one of the elastomers used most frequently for toughening high performance polymer blends. Double bonds render the polymer sensitive to heat and oxygen. Therefore protection of the dispersed elastomer phase is a crucial point in the stabilization of these polymer blends.

Thermal oxidation of PBD involves autocatalytic processes which start with hydroperoxide formation followed by decomposition via radical-induced reactions resulting in different carbonyl products, saturation and crosslinking¹⁻³. Inhibition of the thermooxidative decomposition can be achieved by retardation of chain initiation and interruption of chain propagation. The efficiency of antioxidants depends on their chemical structure, concentration and distribution in the polymer, as well as, on environmental effects⁴.

The aim of the present work was studying the effects determining the stabilizing efficiency of chain breaking primary antioxidants (AO) in PBD under different conditions.

Experimental

Degradation of PBD produced by emulsion polymerization (GE Plastics) and subsequently purified from additives was studied. Effects of two phenolic antioxidants - Stearyl- β -(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionate (AO1) and Triethyleneglycol-bis-3(3-*tert*-butyl-4-hydroxy-5-methyl-phenyl)-propionate (AO2) (Ciba-Geigy) - were investigated. PBD films without and with AO were prepared from emulsion by evaporating the water in vacuum at ambient temperature. The polymer is cross-linked, insoluble in any solvent.

The materials were characterized by FT-IR (Mattson-Unicam), DSC and TMA (Mettler) under nitrogen as a function of temperature. Stabilizing effectiveness of AOs was studied *a)* at high temperatures by DSC in oxygen under isothermal conditions (oxidation maximum time, OMT); *b)* at 100 °C by oven aging. Solubility of the additives in PBD was determined in a wide temperature range.

Results

FT-IR studies of the additives revealed that the OH group of AO1 is non-associating, while those of AO2 are inclined to form hydrogen-bonds. The strength of hydrogen-bonding depends on the physical state of AO2 and the surrounding medium.

AO1 has high solubility (S) in PBD above the melting point of the antioxidant (S=71.5 wt% at 50 °C). Complete dissolution of the polymer is prevented by the cross-links. The solubility of AO2 is low even at high temperatures (S=9.4 wt% at 190 °C), lower than follows from thermodynamic expectations, indicating survival of some hydrogen-bonds.

Degradation of additive-free PBD at low temperature (15 °C) proceeds similarly to that initiated by photons during photooxidation^{1,2}. Thermal and thermooxidative properties of the oxidized material indicate that the polymer chains are cross-linked through oxygen bridges which decompose at elevated temperatures. Oxidation at 100 °C is fast, starting with formation of hydroperoxide groups.

Both of the antioxidants investigated inhibit oxidation of PBD. The effectiveness depends on concentration and temperature. At high temperatures AO2 provides higher oxidative stability in low concentrations than AO1. At higher concentrations the order is reversed. The OMT values measured at 190 °C and plotted as a function of AO concentration cross at around 0.05 mmole eq./gPBD, as the oxidative stability of the films prepared with AO1 increases linearly, while in presence of AO2 the change corresponds to a saturation curve.

Long time stability of PBD with 2 wt% AO was investigated at 100 °C. The mechanism of oxidation with both additives is similar. The ratio of hydroxyl/carbonyl concentrations is considerably lower than in absence of AO. At the initial stage decomposition of the polymer is indicated by weight loss. Further oxidation results in an increase of the polymer weight and cross-linking. The glass transition shifts to higher temperatures and the polymer loses its elasticity. The rate of oxidation of PBD is faster in presence of AO2 at this temperature than with AO1.

Better performance of AO2 at high temperatures in low concentrations, compared to that of AO1, is explained by the difference in OH shielding. Its inferior stabilizing efficiency at 100 °C and at high temperatures in higher concentrations is attributed to hydrogen-bonds, resulting in a decrease of 1) solubility and 2) the number of active OH groups.

The oxidation of PBD proceeds heterogeneously both in absence and in presence of antioxidants.

Conclusions

Stabilizing efficiency of primary antioxidants in PBD is determined by structural factors. The type of the groups adjacent to phenolic OH has a strong influence. Decreasing the shielding effect increases the chemical efficiency. On the other hand, the less shielded OH can form hydrogen-bonds resulting in a decrease of performance.

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CL-23

HIGH PERFORMANCE UV ABSORBERS FOR ENGINEERING PLASTICS

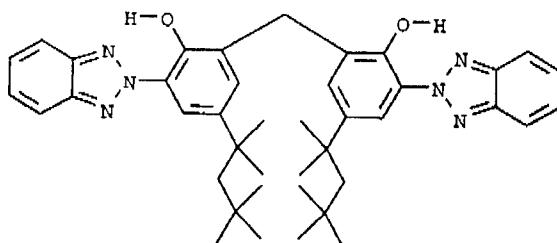
P. HAYOZ

Ciba Geigy Ltd., Additives Division, CH-1723 Marly, Switzerland

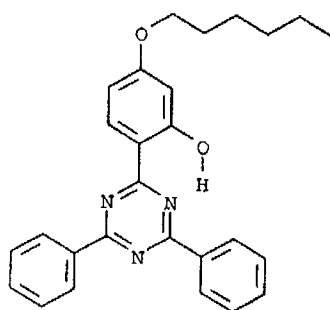
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The mode of action of two classes of UV absorbers (2-(2-hydroxyphenyl)-benzotriazoles (e.g. 1) and 2-(2-hydroxyphenyl)-1,3,5-triazines (e.g. 2)) will be discussed.

Application results of these UV absorbers as light stabilizers in polycarbonate show a better performance of the 2-(2-hydroxyphenyl)-1,3,5-triazine class. This superiority can be explained by theoretical considerations.



1 Tinuvin 360®



2 Tinuvin 1577®

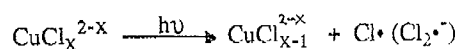
MECHANISMS OF METAL SALTS PHOTOINDUCED DEGRADATION OF POLYMERS

J.F. RABEK¹, L.A. LINDÉN¹, H. KACZMAREK² AND A. KAMINSKA²

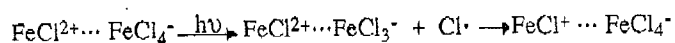
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Inorganic salts are well known photoinitiators of oxidative degradation of polymers in solid state or in solutions. This paper focuses only on copper and iron chlorides photoinitiated degradation of different, mainly water soluble polymers. Along with the presentation of experimental results, a brief overview of redox photo-reactivity and mechanisms will be discussed. Our research was concentrated on photo-degradation of poly(ethylene oxide)(PEO) in acetonitrile (ACN) in presence of CuCl₂ and FeCl₃. Chlorocopper (II) complexes in ACN, a strong π -acceptor, represent an interesting photocatalytic system working under visible or UV radiation. Irradiation of the system in the region of the lowest spin-allowed charge-transfer (CT) excited state result in the photoreduction of Cu(II) metal center to Cu(I) and Cl• radical,



which easily abstract hydrogen from the PEO molecule, producing a polymer radical (P•). Further oxidative steps of the P• radical cause chain scission (in solution) and crosslinking (in solid state). Simultaneously the polymer is partially chlorinated by addition of Cl• radicals to P• radicals. ACN is a solvent that is practically inert toward chlorination. Degradation process can be inhibited by addition of free radical scavengers such as DPPH, galvinoxyl radicals, or nitrones, which effectively trap Cl• radicals. When taking into consideration the changes of the oxidation state of the metal center, three principal types of Cu(II) photochemical reactivity are distinguished: Cu(II) to Cu(I) photoreduction, Cu(II) to Cu(III) photooxidation, and Cu(II) photoredox reaction [Cu(II) → Cu(I) → Cu(II)] without irreversible photoreduction to Cu(I). PEO also form coordination complexes with CuCl₂ and FeCl₃ at different weight ratios. Formation of these complexes has a significant importance in the PEO photodegradation mechanism. The photoreduction of PEO-FeCl₃ complex results in a rapid electron exchange between ions Fe²⁺...FeCl₄⁻ in the ion pair generated in the photoreduction of FeCl₄⁻:



The chlorine radical is responsible for the abstraction of a hydrogen atom from the PEO molecule and formation of P• radical. The role of metal salts in the photooxidative degradation of polymers seem to be quite interesting in improving their photo- and thermal stabilization. Due to the richness of the photoredox pathways, interest in reactivity of metal salt complexes will no doubt remain high. Photooxidation based on the photoreactivity of metal complexes will likely play a very important and promising role, not only in the photodegradation of synthetic polymers and biopolymer, but as well in biological systems (effective in inactivating a variety of microorganisms).

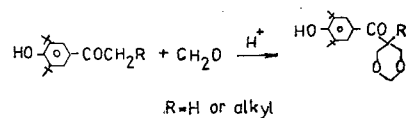
CL-25

SYNTHESIS AND PROPERTIES OF NEW STABILIZERS FOR RUBBERS AND POLYMERS

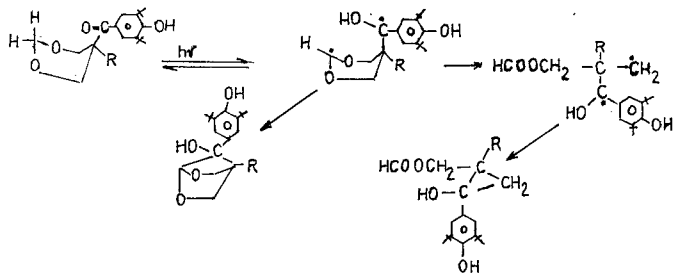
S.S. ZLOTSKY

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We offered carbonyl-containing cyclic acetals - derivatives of sterically-hindered phenols - as photostabilizers for rubbers and polymers. We fulfilled their synthesis by condensation of the corresponding 4-acyl-2,6-di-*tert*-butylphenols with formaldehyde



Photoinitiated transformations of the compounds obtained proceed parallel to formation of bicyclic structures and decomposition of acetal fragment



Influence of conditions onto the course of photoinitiated transformations and reaction mechanism is discussed in the report. The data on inhibition of polymers and elastomers photodegradation are provided.

KINETIC STUDY OF THE THERMAL OXIDATION OF POLYPROPYLENE

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The thermal oxidation of non stabilized isotactic polypropylene (PP) was studied in the 80-150°C temperature range by gravimetric and spectrophotometric (OH and CO groups) measurements. An example of the experimental kinetic curves is shown in Fig. 1.

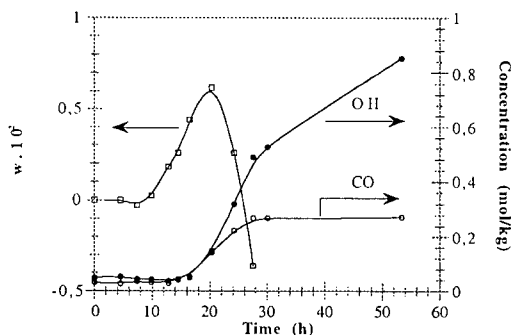


Fig.1 : Changes of weight (w), hydroxyl (at 3410 cm^{-1}) and carbonyl (at 1714 cm^{-1}) concentration with time at 110°C .

It has been recently shown ⁽¹⁾ that a simple kinetic model based on the assumption that unimolecular hydroperoxide (POOH) decomposition is the unique source of radicals and that the hypothesis of stationary state can be applied, allows to predict many important features of the PP thermal oxidation at moderate temperatures, for instance :

- The existence of a steady state due to the fact that POOH destruction equilibrates its formation. A peculiarity of this state is that the corresponding rate is independant of the initiation rate constant, which can be verified in Gijnsman results ⁽²⁾.
- The fact that the duration of the induction period is practically independant of the initial POOH content for relatively "clean" samples.
- The fact that the apparent activation energy of induction period corresponds closely to the apparent activation energy of POOH decomposition.
- The fact that activation energies determined from induction periods and steady state rates are different so that whole oxidation appears as a non arrhenian process.

All the characteristics were confirmed by our results which are in good agreement with the hypothesis of existence of an "universal" Arrhenius plot for induction times, independently of sample origin, morphology, etc...

In addition, a new characteristic feature, also predicted by the kinetic model was found :

- The induction times relative to weight, carbonyl and hydroxyl gain are in the ratio 2 : 3 : 3.

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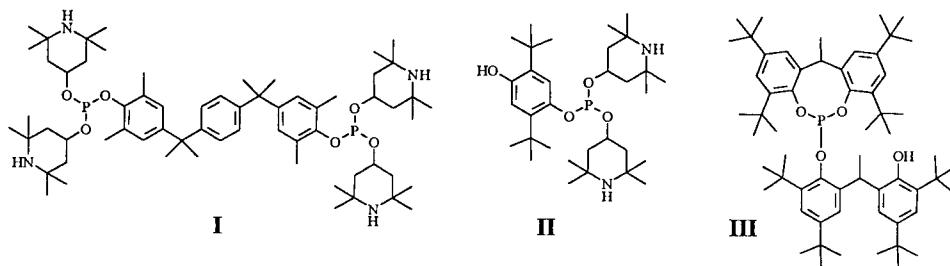
SYNTHESIS OF NEW MULTIFUNCTIONAL STABILIZERS BASED ON ORGANIC PHOSPHITES

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In order to get an overall protection of polymers against different damaging influences it is important to find sets of stabilizers which are able to protect polymers against these influences and which do not give negative interactions. Another idea is to design stabilizers combining the active functionalities in one molecule.

In the past we already reported about multifunctional stabilizers containing HALS and phosphite moieties in one molecule. Here we present some new HALS-Phosphites (see examples I and II) and also multifunctional phosphites containing free phenolic moieties (see example III).



Two synthetic routes starting either from PCl_3 or Trisdialkylaminophosphanes $\text{P}(\text{NR}_2)_3$ are compared. Reactions with $\text{P}(\text{NR}_2)_3$ are more selective and easier in their handling. So it is possible to substitute the diethylamino function step by step with alcohols or phenols. A set of precursors for HALS-Phosphite synthesis could be gained by that way. Disadvantage is the smaller reactivity towards esterification of the phosphorous amides compared to the phosphorous chlorides. Especially some very bulky phenols hardly give any third step substitution reaction at the phosphorus. Test results under application conditions (MFI, YI, CI) of some compounds synthesized are given in comparison to commercial stabilisers. It is shown that their stabilising activity during processing is in the same range as those of the most efficient commercial product PEPQ.

THERMOOXIDATIVE STABILITY OF POLYETHYLENE - POLYSTYRENE INTERPENETRATING POLYMER NETWORK-LIKE SYSTEMS

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A polyethylene - polystyrene (PE-PS) and polyethylene-polybutyl- methacrylate (PE-PBMA) interpenetrating polymer network (IPN)-like systems were prepared by synthesis in situ; they differ from "pure" IPN systems. PS network is partially grafted onto the PE network.

In the first system, PE-PS IPN, the molar ratio between PE and PS was 1:1. Five samples with different amount of crosslinker (0.25, 0.50, 1.0, 2.0 and 3.0 mol. % of divinylbenzene - DVB) were prepared. In the second IPN system (PE-PBMA) the molar ratio of both polymers was also 1:1. Glycoldimethacrylate - GDMA was used as a crosslinker (0, 1, 2, 3, 4, 5, 6 mol. %). At the synthesis of IPN, PE is dissolved in monomer with molar ratio 1:1. The polymerization of monomer solution of PE was carried out in the presence of initiator and crosslinker between two glass plates sealed with PVC tubing. Curing took place at 120 °C [1]. Di-tert.-butyl peroxide (at PE-PS IPN) and Luperox-101 (2,5-dimethyl-2,5-di(tert. butylperoxy)hexane (at PE-PBMA IPN) were used as initiators.

When crosslinker (DVB or GDMA) was added in the increasing amounts to the crosslinked PS or PBMA the influence of the PS or PBMA network became more and more evident: higher moduli and stress at break and lower elongations at break were observed. These effects are attributed to the increasing network density in IPN samples [2].

The samples with different network densities of PE-PS and PE-PBMA IPN systems were underwent to oxidation under dynamic (the rate of heating 5 °/min) and isothermal ($T = 180$ °C) conditions in O₂ atmosphere. The course of oxidation was examined by the measurement of chemiluminescence light emission, which is accompanying the degradation process. As illustrated by Fig. 1 and 2 (for PE/PS) the increase of DVB concentration results in the deterioration of thermooxidative stability of crosslinked systems.

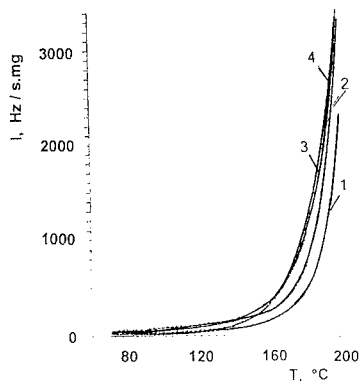


Fig. 1 The dependence of chemiluminescence intensity (I) on temperature (T) for oxidation of PE/PS system. Concentration of DVB [%]: 1 - 0.05; 2 - 0.5; 3 - 1.0; 4 - 2.0.

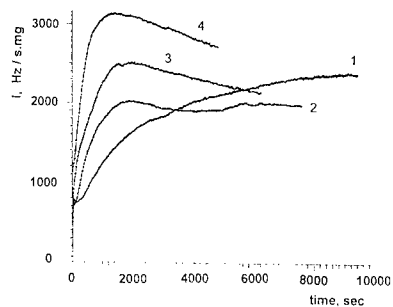


Fig. 2 The courses of intensity of chemiluminescence (I) on time for oxidation of PE/PS at 180 °C in O₂. Concentration of DVB [%]: 1 - 0.025; 2 - 0.5; 3 - 1.0; 4 - 2.0.

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CHEMILUMINESCENCE FROM TETRAMETHYLDIOXETANE IN POLYMER MATRICES

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It has been reported [1] that only a small fraction of polypropylene peroxides decomposing in inert atmosphere causes observed chemiluminescence (CL). This gives a raise the question of a nature of a reaction responsible for CL from oxidised polymers. Until now this problem is not solved. In the number of studies focused on polymer CL the two main elementary reaction have been proposed to be source of light during polymer thermooxidation - decomposition of hydroperoxides and termination of peroxy radicals .

In this work the idea of contribution of polymer dioxetanes decomposition to the chemiluminescence from a thermooxidised polymers is presented. The aim of the present study is to examine the effect of a polymer matrix on the chemiluminescent reaction pattern. For this purpose the low molecular dioxetane - tetramethyl-1,2-dioxetane (TMD) - was used and the kinetics of CL of thermal decomposition of TMD in poly(methyl methacrylate) (PMMA) and polystyrene (PS) has been investigated.

The activation energy of CL of TMD decomposition (E_a) has been evaluated under isothermal and nonisothermal conditions. There is a discrepancy between results of these methods for PMMA matrix and the lower value of E_a obtained at the latter has been discussed in term of the temperature dependence of CL quantum yield caused by the changes of matrix rigidity with temperature.

The effect of chemiluminescence activator, 9,10 - dibromoanthracene (DBA), on the kinetics of TMD chemiluminescence has been also examined. It was found that excited DBA can accelerate TMD decomposition in PMMA but not in PS. The appropriate mechanisms has been suggested.

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AN ESR STUDY OF γ IRRADIATED ISOTACTIC POLYPROPYLENE CORRELATED WITH CHEMILUMINESCENCE

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It is well known that γ irradiations under air create peroxy radicals ($RO_2^\bullet$) in the bulk of polypropylene (PP) (1, 2).

Experiments were carried out on stabilizers free isotactic PP, irradiated at room temperature with a ^{60}Co source. In order to follow isothermal behaviour of these radicals at temperature in the range between 20°C to 140°C under oxygen or inert atmosphere, we used electron spin resonance spectroscopy (ESR) and chemiluminescence (CL) techniques.

The ESR measurements were carried out on an ESR spectrometer working in X band equipped with variable temperature controller. We have observed that at room temperature the $RO_2^\bullet$ decay is very slow (several days) but at high temperature these radicals disappear quickly (a few seconds). The ESR spectra analysis permits also to get information on the peroxy radicals location in the polymer matrix (3). The radicals rotational mobility is expressed in terms of correlation time τ_c , which reflects the local viscosity.

The CL experiments give another view of the $RO_2^\bullet$ decay(4), but it depends on the chosen kinetic scheme. Comparison of ESR and CL data obtained in comparable experimental conditions is expected to give interesting information on the mechanisms involving $RO_2^\bullet$ radicals, especially terminations.

On the basis of these ESR and CL data the mechanism of these processes will be discussed.

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RADIODEGRADATION OF VULCANIZED IIR

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Recovery of vulcanized buthyl rubber waste requires detailed studies concerning the influence of various factors capable of producing "new" material with technological applications.

Structural changes of vulcanized IIR samples were obtained by irradiation with accelerated electrons or gamma rays as dose dependence. They can be assigned to the chain reaction of free radicals, which are formed during the second stage interaction of ionizing radiation with polymer. Because buthyl rubber belongs to the class of degrading materials, its weight-average molecular weight decreases sharply over the first 200 kGy of irradiation dose. Charlesby-Pinner representation (figure 1) shows the influence of absorbed energy on sol fraction. The gel dose values are 52.6 kGy for thermally and mechanically aged rubber and 53.3 kGy for unaged material with the same composition. From the dependence of $S + \sqrt{S}$ on reciprocal dose, it can be determined the ratio of scission to crosslinking yields. It was evaluated that, for the beginning of experiments, 4 scission events are accompanied by one crosslinkage. For advanced irradiation (90 kGy and 250 kGy) the ratio $\lambda = G(S)/G(X)$ becomes 50 and 110, respectively.

Changes in main characteristics of irradiated IIR are presented in figures 2 and 3. Mooney viscosity of γ -irradiated material decreases faster than the same property of electron irradiated

rubber for standard compositions. It can be explained by the lower dose rate in γ -processing. These experiments were performed in air and the presence of oxygen emphasizes scission process by scavenging free radicals.

It is well known that unsaturation level of irradiated IIR increases (figure 2), because in the primary radiation-chemical event a carbon-carbon bond of the main chain is broken. Under such conditions, intramolecular disproportionation is highly favoured on quaternary carbons¹.

Vulcanized buthyl rubber samples irradiated over dose range between 120 kGy and 200 kGy increases its plasticity, which makes it suitable for recycling in new primary mixtures in the concentration range of 10-20 %.

As absorbed dose becomes 400-500 kGy or more, tested material gains adhesive properties, which are suitable in corrosion protection, in manufacture of sealant production or other application.

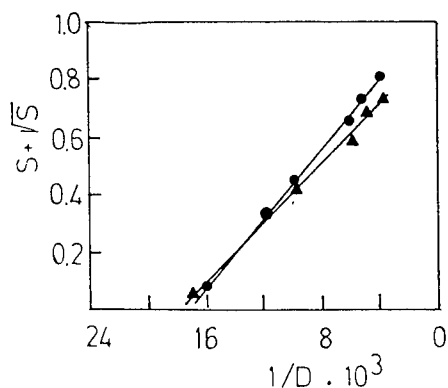


Figure 1. Charlesby-Pinner representation for irradiated buthyl rubber.

- (Δ) thermally and mechanically aged material;
- ($\bullet$) unaged material

In figure 2 is also presented changes in dry gel content. It can be noted that radiation effects of γ -rays and accelerated electrons are smoothly decreased over large dose range, up to 250 kGy, as it was expected. This similarity can be assigned to about the same rate of scission process occurred during these two types of ionizing radiations.

Irradiated product can be added to crude rubber at low concentration. Vulcanized material shows improved properties, such as Mooney viscosity ML_{1+4} (100°C) or mechanical strength (figure 3).

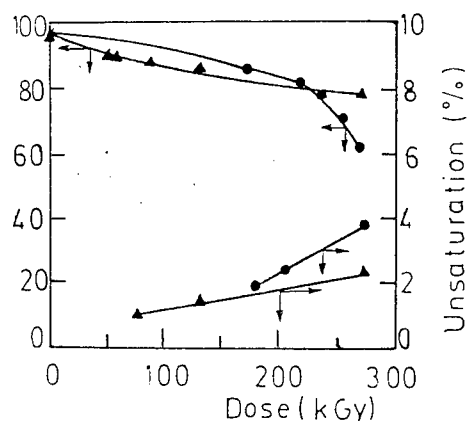


Figure 2. Changes in dry gel content and in unsaturation level with dose by γ ray (●) and accelerated electrons (▲) irradiation

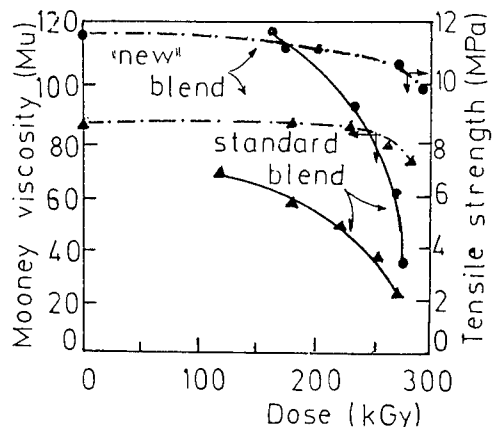


Figure 3. Changes in Mooney viscosity and tensile strength with dose after γ irradiation of vulcanized IIR samples

This communication has intended to present an alternative for reclaiming of IIR wastes by gamma or accelerated electron irradiation, which can be applied in manufacture of various rubber products. Practical interest in improvement of usefull properties for rubber materials requires detailed studies concerning radiochemical way of material recovery².

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**THE INTERACTION OF POLYMER STABILISING ADDITIVES
WITH SILICA FILLERS AS INVESTIGATED BY FLOW
MICROCALORIMETRY, GRAVIMETRIC METHODS AND
MICROWAVE DIELECTRIC SPECTROSCOPY**

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Additive adsorption by fillers in polyolefin formulations is a well recognised problem in industry. Silica is one such filler and is commonly used as an antiblocking agent in the production of packaging films. Flow microcalorimetry (FMC) has successfully been utilised to determine the behaviour of silica with respect to typical antioxidants and light stabilisers used in polyolefins. This technique in conjunction with Microwave Dielectric Spectroscopy (MDS) and traditional gravimetric adsorption methods (GM) has been used to determine the saturation adsorption level (SAL) for Irganox 1010, BHT, Chimassorb 944, Aduvex 12 onto silica. SAL determined by these methods produce reproducible concordant results.

FMC also reveals important information on the nature and strength of interaction between silica as demonstrated by heats of adsorption and desorption. Studies on silicas differing in pore volume show behaviour as predicted from controlled thermo-oxidative and photo-oxidative experiments on filled polypropylene and polyethylene, suggesting that certain silicas are able to remove additive from the polymer matrix reducing their stabilising action whilst others show no excessive debilitating effect.

Chimassorb 944 and Irganox 1010 were examined singularly and in combination in ageing experiments and replica experiments were investigated in flow microcalorimetry by the use of displacement reactions. FMC sequential adsorption studies indicated that Irganox 1010 was not adsorbed over the entire surface of the silica and it may be displaced when Chimassorb 944 is introduced into the system.

ENTRAPMENT OF POLYMER ADDITIVES IN SILICA FOR CONTROLLED RELEASE MECHANISM IN POLYPROPYLENE

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Pigments like silica can markedly influence the properties of polymer materials particularly with regard to their thermal and photochemical stability. Of particular importance is the complex role of catalysis versus stabilisation roles as well as the complex inter-play with polymer additives such as antioxidants and UV stabilisers.

Films of polypropylene were prepared with different commercial additives (0.1% w/w), the additives used were based on hindered phenolic and piperidine structures: Cyanox LTDP, Chimassorb 944, Tinuvin 622, Cyasorb UV-3346, Tinuvin 770DF, Irganox 1010, Irgafos 168. Also films were prepared with a combination of two of these additives, looking for antagonistic and synergistic effects..

Silicas saturated with these antioxidants and UV stabilisers were prepared, and films of polypropylene were made with the additives adsorbed in silica, in order to study the influence of silica's properties on the thermal and photochemical stability of the polymer and its complex inter-play with additives.

The oven and UV ageing were carried in the polypropylene films, until the samples become yellow. Over this time period, the samples are monitored frequently by FTIR for an increase in the carbonyl index. Second derivative UV has also been used , in order to note the disappearance of the additive. The hydroperoxide analysis were made on the oven aged samples to follow the degradation in the films.

From the UV ageing it is observed that in the absence of silica the polymeric HALS outperforms the monomeric HALS (ie. Tinuvin 770). Weak antagonism is observed between the HALS and the hindered phenolic antioxidants whereas strong antagonism is seen between the HALS and sulphur DLTDP. The overall performance of the HALS systems are reduced by almost 50% when bound to silica except for Tinuvin 770 (monomeric HALS) on its own. Here extremely high stabilisation activity is observed; better than in the absence of silica.

During thermal ageing good synergism is seen between the HALS and antioxidants. The performance of the HALS is enhanced when trapped in silica but that of the thermal antioxidants is reduced. However, good synergism is retained when bound to the silica system.

The hydroperoxide changes follow a similar pattern to the C=O index measurement. In the case of silica they are enhanced.

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THE MECHANISTIC ACTION OF A NEW CO-STABILISER (N-PHENYL-3-ACETYL PYRROLIDINE-2,4-DIONE) IN POLY(VINYL CHLORIDE)

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ABSTRACT

The stabilisation performance of a recently patented triketone costabiliser for PVC has been evaluated in the presence of zinc and calcium stearates. The triketone : N-phenyl-3-acetylpyrrolidine-2,4-dione (NPAPD), leads to superior colour retention in the polymer when added at a fraction of the quantity of other commercially available costabilisers. Its performance is associated with a remarkable ability to form co-ordination compounds with the metal soaps, even on simple mixing.

In particular zinc stearate readily complexes with NPAPD at room temperature.

However, zinc complexes have low thermal stability and the zinc stearate is readily released on heating (to scavenge HCl and/or engage in reversible blocking reactions).

The acidic methine of the co-stabiliser is then free to participate in C-alkylation reactions - substituting allylic chlorine and preventing double-bond formation.

Complexation of the co-stabiliser inhibits the formation of prodegradant $ZnCl_2$ in the early stages of degradation and hence considerably reduces sequence length and colour formation in PVC. Evidence for these process is given by FTIR and Luminescence studies on PVC containing 1 phr of a given costabiliser with 3 phr of calcium and zinc stearates (1:2 ratio) aged at 180 °C.

CORRELATION OF DISCOLOURATION AND OTHER PROPERTIES OF STABILIZED PE WITH IRGANOX 1010

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Structure and characteristics of polyethylene can change basically during its processing and application. Polyethylene is sensitive to thermal, thermo- and photo-oxidative degradation during which chain scission and/or recombination take place, modifying the structure of the polymer chain. These structural changes have disadvantageous effect on the physical properties and stability of the polymer, occasionally they may render the polymer unsuitable for use in a given application field. Stabilizers are added to the polymer to protect polyolefins against degradation during processing and application. The most often used stabilizers are the hindered phenolic antioxidants, which react with alkoxy and alkyl radicals due to their electron donor character. Phenolic antioxidants can take part in many transformation reactions during processing. Some of the transformation products may react with the polymer, macroradicals and hydroperoxides (in some cases these are more effective radical scavengers, than the parent antioxidant). Most of the transformation products of phenolic antioxidants have the structures of conjugated dienones, having high extinction coefficients in the visible part of the light, thus they discolour the polymer. The type and quantity of the stabilizer used basically determine the properties of product.

An ethylene/1-hexene copolymer containing different amounts of a phenolic antioxidant (Irganox 1010) are processed by multiple extrusion. Various properties of PE were determined after each extrusion step. Multiple extrusion induced significant changes in the characteristics of the polymer. Colour, oxidative stability, melt viscosity, all changed with increasing processing history and also the mechanical properties of blown film deteriorated considerably. We have found surprising correlations among the determined characteristics. The conclusions obtained are not evident and they are difficult to explain, but indicate that all can be traced back to the chemical and physical changes taking place during the processing of the material.

RADIOCHEMICAL OXIDATION OF ISOTACTIC POLYPROPYLENE

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The γ ray initiated oxidation of isotactic polypropylene was studied by FTIR spectrophotometry, for different dose rates: (600- 800Gy/h). The samples were commercial polypropylene chipped and molded into sheets of 1.8-mm thickness. To obtain the spectrum, the samples were cut and had the thickness of 10, 20, and 40 μ m.

The γ -irradiation was performed in the air, at 23°C, with doses varying between 20 and 1200k Gy. The presence of oxygen greatly affects the radiative degradation of isotactic polypropylene; polypropylene, with its tertiary carbons oxides much more quickly than polyethylene.

The dominant aging process is a radiochemical initiated chain oxidation. The main characteristics of these processes are well known: initiation is non selective so that branching due to hydroperoxide decomposition is not favored; the propagation is selective owing to the relatively low reactivity of peroxy radicals in hydrogen abstractions. Thus, the first products of degradation are hydroperoxide groups: (3000-4000) cm^{-1} . The decomposition of hydroperoxide groups led to chain scission, with the conversion of hydroperoxide groups on the backbone to ketone groups at the chain ends.

Later the bands in the carbonyl region appear, from 1850 to 1650 cm^{-1} [1]. The carbonyl region presents different bands at different doses of irradiation. We noted the appearance of the band 1736 cm^{-1} assigned to the ketone group or ester, as well as the band 1716 cm^{-1} assigned to the group corresponding to carboxylic acid. For greater doses the existence of γ -lactone groups (1774 cm^{-1}) has been identified. In fact, at all doses, the strongest band is the ketone or ester band.

The composition of the carbonyl region of dust particles is different from that of the samples of polypropylene. The dust particles of irradiated PP at 1200 kGy presents two maximums who are the same: the first at 1736 cm^{-1} and the second at 1776 cm^{-1} [1].

Isotactic PP is a semicrystalline polymer; one cannot understand the phenomenon produced in isotactic irradiated PP if the variation of its crystallinity is not taken into account. If it is considered that the variation of PP crystallinity is the same as the variation of its isotacticity, it may be determined through the ratio of the bands 995/974, simultaneously with the ratio of bands 842/810 as well as the intensity of the band 895 cm^{-1} . These bands do not present significant variations. This is a proof that the crystallinity did not change because the irradiation doses are still low.

Thickness distribution of carbonyls in thick samples was determined. The thickness of the oxidized layer appears as an decreasing function of dose rate.

The FTIR mappings at different doses for the interval $1740-1820\text{cm}^{-1}$, which is the domain of esters and γ -lactones have been registered. Also, the FTIR mappings of isotacticity, the carbonyl region at different doses have been analysed. In fig.1. the FTIR mapping for the interval $1740-1820\text{ cm}^{-1}$ at 100kGy is represented.

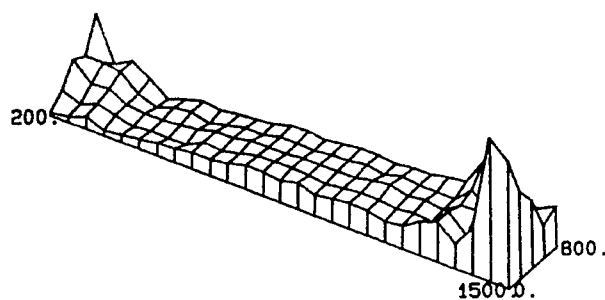


Fig.1

$R=A_{1740}-A_{1820}/A_{2723}-A_{2694}$. Thickness of the samples was $40\mu\text{m}$.

In the registration we performed, we took into account the variation of absorbance due to thickness, through determination of the difference ($A_{2723}-A_{2694}$) (fig.2).

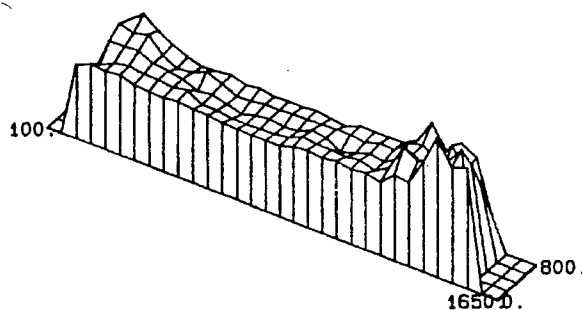


Fig. 2

$A_{2723}-A_{2694}$

At 100kGy , the observation shows that a stabilization of the phenomenon has been produced.

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IMPACT BEHAVIOUR OF DEGRADED NOTCHED HDPE SPECIMEN

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Introduction

The surface layer of HDPE embrittles due to UV-degradation and decreases the life time of plastics products used outdoors. The mechanical behaviour of HDPE versus exposure time was studied in more detail, taking into account the depth of the degraded layer.

Failure of UV-degraded HDPE is often compared with the appearance of a notch. In this summary some results are shown of the three point bending tests on degraded HDPE specimens, which were notched after exposure. Different notch depths were used in order to compare the mechanical behaviour with the thickness of the degraded layer.

Theory

A notched specimen will fail if the stress intensity at the tip of the notch exceeds the critical stress intensity factor K_{Ic} [2]. The stress intensity factor applied (in mode I) is given by:

$$K_I = \sigma Y \sqrt{\pi a} \quad (1)$$

with a the depth of the notch, Y a geometrical factor and σ the nominal stress. K_{Ic} is known as a material parameter in the plane strain or plane stress condition. In HDPE, however, this condition will never be reached, due the nonlinear behaviour of the material. Here K_{Ic} will also depend on notch depth.

Experimental procedure

Unnotched 4 mm thick injection moulded HDPE Charpy specimens were supplied by DSM, the Netherlands. The material was not UV-stabilized. The specimens were photo-oxidized in a SUN-test for exposure times amounting to 28 days. After exposure, the specimens were notched with a razor blade. The depth of the notch was controlled and varied between 0.05 and 2.5 mm. After notching the ultimate depth of the notch was determined using a light microscope. An instrumented three point bending test apparatus was used to determine the force-displacement curves. A carbonyl profile was made by FT-IR [1].

Results

Figure 1 shows the nominal maximum stress versus notch depth for various exposure times. The stress values of the exposed specimen decrease to a minimum at notch depths of 0.3 ± 0.1 mm. The depth, at which the maximum stress decreases, increases with exposure time, but the minimum value of the stress versus notch depth does not decrease below a critical value. No difference of the maximum stress was found above 1.2 mm.

Figure 2 shows the concentration of carbonyl versus depth measured by FT-IR. The thickness of the oxidized layer decreases with increasing exposure time although the damage

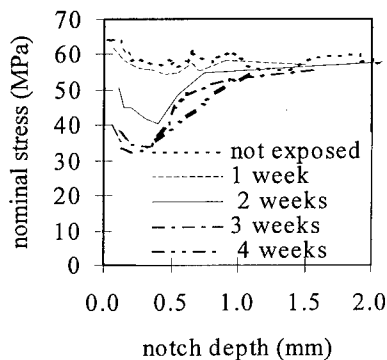


Fig. 1: Maximal nominal stress versus notch depth for different exposure times.

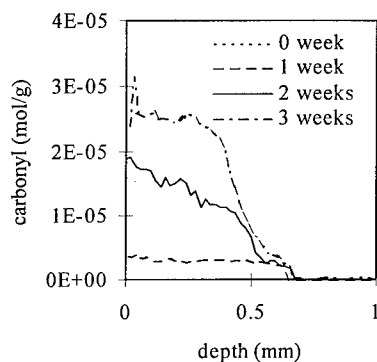


Fig. 2: Concentration carbonyl versus depth for different exposure times.

at larger depths is still there. The depth of degradation of the brittle specimen at one week of exposure is found to be about 0.7 mm.

The K_{Ic} values versus notch depth can be derived from eq. 1 and fig. 1 (not shown). K_{Ic} of the non-exposed specimen increases with notch depth till 1 mm. After 1 mm, K_{Ic} decreases slowly. During exposure K_{Ic} decreases from the original values at notch depths from 0 till 1.0 mm. After 2 weeks of exposure K_{Ic} does not decrease anymore for all notch depths.

Discussion

The depth of degradation in a three point bending test is larger than the depth of degradation found by FT-IR. Specimen with notches between 0.6 and 1 mm are still effected by the degraded layer of 0.6 mm thick. This effect can be explained by the decrease of the plastic zone around the crack tip. The plastic zone in the degraded layer can be assumed much smaller.

Because of the fact that photographs of the fracture surface show degradation depths comparable with the carbonyl profiles the following conclusions can be drawn:

- In a three point bending experiment a crack appears in the degraded area with the size of the thickness of the oxidized layer.
- Although the critical stress intensity value at the interface between brittle and ductile material differs from only ductile material, the residual strength can be calculated using a notch with the thickness of the oxidized layer.

Furthermore these tests can be used as a method to determine the effective thickness of the oxidized layer.

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SPECTRAL AND PHOTOSTABILIZING CHARACTERISTICS OF BIFUNCTIONAL FLUORESCENCE PROBES BASED ON NAPHTHALENE

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Free radicals of N-oxyl type attract attention for two reasons. First of all they are intermediates in the course of stabilization of polymers mainly polyolefins by sterically hindered amines (1). Secondly, the free radicals influence the photophysical and photochemical processes due to their paramagnetic effect (2-4). Fluorescence probes have been prepared in which simple aromatic chromophores were combined with free radical centre of N-oxyl type (5). Formation or decay of the free radical is connected with switching off or on of the chromophore emission as a result of intramolecular quenching.

Spectral properties of esters of 1-naphthoic acid and 1-naphthylacetic acid with methanol 2,2,6,6-tetramethyl-4-hydroxypiperidine (parent amine) its N-oxyl (oxidized amine) and hydrochloride were compared in solution and in polymer matrices as isotactic polypropylene, polystyrene, poly(methyl methacrylate) and polyvinylchloride. Esters of 1-naphthoic acid exhibit broad absorption band which shifts slightly bathochromically in going from non polar to polar solvents. The broad and structureless emission band shifts strongly bathochromically in going from non polar to polar solvents. The same shift is observed in polymer matrices as well. Esters of 1-naphthylacetic acid exhibit absorption and emission spectrum typical for naphthalene chromophore which is not influenced by polarity of solvent or polymer matrix. The different behaviour of derivatives of naphthylacetic acid as compared to 1-naphthoic acid is due to methylene bridge which weakens the interaction of ester group with naphthalene ring. The lifetime of the fluorescence of esters of 1 naphthoic acid is in the range 2-4 ns and emission decays as monoexponential in some approximation.

Intermolecular quenching of esters of 1-naphthoic acid (parent and model compounds) by N-oxyls like 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxyl is effective and proceeds as a diffusion controlled process in solution. Intramolecular quenching, which proceeds in N-oxyls derived from esters of 1-naphthoic and 1-naphthylacetic acids, is equally effective in solution and polymer matrices. Small medium effect on the intramolecular quenching supports the conclusion that the new radiationless channel is opened in the presence of paramagnetic centre for dissipation of electronic energy.

Photooxidation of isotactic polypropylene in the presence of esters of 1-naphthoic and 1-naphthylacetic acid derivatives reveals that the most effective inhibitor is N-oxyl radical. The hydrochlorides for both parent amine were less effective as the parent free amine and oxidized products. No accelerating effect on polypropylene photooxidation was observed for other derivatives of 1-naphthoic and 1-naphthylacetic acid. The absorption and IR spectra show that the naphthalene ring is destroyed early in the course of photooxidation and therefore the fluorescence monitoring is not possible.

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THE INFLUENCE OF NETWORK ON THE INTERACTION PARAMETER χ IN SYSTEM EPDM VULCANIZATE - SOLVENT

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Flory-Huggins interaction parameter χ was determined for the samples of EPDM vulcanizates, Keltan 312, 812 and their mixtures 312/812. Crosslink density was varied by changing the amount of dicumyl peroxide added during milling, then samples were vulcanized. The uniaxial stress-strain measurements were made on networks to determine the crosslink density.

Prepared samples were swelled in following solvents; cyclohexane, m-xylene, n-heptane, toluene, tetrahydrofuran and benzene, which interaction parameters χ are well known. The values of interaction parameter χ_c were obtained for EPDM vulcanizate and quoted solvents by equilibrium swelling from Flory-Rehner equation. The values of χ , known from literature, were compared with obtained interaction parameter χ_c .

Structural factor F'_4 , additionally characterize the investigated networks, was determined by equilibrium swelling.

The difference between the interaction parameters χ_c calculated from Flory-Erman equation, where is structural factor take in count, and Flory-Rehner equation indicate that network has an influence on interactions in system polymer-solvent.

From the results it can be also concluded that the values of χ parameter are distinct for crosslinked and uncrosslinked polymer.

P-15

STRESS INDUCED CHEMILUMINESCENCE FROM INJECTION MOULDED POLYAMIDE 6

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Injection moulded polyamide 6 samples have been studied with stress induced chemiluminescence (SCL). Chemiluminescence (CL) has been found to be a sensitive tool to study oxidative degradation of polymeric materials. CL is thought to be the result of the emission of light originating from an excited carbonyl group, which is formed as a result of oxidative degradation. Stress induced chemiluminescence (SCL) is used to monitor degradation of a polymer subjected to stress. Stress is initiating chain scission in the polymer resulting in radical formation.

The SCL was recorded by using an Instron tensile testing machine modified by attaching a lens system and a photo multiplier tube coupled to a photon counting device.

Two chemiluminescence peaks were observed, one in the strain softening region right after the first neck formation and one in the strain hardening region. Cyclic step strain experiments gave as a reasonable interpretation that the two peaks are of different origin.

THE EFFECT OF FLAME RETARDANTS ON CIS-1,4-POLYISOPRENE THERMAL STABILITY

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Our earlier investigations have revealed that both thermal properties and flammability of cis-1,4-polyisoprene are depended on its crosslink density, network structure, presence of fillers and metal with variable valence [1-7]. In this work an effect of flame retardants on thermal properties of cis-1,4-polyisoprene has been demonstrated.

The objects of our investigations were peroxide vulcanizates of cis-1,4-polyisoprene, Cariflex IR-307, containing the following flame retardants: chloroparaffin, antimony trioxide, mixtures of antimony trioxide and chloroparaffin, melamine cyanurate, pentabromotoluene. Thermal analysis has been carried out with the Paulik-Paulik-Erdey Derivatograph in air atmosphere and with Perkin-Elmer thermobalance in inert gas atmosphere. The thermal curves have been interpreted from chemical reactions of cis-1,4-polyisoprene vulcanizates point of view. Thermal stability indexes T_5 and T_{50} corresponding to 5 % and 50 % loss of mass respectively were determined from TG curves.

Trioxide antimony has proved maximum thermal stability from among investigated flame retardants. The lowest values of thermal stability indexes have been observed in the case of pentabromotoluene although its solid residue at 800°C is relatively high.

The used flame retardants except Sb_2O_3 have changed characteristic of cis-1,4-polyisoprene vulcanizates thermal transitions. The presence of chloroparaffin, pentabromotoluene and melamine cyanurate has eliminated the reaction of combustibility of the residue after vulcanizate thermal decomposition.

The investigations has been supported by State Committee for Research, grant Nr PB 1103.

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CHEMILUMINESCENCE STUDY OF THERMO - OXIDATIVE OF SOME EPDM / IIR BLENDS

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The aim of this study was a thermo - oxidative stability characterisation by chemiluminescence method of some EPDM / IIR * elastomer blends. This sort of blend has been selected to obtain elastomeric materials with improved mechanical properties than base elastomers.

In a first stage, the elastomers were studied as they are received, without removing the antioxidants by extraction.

Sigmoidal chemiluminescence curves (Fig. 1) recorded in presence of air are typical for a radicalic oxidation mechanism (peroxide intermediary).

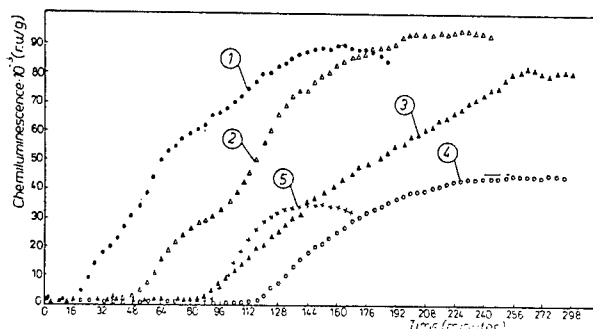


Fig. 1 - Chemiluminescence curves at 192°C from
binary EPDM / IIR blends

1 - 100 % EPDM ; 2 - 75 % EPDM / 25 % IIR ; 3 - 50 % EPDM / 50 % IIR ;
4 - 25 % EPDM / 75 % IIR ; 5 - 100 % IIR

Thermo - oxidative stability (as described both by the oxidation induction time (t_i) and the time necessary for reaching half of the maximum chemiluminescence intensity ($t_{1/2}$)) attain to maximum for EPDM / IIR ratios in range 50 / 50 ; 25 / 75

*EPDM - ethylene - propylene - diene terpolymer ; IIR - butyl rubber

(in weight parts). The enhanced stability of these compositions may be a explanation for maximum of the radiation crosslinking yields observed at irradiation of the same blends /1/ (Fig. 2).

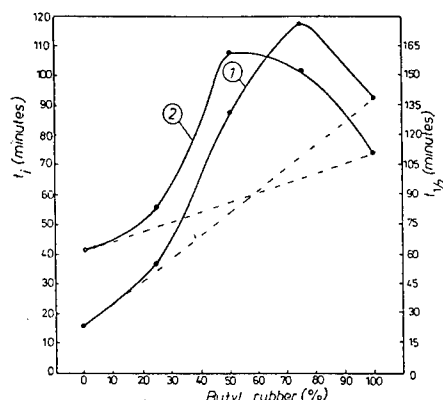


Fig. 2 - Dependence of t_i and $t_{1/2}$ parameters on ratio EPDM/IIR

In order to determine if the stabilization effect is due to interaction of the two elastomers or to added antioxidants, the elastomers were purified by repeatedly solving them in hot o-xylene and precipitating with methanol. Chemiluminescence and infrared data concerning to thermo-oxidative stability and thermal ageing of the blends based on purified elastomers are presented.

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P-18

RADIATION DEGRADATION OF POLYPROPYLENE

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Radiation degradation of polypropylene is due to the scission of macromolecule chains of polymer caused by high-energy electron beam or gamma rays. The consequence of scission of macromolecule chains is a diminution of molecular weight influencing many properties of polypropylene.

Melt flow index changes for pure polypropylene (PP) and its copolymers and blends with polyethylene (PE) in quantity 6% and 30% of PE generated by electron beam irradiation in the range up to 50 kGy have been investigated.

Properties of PP mainly depend on the percentage of crystalline phase and molecular weight. Because of the diminution of molecular weight of PP caused by electron beam irradiation there is significant worsening of mechanical properties of pure polymer. The addition of PE inhibits the decrease of mechanical properties.

Melt flow index changes of PP irradiated with different doses and stored within one month have been investigated

COMPARISON OF HYDROLYTICALLY STABLE PHOSPHORUS STABILIZERS IN POLYOLEFINS

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Phosphorus stabilizers, particularly phosphites, have been used to enhance the stabilizer efficiency of phenolic antioxidants as processing stabilizers for polymers. The use of these phosphorus stabilizers has grown, especially in polyolefins, despite the tendency of these materials to hydrolyze, which has caused handling problems in varying degrees and has affected the performance of the polymer in some applications. There have been efforts to improve the hydrolytic stability of phosphorus stabilizers which has led to the commercialization of several new products. Several different approaches have been taken to improve hydrolytic stability. One approach has been to increase the steric hindrance around the phosphorus atom in the molecule to block the approach of water molecules (T. Lemmen, et. al. SPE Antec '90, p186; D. R. Stevenson & C. N. Slater, SPE Retec Polyolefins IX, 1995, p687). Another approach was to prepare fluorophosphonites which take advantage of the improved hydrolysis resistance of the P-F bond [G. J. Klander, in "Polymer Durability," Chapter 26, p397, Advances in Chemistry Series No. 249, Editors: R. L. Clough et. al. Amer. Chem. Soc. (1996)], while a third approach was to incorporate the amine group into the molecule as an acid scavenger in order to minimize the accelerating effect that trace acid has on the hydrolysis of phosphorus stabilizers (K. D. Cooper, SPE Retec Polyolefins IX, 1995 p 653). Several of these compounds show significant improvement in the relative hydrolytic stability to commercial phosphorus stabilizers that are being currently used in the polyolefin industry. The accelerating effect of hydrolysis products on the hydrolysis of these more stable compounds is demonstrated. The effectiveness of these new phosphorus compounds as processing stabilizers in polyolefins, particularly in combination with a phenolic antioxidant is studied in this paper and relate in some cases, to the thermal stability of the compounds. The effect on processing color and other features of these new secondary antioxidants are also examined.

P-20

**ANTIOXIDANT EFFECTIVENESS IN POLYMERS AS
TESTED BY CHEMILUMINESCENCE: AN ACCEPTED TEST
METHOD FOR INDUSTRIAL USE**

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Abstract

Chemiluminescence imaging of large series of polyolefins with various stabilizers was carried out at different temperatures under oxygen. Sample thicknesses and stabilizer concentrations have been varied to define standardized conditions. The experiments show a good correlation between the oxidation induction time and the embrittlement time observed during conventional oven ageing tests. Therefore we are convinced that the chemiluminescence method can be used for screening purposes to study the antioxidant effectiveness in polyolefins.

NEW INTUMESCENT FORMULATIONS OF FIRE RETARDANT POLYPROPYLENE - FREE RADICALS MECHANISM OF FORMATION OF THE CARBONACEOUS PROTECTIVE MATERIAL

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Uses of polyolefins and most particularly, of polypropylene are often limited because of their bad fire behaviours. A solution to limit the kinetics of their burning mechanisms consists in developing on the outer surface of the polymer a glassy [1] or an expanded [2] shield which may at least partially, limit the transfer of fuel to the gas phase, the transfer of heat from the gaseous phase to the condensed phase and the oxygen diffusion in the condensed phase.

The study compares five new intumescent additives mixtures and a carbonising glassy additives system (IX) with the ammonium polyphosphate - pentaerythritol system (I) and two additives formulations (II and IV) previously developed in this Laboratory in term of fire retardancy of polypropylene-based formulations (Table 1).

Table 1.- *Composition of the additives mixtures.*

Mixture label	CP	CA	SA	CA/(CA+CP) (wt. %)	SA/(CP+CA+SA) (wt. %)
I	APP	PER	-	25	-
II	APP	PER	4A	25	5
III	APP	PA-6	EVA-8	68.8	10.3
IV	PY	PER	-	39.1	-
V	PY	XOH	-	33.33	-
VI	PY	MOH	-	33.33	-
VII	PY	SOH	-	33.33	-
VIII	APB	PER	-	33.33	-
IX	PY	BCOH	-	66.66	-

Glossary : ammonium polyphosphate (APP), diammonium pyrophosphate (PY) or diammonium pentaborate (APB) as **carbonisation catalysts**, pentaerythritol (PER), xylitol (XOH), mannitol (MOH), d-sorbitol (SOH), β -cyclodextrine (BCOH) or polyamide-6 (PA-6) as **carbonisation agents**, zeolite 4A (4A) and an ethylene-vinyl acetate (8 %) copolymer (EVA-8) as **synergistic agents**.

Table 2 presents the FR performances of the PP - additives formulations (additives loading : 30 wt. %).

Table 2.- *Results of the FR tests of the PP-based formulations (NC : not classed by the test)*

Mixture	I	II	III	IV	V
LOI (%)	32	42	28.5	35	24
UL-94	V0	V0	V0	V0	V0
Mixture	VI	VII	VIII	IX	
LOI (%)	23.8	24	24	19.8	
UL-94	NC	V0	NC	NC	

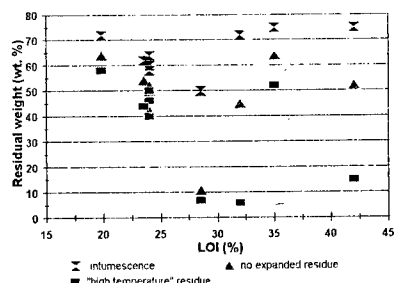


Figure 1. Amounts of residual carbonaceous materials vs. the LOI.

Figures 2 and 3) shows the presence of free radicals in the protective coating (composed of polyaromatic species, partially organised into structures with parallel layers linked by phosphates esters) formed using the additives systems.

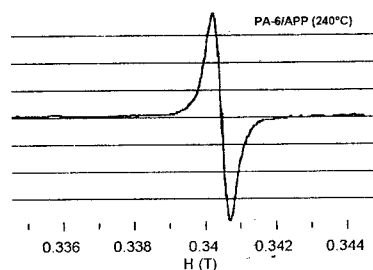


Figure 15. X-band ESR spectrum of the APP - PA-6 mixture heat treated at 240°C under air.

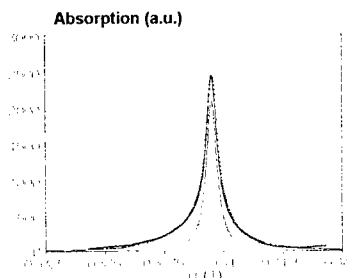


Figure 3. Integrated ESR spectrum (one lorentzian and one gaussian functions) of the APP - PA-6 mixture heat treated at 440°C under air.

A line shapes analysis of the ESR signal brings information about the size of the carbonaceous structures. Moreover, the values of the spectroscopic factor are proposed as probes for the presence of crystalline phases in the coating. The study proposes that spin concentration at least equal to 10^{21} spins/kg in the intumescent and in the no expanded residue is always required to obtain $\text{LOI} \geq 28\%$. Finally, the participation of free radicals in the formation of chemical bonds between the materials produced from the additives and the products of the degradation of the polymer is discussed. These reactions take a part in the FR process via two different steps : they decrease the evolution rate of fuels and are termination steps in the free radical reaction scheme of the pyrolysis of the protective material.

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THE FORMATION OF DIACYL PEROXIDE IN PENDANT POLYMER CHAINS BY PHOTOOXIDATION OF BENZIL MOIETIES IN POLYMER FILM

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Diacyl peroxides represent an important class of reactive compounds in macromolecular chemistry. They are widely employed in preparation and also in modification of polymers. This work describes the formation of diacyl peroxide in side chain of polymer by photooxidation of benzil units in polymer film.

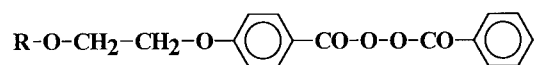
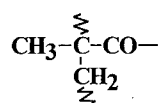
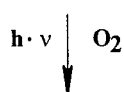
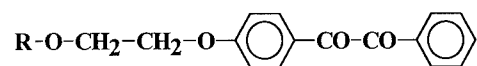
The photooxidation of low molecular benzil [1] and polymer with benzil moieties in pendant groups [2] in the benzene solution results in formation of biphenyl, phenylbenzoate, benzoic acid and a small amount of dibenzoyl peroxide. Photooxidation of benzil in polymer film result almost quantitatively in formation of dibenzoyl peroxide [3].

The photooxidation of benzil moieties in pendant groups of polymer in polymer film has not been studied until now. Therefore we decided to study the photooxidation of poly(1-phenyl-2-[4-(2-methacroyloxyethoxy)phenyl]-1,2-ethanedione) - co - styrene which preparation has benn described [4]. Besides the copolymer photooxidation, the photooxidation of low molecular model compound, (1-phenyl-2-[4-(2-acetoxyethoxy)phenyl]-1,2-ethanedione, in PS film was studied as well.

The polymer films were irradiated by medium pressure mercury lamp at laboratory temperature. The wavelengths longer than 370 nm were isolated using glass filter 730 87112 (Carl Zeiss, Jena, Germany). The course of photooxidation was monitored by IR spectroscopy. In IR spectra the formation of the vibration bands of carbonyl groups of diacyl peroxides in the region $1760-1800\text{ cm}^{-1}$ can be observed. The irradiation of the copolymer film causes crosslinking.

The benzoyl-4-(2-acetoxyethyl)benzoyl peroxide was formed during photooxidation of model compound 1-phenyl-2-[4-(2-acetoxyethoxy)phenyl]-1,2-ethanedione in PS film. The low molecular peroxide was isolated and characterised.

The photochemical transformations of copolymer and low molecular compound in the presence of oxygen can be expressed by equation:



The crosslinking of copolymer is caused by radicals that are formed by thermal or photochemical decomposition of the part of peroxides bound in the polymer.

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PHOTOCHEMICAL CIS-TRANS ISOMERISATION OF PENDANT ENAMINOESTER GROUP IN POLYMER FILM

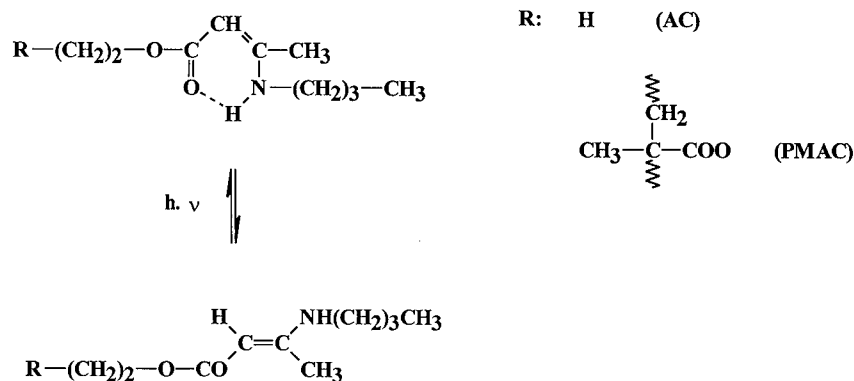
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The influence of the polymer matrix on the photochemical reactions is known [1]. The formation of different products by the photooxidation of benzil in solution and in polymer films has been described [2]. In poly (methyl methacrylate) (PMMA) and in polystyrene (PS) matrix, photooxidation of benzil proceeds specifically via the formation of dibenzoyl peroxide [2]. The reason for the formation of only one product in PMMA and PS films is due to stabilization of intermediate of photooxidation by the polymer matrix. In solution however the common intermediate is decomposed.

The present work also describes stabilization of intermediate of photochemical reaction in the polymer matrix. The studied poly(methacryloyloxyethyl 3-N-n-butylaminocrotonate) (PMAC) was prepared recently [3]. Greater changes of PMAC film irradiated with more intensive light (wavelengths higher than 300 nm) in air were described [4]. On irradiation of PMAC film with monochromatic light of lower intensity at wavelength 313 nm, only cis - trans isomerisation is observed:



This cis - trans isomerisation is not observed during irradiation of PMAC and its low molecular model, ethyl 3-N-n-butylaminocrotonate (AC) in chloroform. In the ground state the aminocrotonate six membered ring of cis form is stabilized by resonance and hydrogen bonding. The trans isomer formed is not stable. In the dark reaction it is transformed to the cis-form with the rate constant equal to 0.00136 min^{-1} . Similarly the isomerisation of low molecular model AC in PMMA was observed. But dark reaction of AC in PMMA is quicker 0.01267 min^{-1} . The course of isomerisation is evidenced by changes in UV and IR spectra. The different rate of the dark trans - cis isomerisation in solution and in polymer matrix caused with restricted rotation around C-C double bond in film. Therefore in the homopolymer, one side of the isomerising group is fixed to the polymer chain, the rotation is more restricted in homopolymer film than in the case of AC in PMMA. The different lifetimes of the trans form in solution and in polymer film is the reason for the difference photochemical product formation from enamino ester group in the polymer film and in the liquid solution.

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HYDROBROMINATION OF POLYCYCLOOCTENE AND SUBSEQUENT REACTIONS

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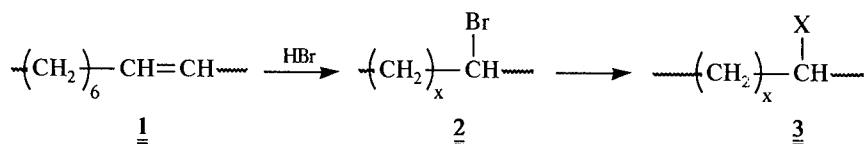
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The common feature in the photoageing of polyolefins is radical formation on the backbone of the macromolecules, followed by the addition of oxygen and formation of hydroperoxides. The hydroperoxides being unstable compounds are gradually decomposed as they are formed. Under the photoageing conditions, various products are formed. To elucidate the exact role of the hydroperoxides in photoageing of polymers, the "pure" polymeric hydroperoxide is needed.

In the course of our investigation to synthesise such a macromolecular hydroperoxide, we found that direct nucleophilic substitution of sulfonates (obtained from corresponding alcohols) by HOO^- did not lead to the desired product.

Second approach was to use brominated polymer, similar to low molecular compounds^{1,2}. As starting material, commercially available polycyclooctene (1) (Vestanamer 8012 - Hüls, Germany) was used. Hydrobromination of double bonds of Vestanamer with gaseous hydrogen bromide at the temperature $-20 / +20^\circ\text{C}$ and slightly increased pressure was quantitative (1 $\rightarrow$ 2).



$$6 \leq x \leq 8$$

X = ONO_2 , OCOCF_3 , OOH , NH-TMP

Nucleophilic substitution of hydrobrominated Vestanamer (2 $\rightarrow$ 3) with HOO^- in the presence of the silver nitrate and silver trifluoro acetate, lead easily to alkyl nitrates (X = ONO_2) and trifluoroacetyloxy (X = OCOCF_3) derivatives respectively. 15 % maximum conversion to hydroperoxide (X = OOH) was obtained in the presence of CF_3COOAg with 50 % aqueous solution of hydrogen peroxide or hydrogen peroxide/urea complex in

tetrahydrofuran solution. Final hydroperoxides were insoluble in organic solvents and probably crosslinked. Hydroperoxides were estimated iodometrically and also as nitrite derivatives by means of FTIR spectroscopy after NO treatment.

In the treatment of hydrobrominated Vestenamer with 4-amino-2,2,6,6-tetramethyl piperidine (TMP-NH₂) polymer containing light stabilizing units, as viscous liquid was obtained. The polymer is soluble in organic solvents. Together with substitution by amino group, dehydrobromination of the original polymer to a small extent was observed. Photostabilizing activity of the polymer obtained was examined.

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AGEING OF POLYDICYCLOPENTADIENE NETWORKS*S. MALLET, B. CHARTIER, M. AUTRAN, P. MOREAU AND B. MORTAIGNE*

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Polydicyclopentadiene (PDCPD) is a thermoset polymer prepared by liquid moulding techniques using formulated liquids based on dicyclopentadiene (DCPD) and a metathesis catalyst/activator system. DCPD resins crosslink via Ring Opening Metathesis Polymerisation (ROMP reaction). One of the great advantages offered by PDCPD is that it can be made via Reaction Injection Moulding (RIM) or Resin Transfer Moulding (RTM) processes, because of the low viscosity of the liquids and the rapid metathesis polymerisation rate. Thermoset PDCPD is well suited for a wide variety of applications, particularly as an engineering plastic, to fabricate large and complex parts with varying thickness. Neat polymers based on DCPD provide an excellent balance of stiffness and impact properties. Unfortunately, the network structure of these materials, which is not again very well known, present a lot of unsaturated double bonds [1,2], and these double bonds are very sensitive to oxidation phenomena.

Degradation of components made from polymeric materials occurs as the result of environment dependent chemical or physical attack, and very often limits the service lifetime. The present work deals with the effects of oxidation on PDCPD network ageing and with the influence of ageing on the mechanical properties, to finally predict PDCPD lifetime under service conditions.

Two PDCPD thermoset polymer (Telene™) modified with polybutadiene elastomer (3.5 and 5.5 weight percent) to increase impact strength were supplied by Telenor society. Plates 300 x 300 mm with different thickness (5, 10 and 20 mm) were moulded by RIM process.

In a first part of this study, we used an infra red technique (FTIR) to look for the thickness of the oxidised layer (TOL) of the moulded plates left for three month in ambient temperature and humidity.

Infra red measurements concerned the analysis of thin sections of the samples and were carried out with a Bruker IFS 88 FTIR spectrometer equipped with a microscope and a narrow bandpass mercury cadmium telluride detector. Thin sections were obtained, by means of a microtome, in the direction perpendicular to the substrate surface. Sections were 10µm thick to allow a transmission analysis with the infra red microscope. Spectra were recorded using a beam diameter ranging from 30 to 50µm, at a resolution of 4 cm⁻¹ and by averaging 100 scans. The evolution of different optical density ratios was determined.

During ageing, chemical degradation increases oxidation absorption bands and decreases carbonyl absorption bands in FTIR spectra. For the FTIR investigation, the skin core profile evolution is obtained by plotting the optical density ratio of carboxyl, hydroxyl and carbonyl bands against distance from the substrate surface. It was showed that oxygen depletion restricted reaction in the interior of plates as thin as 150 to 200 µm.

The process of photo oxidation proceeds by a radical chain process converting the long chain polymer molecule, PH, into a radical, P°, which leads to chain scission by

oxidation. Based on literature [3,4], kinetic oxidation profile were discussed and it was determined that the thickness of the degraded layer was controlled by oxygen diffusion in PDCPD material. The degraded layer is of the order of magnitude of D/k , where D is the diffusion coefficient and k the pseudo first order rate constant for reactant consumption.

The most interesting factor for using this polymeric material concerns its impact resistance, and usually the thickness of degraded layer is of crucial importance in determining the residual mechanical properties of aged samples. In a second part of this study, we look for evolution of polymer mechanical properties after ageing.

The impact strength and the critical stress intensity factor (K_{Ie}), which describes the stress field at a crack tip when crack extension occurs, has been determined to characterise the fracture behaviour of PDCPD under the plane strain and the plane stress conditions. Unnotched Charpy impact specimens 10.60 mm large with 5 mm thickness for testing were used. Crack propagation was studied on CT (compact tensile) mechanical notched samples 40.50 mm large; crack beginning was 0.4 mm length.

Impact initial values for PDCPD plates was 100 to 140 kJ/m², value increasing with increase of thickness plate. It was 160 kJ/m² for 5mm PDCPD plate with 5.5% weight polybutadiene (to be compared with 100 kJ/m² for 5mm PDCPD plate with 3.5% weight polybutadiene). K_{Ie} initial values for all specimens was 4.8 to 5.1 MPa. $\sqrt{m}$.

The PDCPD samples were subjected to thermal ageing at 70°C with Relative Humidity 95% RH for different times up to 400 hours in order to perform accelerated tests. The values obtained for aged specimens were compared to initial values of similar specimens. It appears that impact strength and K_{Ie} initial values decreases in the same amount (near 15%) for the different plate thickness.

The mechanical strength is not a decreasing function of the thickness of the TOL, and seems to have an independent variation. It could be concluded that degradation occurs as the result of physical ageing minimising the importance of TOL on loss of mechanical properties. It appears that during thermo oxidative ageing, the network structure of PDCPD was modified which induce decrease in the mechanical properties of samples. As to consider the small thin of TOL, to be compared with the plate thin (5 to 20 mm), physical ageing is of crucial importance on mechanical properties loss in aged PDCPD network.

Authors would gratefully acknowledge M. Recher and Mongin from Telenor society for technical support and for giving us the PDCPD samples.

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THE EFFECT OF THERMAL AGEING ON MECHANICAL PROPERTIES OF FILLED HDPE

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Thermal treatment of polymers results in a changes in properties of the materials. The reason for these changes can be either physical modification of the structure and morphology of the polymer or chemical changes consisting mainly in thermooxidative degradation.

Mechanical properties are influenced significantly by any of these factors and sometimes it is not so easy to distinguish which effect plays a more important role in the process observed.

In this work, the effect of annealing in air was investigated for two different types of HDPE (linear and slightly branched) and for the same polymers filled with various amounts of carbon black (up to 40 wt %). The effect was evaluated according to changes in mechanical properties (tensile strength at break, strain, Young's modulus), crystallinity as measured by DSC, and oxidation induction period measured by chemiluminescence. The materials were annealed either in lower temperature region, i.e. 100, 110, and 120 °C or at higher temperatures around 180 °C.

It was shown that annealing both at low and high temperatures leads to changes in the mechanical properties, however, significant differences were found in the behaviour of the two HDPEs investigated as well as in the filled composites. A decrease in strain at break and increase in tensile strength and Young's modulus were the main tendencies observed, although several interesting exceptions from these trends were found.

For the samples annealed in low temperature region, DSC data showed the increase in the crystallinity degree indicating a recrystallization of the materials during annealing. Chemiluminescence data did not prove a significant changes in oxidation induction time. Therefore, it was concluded that the annealing at 100 - 120 °C does not lead to a significant oxidation of the material and the physical factors are the only reason for the changes observed. The oxidation in air at 180 °C leads to slightly different results. The comparison of all data indicates that besides the physical factors, thermal oxidation also contributes to the mechanical changes observed as a result of annealing. The presence of carbon black affects the influence of annealing in both temperature regions investigated.

SURFACE PROPERTIES OF POLYPROPYLENE PRETREATED BY OXIDIZERS

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The efficiency of the oxidizing methods for modification of isotactic polypropylene (PP) is comparable to modification by electric discharge [1]. In addition the formers give a more durable results. By using suitable oxidizing agents, such as chromyl chloride [2] or chromosulfuric acid [3], the hydrophilicity in fine surface layer of dimension to 10 μm increases, while the original advantageous physico-mechanical properties of polymer remain preserved [4].

Changes in the surface topography of PP were insignificant for the modification time to 10 min in chromosulfuric acid ($T = 22\text{ }^{\circ}\text{C}$).

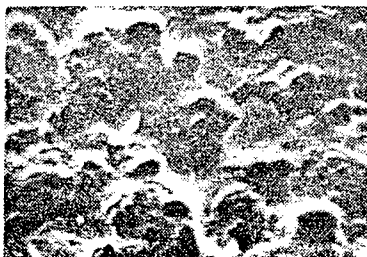


Fig. 1 Modification of PP with chromosulfuric acid ($T = 70\text{ }^{\circ}\text{C}$, $t = 2\text{ min}$) (4000x)

A treatment in warm chromosulfuric acid ($T = 70\text{ }^{\circ}\text{C}$, $t_{\text{ox}} = 2\text{ min}$) had a more pronounced effect on the polymer surface, the whole surface was rough and contained craters with diameters approaching 15 μm (Fig. 1).

The dependence of total free surface energy (TFSE) and its polar component (PFSE) is represented in Fig. 2. According to Fig. 2 the values of TFSE of modified PP increase with rising concentration of carbonyl groups (plot a). However, it level off at certain concentration of carbonyl groups. If the time of modification gradually increases, a part of polar groups in polymer is altered or even inactivated. As a result of this the polarity of polymer is not influenced any more by the increase of carbonyl group concentration. The

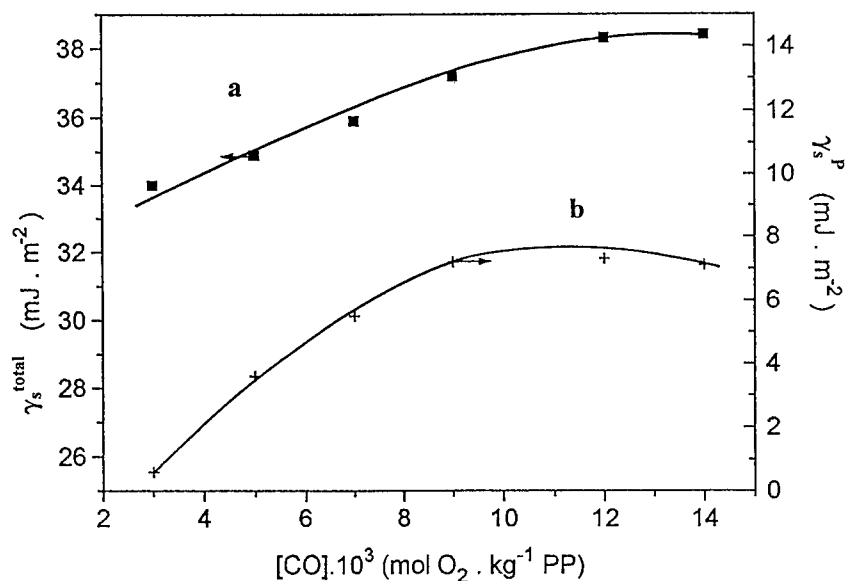


Fig. 2 Total free surface energy and its polar component of PP modified by chromosulfuric acid vs. carbonyl groups concentration

dependence of PFSE exhibits similar character (plot b). In this case the leveling off appears above the concentration $[CO] = 9 \times 10^{-3} \text{ mol O}_2 \cdot \text{kg}^{-1} \text{ PP}$. The increase in the value of PFSE is nine time higher compared to the original value.

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THERMAL HYDROLYTIC DEGRADATION OF POLYOXADIAZOLE DERIVATIVES

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Polyoxadiazole derivatives are known to be the polymers with high thermal and chemical stability and with important dielectric and electrochemical characteristics [1-3]. According to hydrodynamic and dynamo-optical data obtained for poly[(*p*-phenylene)-2,5-diyl-1,3,4-oxadiazole] in conc. sulfuric acid [4], the macromolecules of these polymers are semi-flexible, the equilibrium rigidity of the macromolecules at room temperature being significantly affected by the solvent strength [5].

In this work, the same methods of molecular hydrodynamics and optics are used, for the first time, to characterize the polyoxadiazole derivatives macromolecules degradation observed at higher temperatures in solution in sulfuric acid. Molecular weight is determined at different stages of degradation using the diffusional and viscometric data. Specific parameter of degradation velocity is determined, and activation energy of the process is evaluated. Results are compared with the data known for other heterocyclic polymers to establish the nature (oxidative?) of the macromolecules degradation, possible application of the effect for analytical purposes, and strategy for the macromolecule stabilization via changes in the repeat unit chemical structure.

Acknowledgements This work was supported by the International Science Foundation and Russian Government under Grant No. JAA100.

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STABILITY OF POLYPYRROLE CONTAINING CONDUCTING POLYMER COMPOSITES

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The combination of conventional polymers with conductive polymers or fillers allows to create new polymeric materials with unique electrical properties. Polyolefines can find new applications by blending with polypyrrole, polythiophene, polyaniline or other conducting polymers. The problem of surface static charge of poly(methyl methacrylate) can be solved also by blending with conductive polymers. In such composites the insulating polymer provides good mechanical properties and processability and the conducting polymer provides electrical conductivity. From practical point of view the investigation of the composites stability is also important.

Conducting polymer composites of polypropylene and polypyrrole (PP/PPy), and poly(methyl methacrylate) and polypyrrole (PMMA/PPy) were prepared by means of chemical modification method [1, 2] resulting in a network like structure of polypyrrole embedded in the insulating polymer matrix. The content of polypyrrole determined by elemental analysis varied from 0.25 to 17 wt. %. Electrical conductivity of compression moulded samples depends on the concentration of polypyrrole and reached values from 1×10^{-11} to 1 S/cm. The morphology of the composites was investigated by low-voltage scanning electron microscopy.

The stability of the electrical properties of PP/PPy composites was investigated by conductivity measurements during heating-cooling cycles. There is only a small drop in conductivity by annealing of PP/PPy composites in air at temperatures up to 80 °C.

The thermogravimetric stability of PP/PPy and PMMA/PPy composites was examined by thermal analysis. The thermogram of pure PP was characterized by one continuous process of weight loss starting at 250 °C (1 % weight loss), which did not leave any residue at 437 °C. For chemically prepared PPy the beginning of weight loss was observed at 67 °C, caused by water and solvent vapourization. Pure PPy has hygroscopic properties, and solvent can also be incorporated into the polypyrrole [3]. The weight loss proceeds quite steadily, with a residue of about 35 % remaining at 700 °C.

The decomposition of PP/PPy composites followed a similar tendency to that of pure PP. However, the conducting PPy exerted a stabilizing effect on the composites. Table 1 presents the thermogravimetric characteristics of the samples. We used the temperature values at 10 % weight loss for comparison of the samples because of the overlapping of the real decomposition and solvent evaporation especially in samples

with high PPy content. The thermal stability is shifted to higher temperatures with increasing PPy content. The temperature of maximum of derivative curves also increased from 410 °C for pure PP to 466 °C for PP/PPy composite containing 10.4 % PPy. In all composites a residue remained at 527 °C. The amount of the residue correlated with the PPy content in the composite. A similar stabilizing effect of PPy was also observed in PMMA/PPy composites.

Table 1. Thermogravimetical characteristics of PP, PP/PPy composites, and chemically prepared PPy.

Sample	Temperature of 10 % weight loss (°C)	Maximum of DTG peak (°C)	Residue at 527 °C (wt. %)
PP	319	410 - 415	0
PP/PPy (1.1 wt. %)	335	437 - 441	0.8
PP/PPy (8.9 wt. %)	350	438 - 447	7.3
PP/PPy (10.4 wt. %)	373	462 - 466	7.5
PPy	240	-----	55.0

Large amounts of material with good antistatic and conductive properties can be prepared by an inexpensive way using the chemical modification method. These conductive composites may find applications as antistatic packaging and as materials for electromagnetic radiation shielding. The results of thermogravimetric analysis show a stabilising effect of PPy on the stability of PP/PPy and PMMA/PPy composites against thermal degradation.

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THE OXIDATIVE STABILITY OF PARTICLE-BEAD METHACRYLATE-ACRYLATE POLYMERS

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The thermal volatilization process of polymethylmethacrylates (PMMA) polyacrylates (PBAC) and their copolymers has been investigated during the last decades to the great details, both in the absence and in the presence of oxygen. Among the possible sources influencing the thermal weight loss of these polymers are polymer structure, shape of the sample, sample size and presence of gases. In the present poster we describe the non-isothermal weight loss curves of submicrometric particle beads consisting from PMMA core, crosslinked PBAC interlayer and upper PMMA shell. The particle polymer systems were synthesized in three step water emulsion polymerization.

The oxidative degradation of powder samples differs from the course of volatilization in nitrogen. (Fig 1). The weight loss of samples heated in nitrogen (curve 4 and 5) proceed in two stages which characterize the degradation of PMMA (more sensitive component) and crosslinked PBA (more stable component). In the oxygen a weight loss of sample proceeds fluently in one stage. Molecular oxygen protects PMMA against depolymerization at temperatures below 500 K, however at higher temperatures polymer degrades with higher intensity. The main-chain cleavage reaction mechanism due to H-abstraction from backbone carbons is proposed by [1]. The volatilization curves on figure 1 show also a dependence of the volatilization rate on the heating rate of the sample. The slower production of reaction products, when heating rate of the sample was changed from 10 ° to 1,25 ° / min, moved the weight loss curves to lower temperatures for the same polymer sample. This observation corroborates well with a conception that all the factors which enhance transport of reaction products from a place of reaction accelerate a weight loss of the sample.

The samples from processed particle bead polymers (foils press molded, shear stressed bulk polymer, even the polymer foils from dried emulsions) show in the beginning of volatilization in nitrogen the thermal stability corresponding to the more stable PBAC polymer alone. Nevertheless on oxygen the sensitivity to degradation of the three stage particle polymer increases.

The pure component PMMA is more stable in oxygen (50 w % loss at 645 K) compared to 50 % weight loss at 620 K in nitrogen. We have not observed any significant difference in stability of the crosslinked PBAC in nitrogen or oxygen. The non crosslinked PBAC is somewhat less stable than PBAC network crosslinked with diallylphtalate. The following conclusion can be drawn from dynamic thermal weight loss study of multilayer PMMA-PBAC polymer particles in oxygen and nitrogen:

1. The powder polymer isolated from emulsion by freeze-thaw procedure is slightly less sensitive to volatilization in oxygen than in nitrogen. Moreover the difference between the PMMA and PBAC polymer components degradation is less pronounced. It is due to the oxidative initiation of the chain scission [1].

2. In the systems densified by melting the powder in press, the stability of polymer in nitrogen considerably increases more of the 60 K. (Fig.2)

3. The increasing rate of heating in oxygen has only a little effect on shifting the volatilization to higher temperatures namely in the first stages before 50 w % loss of a sample. In the nitrogen this effect is more evident already at the beginning of volatilization.

4. The differences among the thermal weight loss of PMMA and PBAC composites and pure components are caused by different initiation step of volatilization in nitrogen and oxygene.

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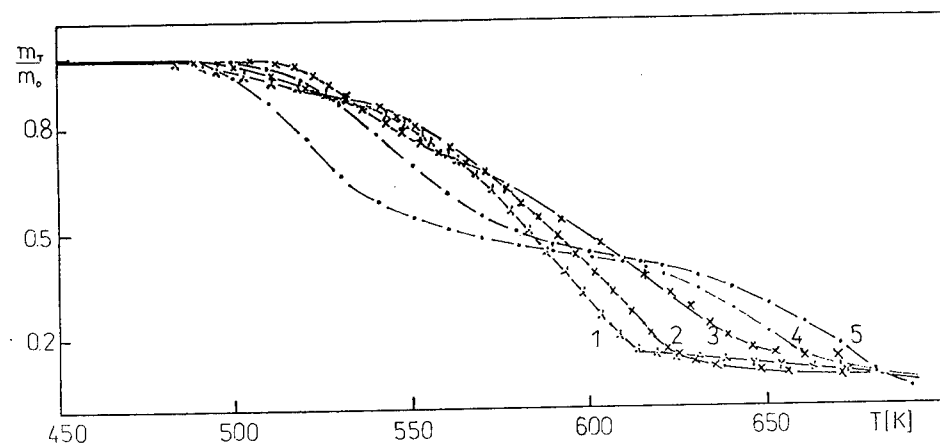


Fig.1 The dynamic TG analysis of the three layers particle-bead powder polymer: PMMA core(45.3 w%), PBAC network interlayer cross-linked with 4.2 w% of diallylphtalate(36.5 w%) and PMMA shell (18.2 w%). Rate of heating[°/min]: curves 1 - 1.25; 2 - 2.5; 3 - 10; (oxygen) and 4 - 2.5; 5 - 10; (nitrogen)

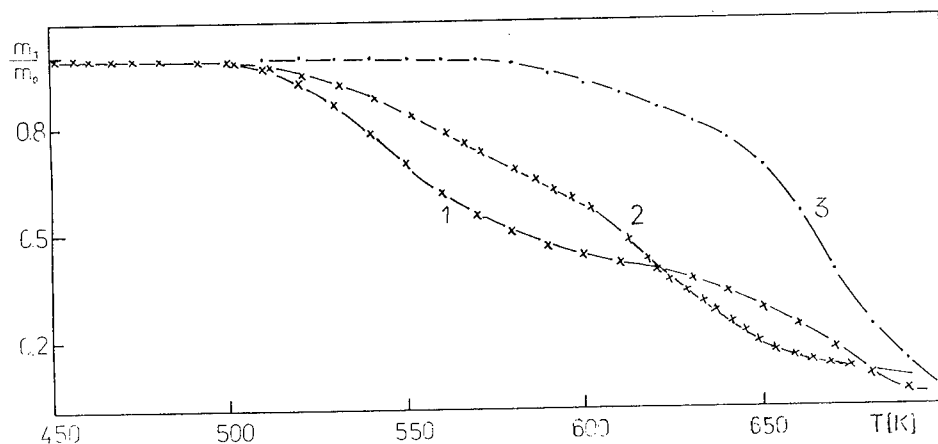


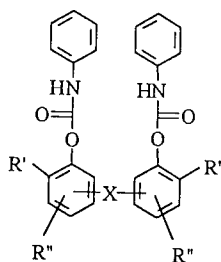
Fig.2 The dynamic TG analysis(10°/min.) of the three layers particle-bead core-shell polymer PMMA-PBAC-PMMA (composition as in Fig.1). Curves: 1 - powder in nitrogen; 2 - sheare stressed melt in oxygen; 3 - sheare stressed melt in nitrogen.

MODIFIED STABILIZERS CONTAINING URETHANE STRUCTURES

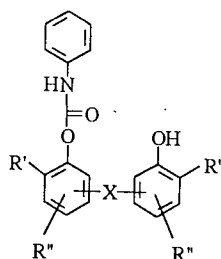
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Various substances with antioxidatively acting structures have been modified by the reaction with isocyanates (phenyl isocyanate, TDI, MDI). The synthesized products of the general formulae **I-IV** have been investigated regarding their thermal behaviour. First tests concerning their efficiency as antioxidants have been carried out.

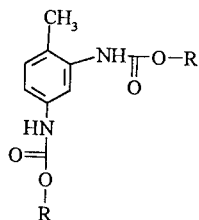


I



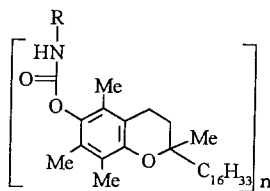
II

R', R''...alkyl
X...S, CH₂, C(CH₃)₂, CH(CH₃)



III

R...2,6-di-t-butyl-4-methylphenyl,
2,2,6,6-tetramethyl-piperidine-4-yl,
1,2,2,6,6-pentamethyl-piperidine-4-yl



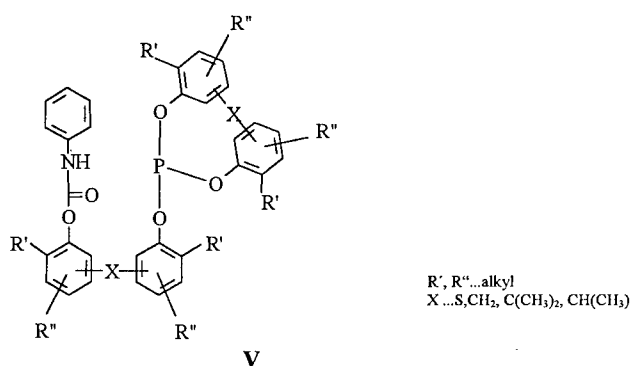
IV

n=1: R...phenyl,
n=2: R...methylenebis-4,4'-phenylene

It is shown that thermal degradation of compounds **I**, **II**, **III(a)**, and **IV** under N₂-atmosphere proceeds in two steps, where the first one is the cleavage of urethane bond, while the second one is characteristic for volatility / decomposition of the parent (phenolic) compound. The cleavage temperatures of the urethane bond in the investigated compounds are found to range

from 160 to 260°C, that means, the antioxidatively acting (phenolic) compound should be released under thermal stress, i.e. under processing conditions.
Using these products in thermooxidation of polypropylene, an improvement of the induction period is observed.

In addition, structure II was modified by the reaction with phosphorous compounds to give structure V:



To test the stabilizing ability of the synthesized compounds under processing conditions, extrusion experiments have been carried out.
First results of our investigations give rise to hope for using the compounds as new stabilizers against thermooxidation as well as during processing.

THE INFLUENCE OF OLIGOMER HALS ON THE STABILIZATION EFFICIENCY IN POLYPROPYLENE FILMS AND FIBRES

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1. Introduction

Generally, the efficiency of stabilizers in a polymer is determined by their chemical structure and ability to stop or retard degradation processes, and on the other hand by physical interactions and mutual compatibility with the polymer (1,2).

Over the last years, in order to fulfil higher requirements on photostabilizers, new UV absorbers of the oligomeric HALS type with very low volatility and good compatibility with a variety of polymers were developed. The molecular aspects of HALS with different molecular weight and their effectiveness in polyolefins are discussed in many works (e.g. 3,4).

This paper reports the results of investigation of the influence of molecular structure of sterically hindered amines on their efficiency in polypropylene films and polypropylene fibres.

2. Experimental

Polymer: Polypropylene HPF (Slovnaft co.) MFI = 9.97 g/10 min
 Light stabilizers: HALS 1/1 - HALS 1/5, on the base of sterically hindered amines (laboratory product)
 HALS 2 - Chimasorb 944
 HALS 3 - Uvasorb HA 88 (fa Sandoz), comm. prod.
 HALS 4 - Hostavin N 30 (fa Hoechst), comm. prod.

Preparation of PP foils and fibres was carried out in two stages:

a/ blending and homogenization of the powdered polymer and the classical stabilization system together with the tested HALS ; remelting and granulation in the Brabender plastograph at a temperature of 200 -240°C and revolution 35 min⁻¹

b/ preparation of pressed foils with a thickness of 0.12 and 0.5 mm at 200°C,.

preparation of fibres by a laboratory extruder (φ 16mm) at a temperature of 230°C (nozzle with 13 holes, feeding rate 8.3 g/min, take up velocity 300 m/min). Fibres were elongated by means of a laboratory equipment to a ratio λ = 3.5. The part of fibres was thermally fixed at 120°C for 3 min. The efficiency of light stabilizers was evaluated after exposure (xenotest) by measuring the content of carboxylic groups (foils) and by the determined of mechanico - physical properties of fibres.

3. Results and conclusions

- The efficiency of oligomeric polymer stabilizers in polypropylene fibres and foils significantly depends on the history of preparation of samples
- The influence of the molecular weight of the stabilizer on its efficiency is ambiguous and different for fibers: foils (Tab.1)
- The efficiency of HALS 1/1 - 1/5 in foils decreases with the molecular weight. Distinct is also the influence of the distribution of molecular weight at higher values
- The influence of the molecular weight of HALS 1/1-1/5 on the light - stabilization efficiency of fibers is manifested by a lower decrease of the tenacity at $M_w = 2500-4700$
- In comparison with commercial oligomeric stabilizers HALS 2 - HALS 4, oligomeric HALS 4 of triazine types prepared in laboratory have a comparable light - stabilization efficiency

Table 1 The influence of molecular weight of oligomer of sterically hindered amines on the stabilization efficiency

Stabilizer	M_w	MFI PP (stab.), g/10min	Absorbance $\Delta A_{CO} = 0.3$	Tenacity fibers after xenotest 1300 h, %
HALS 1/1	1800-2063	9.69	4217	39.6
HALS 1/2	2530-2770	9.88	4068	54.3
HALS 1/3	3600-3700	10.03	3930	51.2
HALS 1/4	4080-4460	9.85	4155	56.7
HALS 1/5	4770-4780	9.37	3740	60.7
Chymasorb 944	-	10.15	4300	61.8
Uvasorb H88	-	9.72	5300	55.9
Hostavin N30	-	9.51	3350	62.7

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**MEASUREMENT OF ABSORBED DOSES NEAR INTERFACES AND
DOSE MAPPING USING GAFCHROMIC DOSIMETRY MEDIA**

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In radiation processing the sharp variation of absorbed dose near interfaces especially in case of large differences in electron densities of the materials making up each interface is a serious problem facing the irradiation of electronic devices which consists of multilayer materials.

GafChromic Dosimetry Media is a thin-coated films consists of 6 μm thick radiation sensitive layer microcrystals of radiation sensitive monomer dispersed in a gelatin binder coated on a 100 μm thick polyester base. The film is sensitive to electron beam and gamma radiation and produce high resolution radiation image.

The effects of dose, dose rate, storage, temperature and relative humidity during irradiation on the dosimeter film performance have been investigated.

The films were irradiated for calibration in the dose range from 0.1 to 50 kGy using electronic equilibrium layers of polystyrene (5 mm thick). The films show increase in absorbance in the whole spectrum. The response curves were established in terms of the increase in absorbance at 400 nm, 600 nm, and the increase in trace area under the wavelength ranges 395-405 nm and 320-450 nm. The coefficient of variation percent of each group of films (4 pieces) is ranging from 0.31% to 1.59% over the whole dose range.

The interface materials in all cases are thin layers of either copper (0.4 mm), aluminum (0.5 mm), stainless-steel (0.5 mm), iron (0.75 mm) or air (~ 80 mm). The spacers are polyester (Mylar) to match the GafChromic Dosimetry Media films. The measured dose as a function of thickness of interface shows the high-resolution properties of studied films made it possible to determine fairly the differences in dose enhancement close to high-z interfaces and build up near an air interface.

The plaque-source irradiator of Egypt's Mega-gamma-1 processing facility is designed to give a two-sided irradiation of a rectangular product package. The dose distributions in a dummy product box irradiated along with other dummy product boxes were measured by placing about 500 individual GafChromic film at different calculated locations at various planes throughout the dummy box. The obtained results can be recommended for dose mapping inside irradiated boxes.

CHEMILUMINESCENCE METHOD FOR STUDYING THE RADIO- AND THERMO-OXIDATIVE DEGRADATION OF POLYMERS

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The aim of this work was to test the capability of chemiluminescence (CL) technique, recently developed in ICPE, for studying of damaging effects produced in some polymeric materials (such as polyethylene or polypropylene) by thermo- or radio-oxidation.

Several works relating to the great sensibility of chemiluminescence both in antioxidant effectiveness assesment and in study of polymer degradation were reported [1-9].

We found a linear dependence between the initial chemiluminescence intensity and 1710 cm^{-1} absorbance for γ -irradiated unstabilized polypropylene; a similar dependence is found for thermal oxidation of the unstabilized polyethylene [9].

Considerable differences in CL response between some stabilized polyethylene samples exposed to various thermal ageing conditions is found (Fig. 1) in spite of the fact that 1710 cm^{-1} absorbance is actually unchanged.

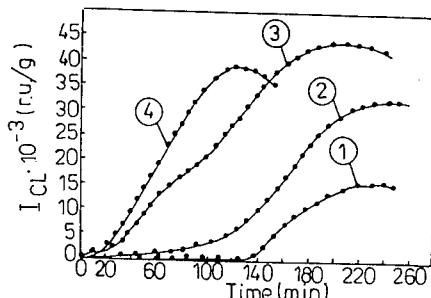


Fig. 1 - Chemiluminescence curves from polyethylene aged in various conditions
1 - unaged; 2 - 1100 hours / 80°C in air (5 atm); 3 - 1758 hours / 80°C in air (5 atm); 4 - 7250 hours / 98°C in air (1 atm)

Using the oxidation induction time values and the formula of stress additivity [10], the durability to various ageing conditions can be easily estimated, e.g. ~ 8500 hours at 98°C in air (1 atm) and 1900 hours at 80°C in air (5 atm) were determined for LDPE.

The specific shape of chemiluminescence curves (Fig. 2 and 3) can be correlated both with the crosslinking effect intensity in polyethylene and the strong radiation induced damage in polypropylene. The efficiency of Santonox - R in

radiooxidative protection of polyethylene seems to be slightly greater than that of Irganox - 1010 although the efficiency in thermo - oxidative protection of Irganox - 1010 is considerably higher.

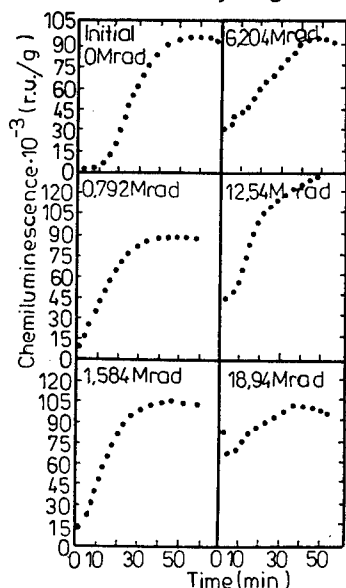


Fig. 2 - Chemiluminescence curves from γ - irradiated polypropylene at various doses

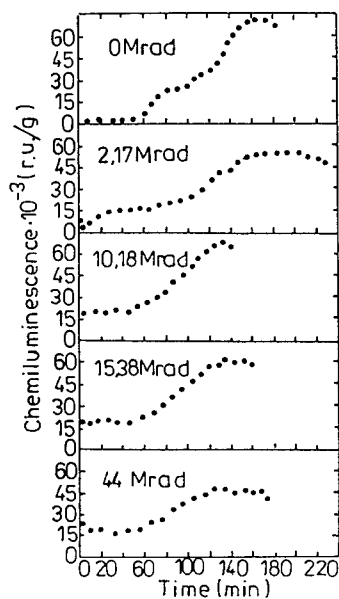


Fig. 3 - Chemiluminescence curves from γ - irradiated polyethylene at various doses

By mean of the oxidation profile obtained also from chemiluminescence data, the unhomogeneity oxidation of a γ - irradiated thick polyethylene sample is pointed out. In order to describe quantitatively the degradation level of the material an adequate parameter based on chemiluminescence is also proposed.

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POLYAMIDE-6 : A CARBONISATION AGENT FOR FIRE RETARDANT INTUMESCENT FORMULATIONS OF POLYETHYLENICS.

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In recent years, there was much interest in the development of alloys based on engineering polymers such as polyamides. For example, blends of polyamides with polyolefins offer good chemical resistance, low water sorption, mechanical properties of interest. The fire retardant properties obtained using PA-6 as carbonizing agent in polyethylenic-based alloys are of additional interest.

Table 1 : COMPOSITION OF THE MIXTURES AND FIRE RETARDANT PERFORMANCES.

PA-6 (g)	APP (g)	EVA-8 (g)	L.O.I. (%)	UL94
250	0	49.8	20	NC
216	84	0	24	NC
192.6	75	32.1	21	NC
180	90	30	29	V0
128.4	150	21.4	56	V0

Glossary : L.O.I. (minimum oxygen concentration to support candle-like combustion of plastics); UL94 (qualitative classification of the samples : V0, V1, V2 and not classed NC labelled samples).

This laboratory develops several fire retardant polyamide-based formulations in association with polypropylene or ethylene propylene rubber. More particularly, it formulates a mixture of polyamide-6 as carbonization agent, ethylene-vinyl acetate (8%) copolymer (EVA-8) as synergistic agent and ammonium polyphosphate (APP) as carbonization catalyst (table 1) [1].

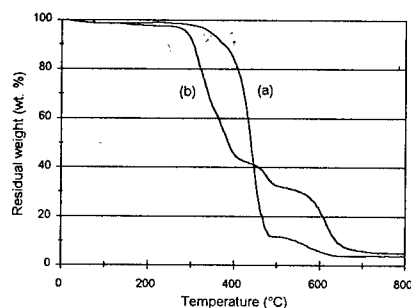


Figure 1 : TG CURVES OF THE PA-6/EVA-8 (CURVE A) AND PA-6/EVA-8/APP (CURVE B) SYSTEMS UNDER AIR FLOW.

In this study, we present the thermogravimetric analyses of the PA-6/EVA-8 and PA-6/EVA-8/APP systems (figure 1). The mixture degradation begins earlier. Reaction between the polymers and APP begins at about 250°C. It leads to the formation of a carbonaceous material which is relatively stable in the 400-470°C range. This material degrades to give a residue stable in the 500-590°C range.

From the thermogravimetric curves, invariant physico-chemical parameters are given (table 2): activation energy E_{inv} and pre-exponential factor A_{inv} . These parameters are independent from the experimental conditions (heating rate) [2]. The activation energy of the mixture PA-6/EVA-8/APP is about 1,7 times smaller than the PA-6/EVA-8 one.

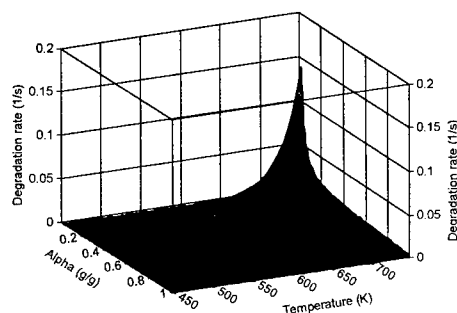
POLYAMIDE-6 : A CARBONISATION AGENT FOR FIRE RETARDANT INTUMESCENT FORMULATIONS OF POLYETHYLENICS. SIAT C. et al.

11th Bratislava Int. Conf. on Polymers (1996)

Table 2 : E_{inv} AND A_{inv} VALUES.

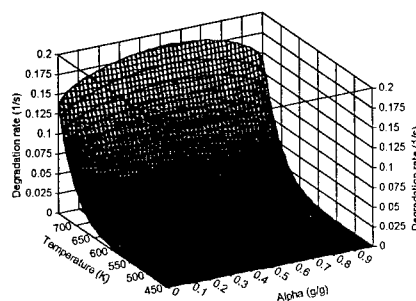
Sample	E_{inv} (kJ/mol)	$\log A_{inv}$ ($A : s^{-1}$)
PA-6/EVA-8	176	10.2
A-6/EVA-8/APP	99	6.0

Figure 2 : DEGRADATION RATE $f(\alpha, T)$ FOR THE PA-6/EVA-8 SYSTEM.



The distribution of the probabilities associated to kinetic functions is computed; it leads to predict the degradation mode of the material [3]. The kinetics models are : a diffusion model for the polymers and a phase boundary reaction for the mixture. The degradation rate $f(\alpha, T)$ is then modelised (figures 2 and 3).

Figure 3 : DEGRADATION RATE $f(\alpha, T)$ FOR THE PA-6/EVA-8 /APP SYSTEM.



The comparison between the two systems shows that the degradation rate of the fire retardant system is always higher than the rate of the blend. We may propose that the protection of the FR material results of an « ablative » process : as noted using several intumescent formulations [4], the FR property depends on an easy degradation step which allows the formation of a protective carbonaceous coating when the conversion degree and/or the temperature are low.

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INTERACTIONS BETWEEN LIGHT STABILIZERS AND FIRE RETARDANT IN POLYPROPYLENE

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Abstract :

Polypropylene samples containing decabromodiphenyl ether as fire retardant and hindered amine light stabilizers were exposed to artificial weathering in accelerated photoageing conditions. The IR analysis of irradiated samples showed that no stabilizing effect were obtained in the presence of decabromodiphenyl ether.

In order to explain the antagonism between the used HALS and the fire retardant, a complete study of the influence of decabromodiphenyl ether on the photooxydation of polypropylene has been first carried out. Because the samples contained important concentration of fire retardant, the photochemical reactor obtained appeared rather complex and had to be fully characterized, in order to understand the kinetic aspect of the evolutions. Different aspects due to the fire retardant were observed : inner filter effect competing with the initiation of the oxidation by the radicalar species obtained by irradiation of decabromodiphenyl ether. The combination of these two antagonistic effects was observed to be concentration dependant.

Concerning the association fire retardant/hindered amine light stabilizers, the inefficiency of the studied HALS to stabilize polypropylene was related to the degradation of the stabilizer by the radicals formed on photolysis of the fire retardant.

P-37

**POLYIMIDE - POLYSILOXANE COPOLYMERS WITH ENHANCED
THERMO-OXIDATIVE STABILITY**

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Polyimide - polysiloxane copolymers show the majority of the properties of polyimides, and in addition to that, e. g. enhanced solubility, reduced moisture sorption and higher toughness and impact resistance.

On the other hand, the thermo-oxidative stability of this type of copolymers is reduced in comparison with polyimides. In our laboratory we have intensively studied the reasons of this drop.

In this contribution the results regarding the thermo-oxidative stability of the polyimide - polysiloxane copolymers differing in the character of polysiloxane moieties will be summarized.

THERMO-OXIDATIVE STABILITY OF POLYIMIDES WITH CONTROLLED MOLECULAR WEIGHT

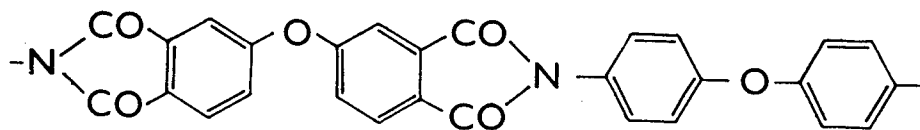
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The properties of polymers are governed by their chemical composition, morphology and molecular weight.

In this work we focus attention on the molecular weight - thermal properties relationship of the polyimides based on oxydiphthalic anhydride and 4,4'-diaminodiphenylether



ranging in the theoretical molecular weight M_n from 5000 to 20000 g/mol.

Dependences of the weight loss, activation energy of the thermo-oxidative degradation and glass transition temperature on the molecular weight will be presented.

THERMO-OXIDATIVE STABILITY OF POLYIMIDE- SILICA HYBRID MATERIALS VIA A SOL-GEL PROCESS

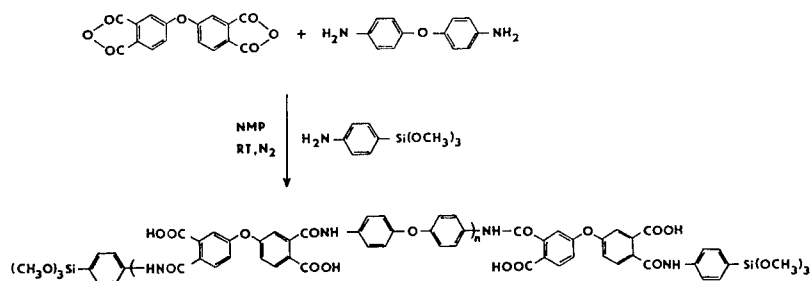
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Polyimides show an excellent thermo-oxidative stability (long-term applications at 250 - 300 °C) in comparison with common organic materials. Nevertheless, some anorganic materials are much more resistant to this attack. Therefore a combination of polyimides and anorganic materials should bring an improvement of the thermo-oxidative stability of resulting products.

Classical filling of polyimides and a preparation of polyimide composites lead to heterogeneous materials. The sol-gel method should provide a highly homogeneous polyimide-silica hybrid material.

In this work we focus attention on characterization of the thermo-oxidative stability of polyimide - silica hybrid materials with covalently bound phases based on p-aminophenyltrimethoxysilane terminated polyamic acids



The controlled molecular weight of polyamic acids employed governs the concentration of covalent bonds.

Dependences of the thermo-oxidative stability on the silica content will be presented.

Acknowledgement

This work was financed by the Grant 143156109 of the Institute of Chemical Technology, Prague.

HYPHENATED CHROMATOGRAPHIC TECHNIQUES FOR THE IDENTIFICATION AND QUANTIFICATION OF ADDITIVES EXTRACTED FROM POLYMERIC MATERIALS

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Polymeric materials are commonly formulated with an extensive additive package, which may contain primary and secondary antioxidants, UV-absorbers, processing aids, flame retardants, antistatic, cross-linking and slip agents, optical brighteners, blowing compounds, colorants etc. The paramount importance of the additive package in polymeric materials, often in conjunction with fillers, lies in the fact that it actually upgrades polymers to products with designed properties. On the other hand, the cost of the additives influences the price of commodity polymers to such an extent that minimising the additive dose has become essential. Identification and subsequent quantification of complete additive packages is a challenge for analytical laboratories. Apart from the direct quantification of well known additives also unknown mixtures, complaint samples and discoloured or aged materials are to be analyzed. The latter, here referred to as unknown samples, require a specially designed procedure in order to identify all components. A comprehensive overview of the literature on additive analysis is given by Freitag of Ciba Geigy.⁽¹⁾ Other reviews have been published by Crompton⁽²⁾ and by Hummel *et al.*⁽³⁾ Most papers on additive analysis deal with a specific subject or analytical technique. An additive analysis procedure for samples of unknown composition must take into account that: (1) the additives are imbedded in a polymer matrix, (2) suitable extraction procedures are to be used, (3) the number of components to be analyzed is unknown, (4) the amount of each component is unknown, (5) complex mixtures of additives may contain unknown reaction products (especially in aged polymer samples), (6) additives are present in a wide range of concentrations (10 ppm - 5 %)

The above mentioned problems can only be dealt with efficiently by screening techniques that combine powerful separation with equally powerful identification properties. In this paper emphasis is laid on HPLC-Photo Diode Array, GC-MS, and GC-AED as the hyphenated techniques in use for additive analysis in an industrial environment. To meet the current efficiency demands the analyses are designed in such a way that identification and quantification are performed in a single analytical experiment.

HPLC-PDA

In this paper a screening HPLC method was developed on the basis of gradient elution starting with 60 v,v% acetonitrile (MeCN) and 40 v,v% water. The final eluent of the gradient was 100% MeCN. Irganox 1063 is chosen as an internal standard since it is not encountered in commercial polymers, it elutes from the column where no other additive elutes and has good UV absorbency. A PDA detector is used for recording one UV spectrum

per second during the experiment. Chromatograms are integrated at a wavelength of 220 nm since all additives have fair UV-absorption at the given wavelength. Prior to quantification it is imperative to check if the peaks describe a single pure component or a mixture. This is verified by the software package by comparing UV spectra on the top and on the slopes of the peaks. After reassuring peak purity, verification of the type of additive is primarily performed on the basis of the retention time relative to the internal standard Irganox 1063. As this is not always sufficient for unambiguous verification of the additive type comparison of the UV spectra of the peaks with a spectral library is introduced. The spectrum comparison is performed by the software on the basis of vector representation of the spectra. Differences between the spectra are quantified in a so called *match angle*. Quantification of the additives is performed utilizing calibration factors relative to the internal standard Irganox 1063.

GC-MS

We have also developed a screening GC method in order to achieve a good separation between frequently encountered additives in polymer materials. The HT-GC method was designed for two objectives: (1) ability to verify the type of additive as a stand alone technique without the aid of identifying detectors, (2) suitability to serve as the GC-method in GC-MS analysis. Verification of the additive type is performed on the basis of a retention time relative to an internal standard (Tricaprine). Quantification of components is performed utilizing calibration factors relative to the internal standard. Method development for GC-MS was focused on two aims: (1) recording proper MS spectra of additives separated by the HT-GC method, (2) verification of the type of additive using reference MS spectra from a home made additive MS spectral library. From the spectra it becomes clear that all the additives that elute into the FID (Flame Ionisation Detector) in the HT-GC method, also elute past the GC-MS interface into the MS. The mass spectra are very specific. The molecular ion is present in the spectra for most additives in this investigation.

GC-AED

Recent literature publications have urged evaluation of additive analysis utilizing GC with Atomic Emission Detection (AED) as an element specific detection. A series of frequently encountered additives has been separated by GC and detected by AED. The results are promising since element specific information can be obtained from additives, which is of great help in identifying additives in unknown samples. However the signal-to-noise ratio of AED for the detection of additives on the basis of element, S, Cl, P or N detection is much lower as compared with the standard means of detection FID and should be improved. From this evaluation it becomes clear that GC-AED is not yet a routine tool for additive analysis in our laboratory but may be used for specific problems in combination with mass spectrometry.

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CHEMILUMINESCENCE STUDIES ON THE THERMOOXIDATIVE STABILITY OF POLY(1,4-PHENYLPHENYLENE VINYLENE)

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Introduction

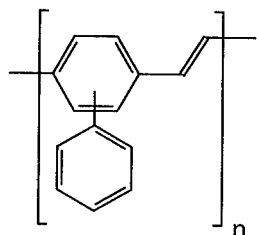


Fig. 1 P-PPV

Poly(1,4-phenylphenylene vinylene), P-PPV, is a conjugated polymer (Fig. 1). It is among a group of oligomers and polymers that currently are under thorough investigation in terms of their applicability as optoelectronic devices [1-2]. So far, the major obstacle to its use lies in lacking stability. Its electroluminescence efficiency ceases already after hours of use to remain then at this low value. The reasons are to be determined in order to either define more suited preparation conditions or to find improved alternative systems.

The hypothesis followed in this work is that trace oxidation of the polymer might reduce the conjugation length and hence cause the observed deterioration of electroluminescence properties. As established analysis techniques, such as IR and NMR spectra and TG-MS measurements, only were able to reveal thermooxidative changes after severe heating, the chemiluminescence technique was chosen which for other polymer systems already proved its sensibility for oxidation processes.

Results and Discussion

The P-PPV, as received from A.Greiner, Marburg, was synthesized in a palladium catalyzed arylation of ethylene with 2,5-dibromo biphenyl (Heck reaction) [3-5]. The fusible, soluble polymer was spincoated (film thicknesses 3-50 μm) and then heated in the temperature range from room temperature to 140°C ($T_g=145^\circ\text{C}$) while the chemiluminescence emission was recorded, both as total intensity and in spectral resolution.

Heating spincoated P-PPV films (Fig.2) for the first time in air results in a chemiluminescence intensity vs. time curve which shows a sharp peak during heating up ($\sim 80^\circ\text{C}$). It ceases while temperature rises further and it is followed by a plateau value in intensity, which is a function of the height of the final temperature level reached. For subsequent heating/cooling cycles only the plateau intensity is repeated, but the heating-up peak no longer occurs.

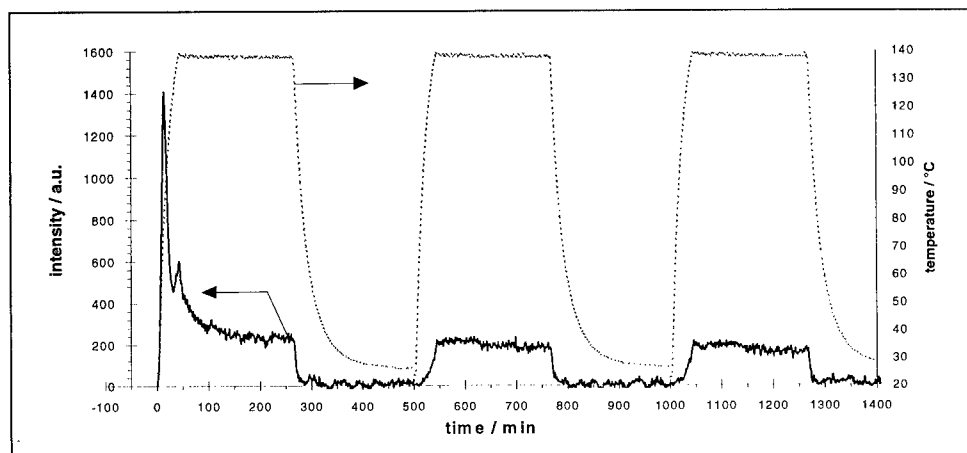


Fig. 2 CL-curve for three heating/cooling cycles of a P-PPV film in air

Conclusions

The observed thermooxidative behavior is different from olefinic polymers which only contain unsaturations at low levels. The lack of induction time and the sharp peak during heating up (which does not occur for a nitrogen conditioned sample) indicate that P-PPV is being readily oxidized. The P-PPV chemiluminescence seems to be governed by two separate mechanisms with different activation energies, the first of which being responsible for the transient peak during initial heating while the second produces the slowly declining plateau. Spectral resolution suggests that the emitting chromophore most likely is the same for both cases.

Taking into consideration that temperatures measured in an actual electroluminescent device can reach up to 100°C, it is assumed that the mechanism associated with the transient peak is responsible for the observed degradation of electroluminescent properties of the material.

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THERMAL OXIDATION OF EPDM/IIR SYSTEMS

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INTRODUCTION

Blends of ethylene - propylene terpolymer with buthyl rubber can be used for manufacturing electrical insulation. Studies on stability of these polymeric systems^{1,2} point out that presence of IIR enhances the oxidation strength.

EXPERIMENTAL

Ethylene-propylene terpolymer was provided by ARPECHIM Pitesti (Romania). It contains 29 % propylene and 3.5 % ethylidene norbornene. Buthyl rubber (BK - 2045, Rusia) presents a unsaturation level of 2 %. These materials were used in unpurified state, because the main purpose of this work consists of simulation of industrial conditions in polymer processing.

Temperature range for oxidation tests was chosen between 150°C and 190°C.

Stability evaluation of rubber materials was performed on thin films obtained by solvent (CHCl₃) removal from 1 % solutions. Infra red spectroscopy was used for measurement of chemical changes occurred in oxidized samples. Records cover spectral range from 4000 cm⁻¹ to 600 cm⁻¹. Characterization of oxygenated group (carbonyl/carboxyl) production is accompanied by gel fraction tests and calculation of unsaturation level.

DISCUSSION

The most important change in infra red spectra of thermally aged elastomers can be found in the band at 1720 cm⁻¹, which describes C=O accumulation. Kinetic parameters, for exemple induction time (table 1), were determined. It can be noted the longer induction time for 1:1 mixture of the two elastomers in comparison with similar parameter of the components.

Table 1. Changes in oxidation induction time

Elastomer	Induction period (min)		
	150 °C	175°C	190°C
IIR	155	50	25
EPDM	220	65	40
IIR/EPDM	325	82	60

Unsaturation level represents an useful characteristic for stability evaluation of any polymer. In the case of studied materials, unsaturation changes in different manner (table 2). It increase in large extent for EPDM. Equimolar blend of ethylene-propylene-diene terpolymer and buthyl rubber shows moderate increase of unsaturation, while IIR presents decreasing process of unsaturated unit content. This fact can be assigned to reactions of active centers which promote crosslinkage.

Table 2. Changes in unsaturation level

Elastomer	20°C	Unsaturation level (%)		
		150°C	175°C	190°C
IIR	2.0	1.4	1.2	0.9
EPDM	3.5	5.0	8.0	12.0
IIR/EPDM	-	3.8	5.3	7.8

Table 3 presents changes in gel content for individual and blended polymers. Gel fraction increase when temperature increases. EP elastomer can thermally crosslinked in a larger extent than buthyl rubber. In can be explained by higher probability of double bonds (initially contained or thermally formed) to be splitted and to generate randomly new bridges between macromolecules.

Table 3. Changes in gel content

Elastomer	20°C	Gel content (%)		
		150°C	175°C	190°C
IIR	1	1.4	5	4
EPDM	2	7.0	20	42
IIR/EPDM	-	3.0	12	28

Thermal oxidation of studied materials takes place on different ways. Ethylene-propylene terpolymer is oxidized, but it is also crosslinked; buthyl rubber forms exclusively oxygenated products by reaction of macromolecular radicals. Activation energy calculated for oxidation process keeps close values for tested systems (97 kJ/mol for IIR, 98 kJ/mol for EPDM and 102 kJ/mol for 1:1 blend)

CONCLUSION

Polymeric mixture of EPDM and IIR can be used for manufacture of new products with high chemical stability, if technological procedure is able to convert unsaturation structure of the blend into a stable configuration of macromolecular network.

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RADIOCHEMICAL PROCESSING OF EPDM/IIR BLENDS

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Gamma irradiation of EPDM/IIR blends was performed in order to obtain a new material with improved strength to the damage action of various factors (heat and ionizing radiations). Mixing ratio of EPDM and IIR covers the whole range of concentrations (0 %, 25 %, 50 %, 75 % and 100 %). Polymeric samples were irradiated in air inside a machinery provided with ⁶⁰Co source. Dose rate was 0.54 kGy/h. The gel content of these mixtures was evaluated by boiling polymeric samples in o-xylene for 24 h. Changes in the amount of insoluble fraction emphasise the highest rate of crosslinking process for terpolymer free of buthyl rubber; the presence of IIR hinders the increase of gel content over the first 0.20 MGy (figure 1). When absorbed dose exceeds 0.20 MGy, samples containing 100 % EPDM begin to be degraded, but 25 % of IIR keep constant the level of gel content. Increase of rubber content slows the development of gel. It can be assumed that during the first stage of irradiation, terpolymer becomes free radical source, because it contains ethylidene-2-norbornene (3.5 %), which can be easily splitted. The enhancing quantities of IIR promote the uptake of elastomeric radicals. As the received dose increases, rubber macromolecules are splitted, providing new position for crosslinking simultaneously occurred with cleavage of double bonds contained in terpolymer.

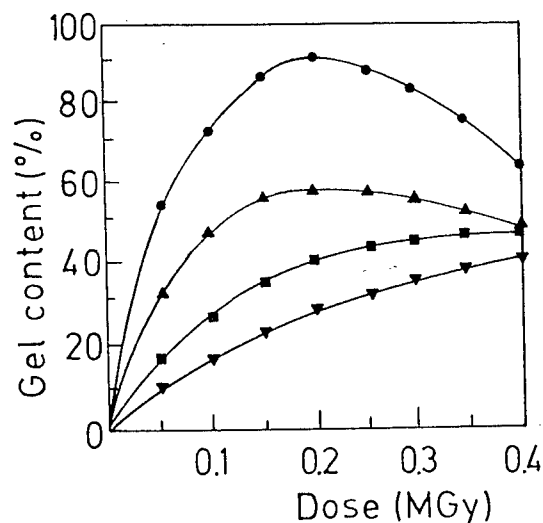


Figure 1. Dependence of gel content on dose
(●) EPDM 100 %; (▲) EPDM/IIR=3:1;
(■) EPDM/IIR=1:1; (▼) EPDM/IIR=1:3;

Thermal stability of irradiated samples was evaluated by oxygen uptake method. Measurements of consumed oxygen were carried out in isothermal and isobaric conditions by means

of equipment built up in our laboratory¹. Oxidation atmosphere was air at normal pressure. Testing temperatures were chosen between 185°C and 210°C. Some characteristic oxygen uptake dependences on time at various temperatures are presented in figures 2 a, 2b and 2c.

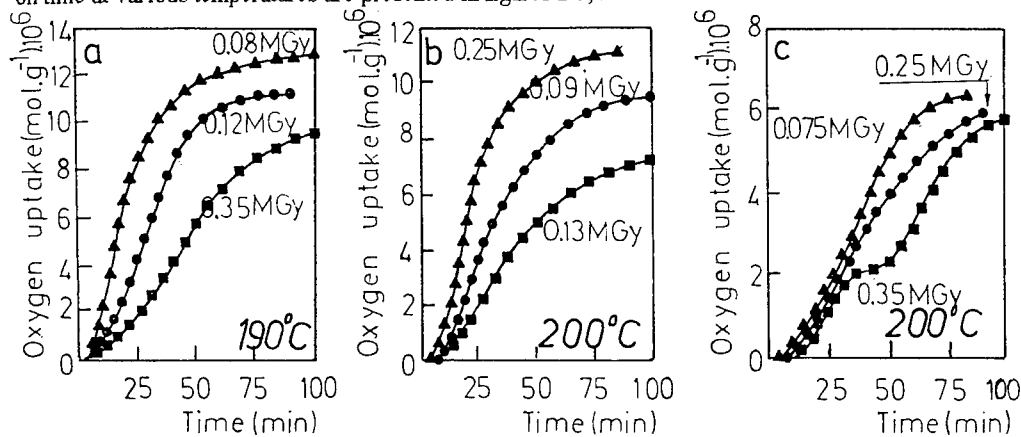


Figure 2. Time dependence of oxygen uptake for irradiated EPDM (a), IIR (b) and EPDM/IIR=1:1 (c)

Some remarks can be made concerning radiation stability of tested systems:

- * ethylene-propylene elastomer is less stable than buthyl rubber, because it contains diene which is easy splitted to form macromolecular radicals;

- * γ radiation produces free radicals which are involved in two main reactions: oxidation and cross-linkage; because EPDM belongs to the type of crosslinkable polymers, the rate of network formation exceeds molecular scission rate². By contrary, IIR is largely degraded because of molecular chain branching;

- * the greater the absorbed dose, the higher the crosslinking rate up to a dose of about 0.15 MGy;

- * for low doses, buthyl rubber is also crosslinked, but its network is damaged when irradiation dose exceeds 0.07 MGy.

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EVALUATION OF IRRADIATION EFFECTS IN ETHYLENE- PROPYLENE ELASTOMERS IN SALT SOLUTIONS

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Radiation stability of ethylene-propylene copolymers can be evaluated by means of various methods, for example, by infra red spectroscopy. This irradiation environment was chosen to check the degradation effect of salt presence on electrical insulation material like EP elastomers.

EXPERIMENTAL

Tested polymers (EPDM and EPR) were provided by ARPECHIM Pitesti (Romania). Propylene amount of these elastomers were unlike. Terpolymer contained 29 % propylene and 3.5 % ethylidene norbornene as added diene; copolymer contained 48 % propylene. This large difference in propylene fraction was selected to emphasize the effect of molecular structure on the oxidation rate.

Concentration range of NaCl (spectral grade) is wide. Four aqueous solutions were prepared in three distilled water, whose concentrations were 0.1 %, 1.0 % and 10 %. Irradiation in distilled water was also carried out to provide reference data.

Elastomer samples were obtained by solvent removal from CHCl_3 solutions. Polymers were not previously purified because it was desired to study these materials in manufacturing conditions.

Irradiation was performed by exposure of polymer samples to a ^{60}Co source at dose rate of 0.34 kGy/h.

Infra red spectra were recorded after fast drying performed on the end of each irradiation step over the whole IR range, divided into two regions: 4000-2000 cm^{-1} and 2000-400 cm^{-1} .

DISCUSSION

Previous studies^{1,2} concerning thermal and radiochemical stability evaluated by IR spectroscopy and oxygen uptake method, respectively, proved that advanced degradation can be easily obtained in solutions of NaCl. In the case of γ radiolysis of salt solutions, chlorine atoms are formed by electron ejection as the primary effect of interaction of γ radiation with chloride ions. They are involved in oxidative polymer degradation by electrical charge transfer from radiolytic $\text{HO}^\cdot$ or by hydrogen atom abstract from hydrocarbon chain. These processes can initiate other reactions which yield free radicals. Moreover, radiolysis products ($\text{H}_3\text{O}^+_{\text{aq}}$, $\text{HO}^\cdot$, e^-_{aq} , H_2O_2 , H_2) overlap their effects of the damage action of chloride ions³.

Table presents oxygenated product concentrations measured by IR spectroscopy at various irradiation doses. It can be noted that C-OH unit is formed at greater rate for advanced doses, exceeding 70 kGy. The same behaviour is met in the case of C=O generation for doses greater than 0.04 kGy (solutions 1 % and 10 %). It can be pointed out that lower concentration of NaCl shows faster degradation action on ethylene-propylene elastomer (EPDM). In spite of greater concentration of propylene in EPR, radiation stability of copolymer is pronounced. It begins to be oxidized after receiving of 0.1 MGy. Thus, the presence of double bonds in terpolymer has worthen effect on stability than tertiary and quaternary carbons.

This behaviour has not happen during irradiation in air. It means that chloride ions contained in aqueous solutions are more reactive than diffused oxygen.

Table Development of oxygenated groups during irradiation of EPDM in salt solutions

Dose (kGy)	Organic function	Concentration of organic function, c (mol.g ⁻¹) .10 ⁶			
		Salt concentration (%)			
		0	0.1	1.0	10
4	C=O	3.3	3.4	1.7	2.2
7	C=O	4.8	4.4	4.3	5.8
10.5	C=O	6.7	4.9	7.8	7.7
4	C-OH	4.9	4.0	7.6	5.2
7	C-OH	10.4	8.5	10.4	7.1
10.5	C-OH	14.6	9.8	15.6	15.0

In order to understand the degradation mechanism of ethylene-propylene-diene terpolymer irradiated in salt solutions, band at 1720 cm⁻¹ was recorded in detail. It shows different rate formation for carbonyl and carboxyl products. This fact emphasizes that attack of chloride atoms takes preferentially place on weaker bonds, followed by specific reactions of free radicals.

Gel content measurement proved that advanced γ irradiation of thicker terpolymer pieces in NaCl solution promotes in a large extent (more than 80 %) crosslinkage of material.

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STUDY OF AUTOSYNERGISM PHENOMENON IN STABILISATION OF POLYPROPYLENE AGAINST THERMAL OXIDATIVE DEGRADATION

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Some of antioxidants with two different functional groups in a single molecule in comparison with antioxidants of similar structure containing only one type of functional group show special stabilisation effect due to autosynergism phenomenon. This has been studied by comparing the stabilisation effects of phenolic arylphosphites [4,5,6] with a sterically hindered phenol [7] and an arylphosphite [8] in thermal oxidative degradation of polypropylene. The comparison is, also, made between the stabilisation effects of hydroquinone [1] and two alkylated hydroquinones [2,3] on the basis of their molecular weight and symmetry.

The results show when the two functional groups are present in a single molecule the stabilisation ability of the related compound increases greatly. This shows the autosynergistic behaviour of the two groups in a molecule which converts peroxy radicals to hydroperoxide and decomposes hydroperoxides into non-radical products.

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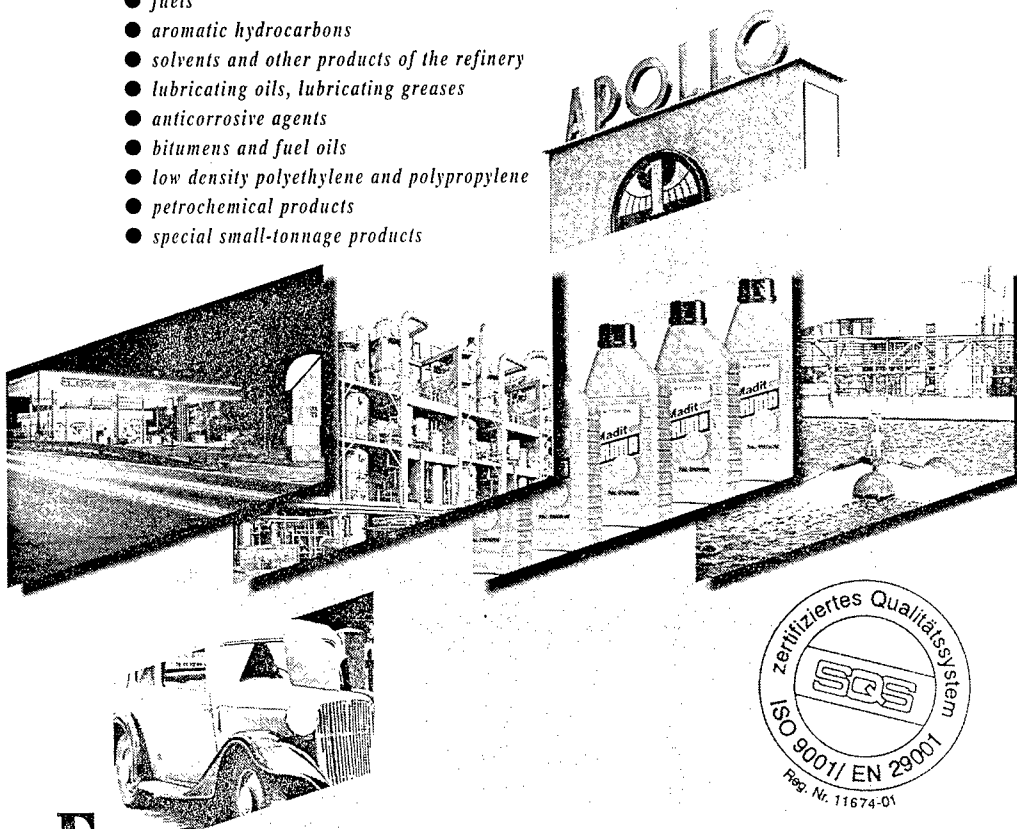
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