DEGRADATION EFFECTS IN POLYMERS

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Abstract. The extremely long molecular chains of polymers can be broken easily by the absorption of a quantum of energy above the energy of the covalent bond of the main carbon chain, which typically is in the range of 5 – 10 eV. The energy of beta and gamma photons of 1 to 10 MeV surpasses by many orders of magnitude this minimum value, representing a high risk of degradation to all kind of polymers, naturals and synthetics alike.

The protection of polymers against high doses (20 – 1000 kGy) requires efficient additives preventing and/or stopping chain reaction type oxidative degradation. Primary and secondary antioxidants work well here in synergy. Commercial raw materials are available for radiation-sterilizable medical devices made out of polyolefins and other thermoplastics. Similarly, polymer compounds of suitable formulae are offered commercially for high-dose applications of polymers in nuclear installations.

The controlled degradation of polymers of large molecular mass – or even of cross-linked molecular structures – is a promising field of radiation application.

One area here is related to recycling non-accessible polymers such as fluorinated plastics of cross-linked rubber products. Another large possible area is the controlled radiation degradation of natural polymer systems. Radiation may facilitate the access to cross-linked natural polymer systems, such as wood, plant cellulose and biomass in general, decreasing to use of aggressive chemicals. The result is energetically favorable, environmentally friendly new procedures and raw materials of natural origin.

A limited dose applied to polymers – although may cause some degradation – however may initiate new bonds on the "wounded" chain. The popular graft-copolymerization technique can be applied in new, up-coming polymer processing technologies such as alloying, composite processing and reconstitutive recycling. By this way, even those polymers described earlier as radiation-degrading types, can be cross-linked by radiation in the presence of reactive additives

Introduction

Polymers, as giant organic molecules with their sophisticated structure represent one of the most organized type of materials, leading up to the functions of life. No wonder if these macromolecules are sensitive against excessive energy transfer. The extremely long molecular chains can be broken easily receiving a quantum of energy above a certain level, causing degradation in structure and properties. The minimum energy required to open the covalent bond of the main carbon chain is in the range of 5 – 10 eV. Consequently the energy of beta and gamma photons of 1 to 10 MeV surpasses by many orders of magnitude this minimum value, representing a high risk of degradation to all kind of polymers, naturals and synthetics alike. In spite of the big difference in energetic level, the degradation caused by ionizing radiation, or UV light, and other lower energies of radiation – is not differing in basic principles.

The degradation effects of ionizing radiation on polymers can be classified from the point of view of the targeted practical applications:

1. – Degradation against which the polymer product should be protected.
    - Assuring radiation tolerance of radiation sterilized polymer devices,
    - Providing stability for polymers in nuclear installations,

2. – Degradation targeting a controlled way of significant decrease in molecular mass
    - Diminishing mol. mass of natural polymers, e.g. cellulose, natural rubber, chitosan, etc.
    - Reuse of (cross-linked) polymers after degradative recycling,

3. – Limited degradation of polymers for creating active, initiation centers fur further modification and/or compatibilization, such as
    - Cross-linking,
    - Grafting,
    - Composite processing,
    - Alloying,
    - Reconstituting – recycling: ‘up-cycling’.

Behind all those degradation effects there are very complex phenomena described in detail in the last four decades [1–4].

Considering the sequences of physical and chemical events, at the beginning an extremely rapid energy deposition occurs in the first 10 x e^{-18} to 10 x e^{-12} s time interval. The chemical processes follow in the next milliseconds (10 x e^{-3} to 1 s). Some „transitional" degradation products however are much more stable in polymers. The frozen-in free radicals are long living enough (10 x e^{3} to 10 x e^{9} s, or more: up to years!) to use them for later practical applications [5, 6].

Protecting Polymers against Undesired Radiation — Degradation

There are broad industrial application fields of plastics where radiation protection of the polymer is a basic requirement. The radiation-sterilization of single-use, disposable medical devices, applies typically a gamma or EB dose of 25 kGy. This dose is high enough to produce substantial damages in the unprotected polyolefins, used as e.g. PP syringes. The task here is not only to protect the given thermoplastics during the radiation, but also to assure a relatively long storability, 3-5 years of shelf life for the sterilized disposable product without any significant degradation [7].

Even more difficult task is to protect the polymeric structural materials in nuclear installations, such as electrical cables or decontaminable flooring in a nuclear power station or industrial gamma irradiator. The required dose-tolerance here can be as high as 1 MGy and a risk-increasing factor is here the low dose rate, sensitizing even the cross-linked polymers against radiation degradation. The warranted life time span here is typically 30 years, and safety aspects are extremely important.

The protection of the polymers against low doses occurring in the food irradiation may seem as a simpler task. The packaging films of irradiated food should tolerate much less dose, in the range of 1 kGy or less, but the extract-free stability of those materials in food-contact is even more important than the possible mechanical consequences of radiation degradation.

The practical solution of these protection tasks are connected to specific chemical agents, well engineered polymer additives, elaborated mainly for the stabilization of general purpose polymers [8]. The radiation stabilizers, called "antirads" represent only a modest, but flourishing fraction of that thermo-oxidative- and UV stabilizers.

The reason behind the parallel technical development of conventional and radiation stabilizers is related to the fact, that the UV degradation and thermo-oxidative degradation as well as radiation degradation of polymers are all similar *chain reactions*. As such, these processes consist of several steps of: chain initiation, chain propagation, chain branching and chain termination. The scheme according to which these reactions proceed on a H containing polymer chain P is seen in Fig.1.

In spite of the differences in fine details the task is similar in all the three main (thermo oxidative- UV- and radiation) degradation processes, namely to control and/or diminish the danger of deterioration of properties either by

- Preventing chain *initiation*, and/or
- Stopping chain propagation.

In controlling the route of those oxidative chain reactions, there are two main types of antioxidant stabilizers:

- *Primary*, or chain-breaking antioxidants interfere with the chain propagation step. That step is the main carrier of the oxidative degradation.
- *Secondary*, or preventive antioxidants destroy hydro-peroxide groups, responsible for chain initiation and chain branching.

Chain initiation

$$PH \xrightarrow{\Delta} P^{\bullet} + H^{\bullet} \qquad (1)$$

$$PH + O_2 \xrightarrow{\Delta} P^{\bullet} + HO_2^{\bullet} \qquad (2)$$

$$\text{Catalyst residues} \xrightarrow{\Delta} \text{Free radicals} \qquad (3)$$

Chain propagation

$$P^{\bullet} + O_2 \longrightarrow PO_2^{\bullet} \qquad (4)$$

$$PO_2^{\bullet} + PH \longrightarrow POOH + P^{\bullet} \qquad (5)$$

Chain branching

$$POOH \xrightarrow{\Delta} PO^{\bullet} + {}^{\bullet}OH \qquad (6a)$$

$$POOH + PH \xrightarrow{\Delta} PO^{\bullet} + P^{\bullet} + H_2O \qquad (6b)$$

$$2\,POOH \xrightarrow{\Delta} PO^{\bullet} + PO_2^{\bullet} + H_2O \qquad (7)$$

$$PO^{\bullet} + PH \longrightarrow POH + P^{\bullet} \qquad (8)$$

$${}^{\bullet}OH + PH \longrightarrow H_2O + P^{\bullet} \qquad (9)$$

Chain termination

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow POOP + O_2 \qquad (10a)$$

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow PO^{\bullet} + PO^{\bullet} + O_2 \qquad (10b)$$

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow \text{inactive products} + O_2 \qquad (11)$$

$$P^{\bullet} + PO_2^{\bullet} \longrightarrow POOP \qquad (12)$$

$$P^{\bullet} + P^{\bullet} \longrightarrow P{-}P \qquad (13)$$

FIG. 1. Scheme of the polymer (thermo-oxidative) degradation as a chain reaction.

The chemical industry of the world is producing in our times yearly more than 200 Mtons of synthetic polymers, is requiring more than 100,000 tons (0.05% of plastics) of antioxidants for the stabilization against degradation. Two thirds of those antioxidants is going to be applied for PE and PP, just requiring the more protection against radiation as well.

Typical primary antioxidants, interfering with the chain-carrying radicals are the ortho-disubstituted phenols, alkylphenols, hydroxyphenyl propionates and hydroxybenzyl compounds, presented on Fig.2. The AO-4 compound, the pentaerythrityl-tetrakis-3,5 di-tertier-buthyl-4-hydroxyphenyl propionate is one of the most important additive (under a commercial name of *Irganox 1010,*) protecting PE and PP in radiation sterilization. It is important to note, that such stabilizers are never used alone. Secondary antioxidants represent an even greater group of sophisticated organic molecules: aromatic amines, organic sulfur compounds (typically thiobisphenols and thioethers) as well as phosfites and sterically hindered amines. These two latter type of compounds are successfully applied in the radiation-stabilization of PP [7].

It is an important fact, that there is an explicit synergistic effect observed by combining primary and secondary antioxidants. A well known example of such synergistic mixtures is the use of thiodipropionates together with sterically hindered phenols for long-term stabilization of polyolefins. Of course, the different polymers and different applications require laborious optimization of each case.

Clearly, the radiation-protection stabilizer systems should fulfill a whole series of other requirements such as chemical, physical and toxicological safety. Take for example the blood-taking and transfusion sets, made out of plasticized PVC, radiation sterilized and then stored (standing by) for years, later filled with chemically stabilized blood, and cooled and stored again. During all these procedures the protected polymeric material should be stable, should not loose its elasticity, and in the last steps there are strict limitations on traces of all chemicals extractable by the blood.

Fortunately, after long years of research and development works, at the beginning of the 21st century the biggest producers of PE, PP, PVC, PA, POM, PC, polysulfons, flouropolymers, thermoplastic elastomers etc. are almost all offering specially stabilized commercial variants of their raw materials stabilized against radiation degradation.

Controlled radiation-degradation of polymers

Another field of application is actually emerging in the polymer engineering, where the radiation-caused degradation is used in a controlled manner to degrade the undesired high molecular mass. This field may be subdivided into:

- Controlled degradation of natural polymers facilitating the next processing step, and
- Reuse of polymers after degradative recycling.

Natural polymers, serving the sustainable development are of increasing importance in the next century. In spite of the extreme rapid development in the synthetic polymers, the yearly yield of the renewable natural polymers, the biomass — is still three order of magnitude higher (hundreds of billion tons/year!) than the production of plastics worldwide (200 Mt/a).

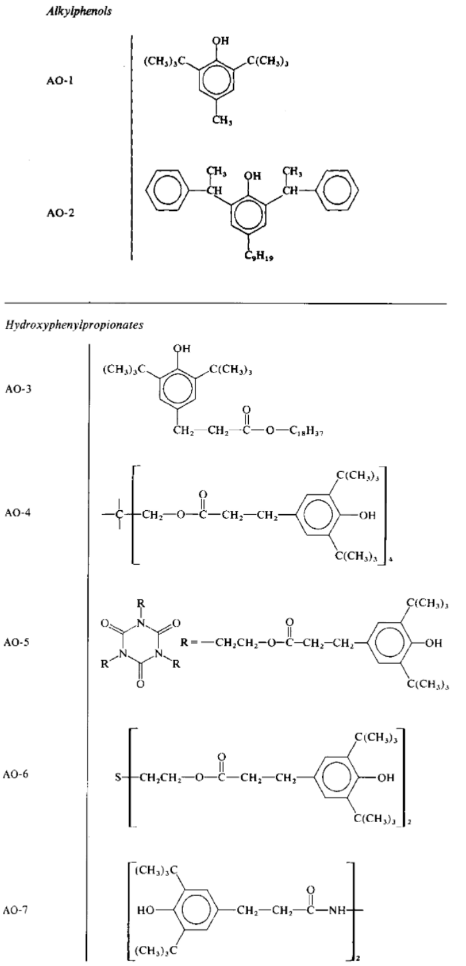
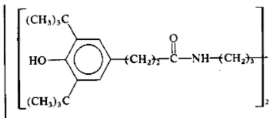


FIG. 2a. Typical primary antioxidants protecting olefin polymers

AO-8



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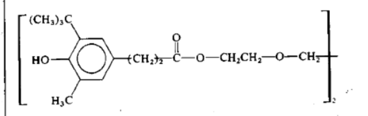

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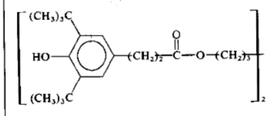

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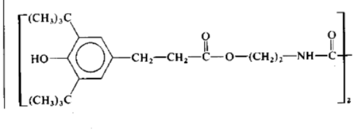


Hydroxybenzyl compounds

AO-12

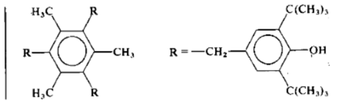


FIG. 2b. Typical primary antioxidants protecting olefin polymers (continuation).

Nature is generous. The molecular mass of most natural polymers is over 1 MDalton, and very often the structure of biopolymers is three-dimensionally cross-linked. The wood, and the similar cellulose-based biopolymers, the most abundant member of the biomass family, is even more complex. In fact, it is a double networked, composite system of cross-linked cellulose reinforcement (fibrous, crystalline, linked through strong H-bonds), embedded in another three-dimensional polymer network if lignin. That is what we call an *interpenetrating polymer network (IPN)* in the polymer material science and engineering. That is contributing to the well known stability against degradation of the wood in the hundred years old houses, in the underwater wooden pylons of Venice (several hundreds of years old), as well as in the thousand years old and still living Sequoias of California. On the other hand this causes the main difficulty in the cellulose and paper production. The IPN is very difficult to open, that is why the pulp and paper industry (bigger than the plastics industry itself) consumes so much aggressive chemicals, resulting in enormous environmental pollution.

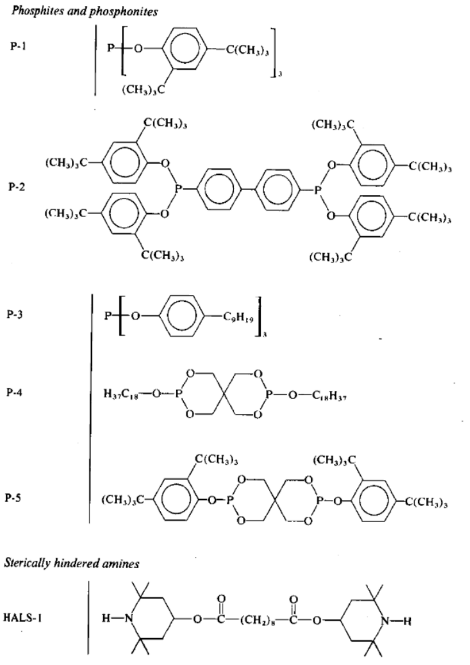


FIG.3. Secondary antioxidants.

Controlled radiation degradation renders the IPN ligno-cellulose composite more easy to open in a subsequent acid hydrolysis in the next processing step, up to form mono- and oligosaccharides [9]. This effect could bring about significant improvements in the cellulose and paper industry [10]. On the other side this radiation degradation could make sawdust or any other agricultural waste of biomass digestible, good enough for animal feed [11]. There is a whole new trend to degrade by radiation different natural polymers, typically byproducts of the food industry, from the empty fruit bunch of the coconut, up to the final waste of the fish processing. The radiation-facilitated accessibility is opening new ways of producing intermediary products for foods, cosmetics or even medicine, see Fig. 4 [9].

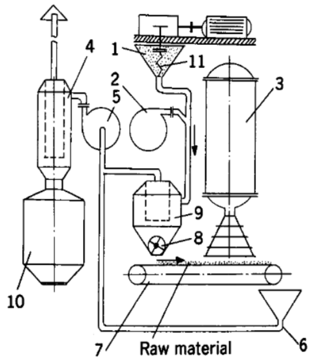


FIG. 4. Irradiation facility to convert cellulose wastes to animal feed [9].
1- hopper-meter; 2, 5 - ventilators; 3 - electron accelerator; 4, 9 - cyclones;
6 - pneumatic transport; 7 - conveyor; 8 - metering device; 10 - product hopper; 11- screw

Another big field of potential application is the controlled radiation degradation in reprocessing and recycling of polymers. Radiation-induced degradation is applied to convert poly-tetrafluoroethylene (PTFE) scrap into useful, recycled products [9]. Teflon waste is formed during the special processing technologies of this corrosion- and heat resistant polymer. The highly crystalline PTFE cannot be extruded or injection molded as other thermoplastics. High pressure pre-forming is applied on the powder, which is sintered afterwards, similarly to the powder-metallurgy of metals. In the final step of PTFE processing often shaving, milling or drilling is applied, producing a significant amount of scrap. The radiation dose required to degrade such PTFE scraps is relatively high, more than 500 kGy. The G-value of degradation is growing with the increasing temperature: $G = 0.3$, 0.9 and 2.1 scissions/100 eV at 100, 300, and 500 °C, respectively. The perflourohydrocarbons produced here form a range of chains of 6 to 14 Carbon atoms, and pulverized PTFE as well. The powdered Teflon polymer has additional functional groups that are not present in the original PTFE, e.g. carboxylic acid groups, if irradiation is carried out in the presence of oxygen or air. The PTFE powder is blended with other materials for use as lubricant, other fluorinated products are employed as surfactants.

The degradative radiation-recycling of PTFE led to a successful pilot-scale plant producing 12 tons/year recycled powder at Sumitomo, Japan [9]. For similar polymer-degrading industrial developments several other candidates are very promising. Among other synthetic polymer products, discarded automobile tires represent a major environmental concern, in an amount close to 10 Mtons/a. A promising method is mentioned in the literature [9] in which the vulcanized rubber product is crushed at low temperature, irradiated at a dose rate of 100 kGy, and milled repeatedly, if necessary. The reclaimed "de-crosslinked" material can be added to an extent 10 – 15% to various new rubber blends.

Radiation degradation may help in solving the biodegradability of the plastic wastes as well, but in that field even the first exploratory works are missing, probably because of the involved cost and required time [12, 13].

Reactive compatibilization through (limited) radiation of polymers

Degradation or build-up (cross-linking) processes as effects of radiation are not excluding each other. Classifying polymers according their behavior under radiation into *degrading* type and *cross-linking* type — may be considered rather an oversimplification today. A limited degradation may be combined with advantageous build-up processes of the polymer structure, such as blending, alloying, grafting, composite processing and new type of composite processing routes, developed from those earlier processes.

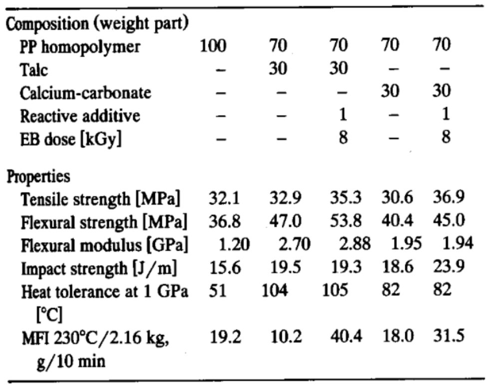
Degradation and cross-linking are not exclusive alternatives. This is shown in an extremely interesting recent study of a large Japanese research team in Takasaki [14]. PTFE, known since long as degrading type of polymer under radiation effect, has been cross-linked and grafted at a relatively low dose rate of 3 kGy/h. Radiation cross-linking of PTFE occurs in molten state at 340 °C, just above the melting temperature of Teflon, under Argon pressure of 0.5 Torr, with a dose ranging 60–320 kGy. In a second step of irradiation a graft-copolymerization process may be initiated to modify the reactivity of Teflon by polystyrene side-chains. The copolymer membranes have been chloro-sulfonated thereafter, to make proton-exchange membranes for fuel cell [14]. The procedure may be considered as a successful realization of an earlier attempt [15].

In fact, the numerous literature sources (a full library! see e.g. Refs 2, 9) on radiation grafting is related to the question of limited radiation degradation, followed by a reconstitutive polymerization. A separate lecture is devoted also here, at the present Consultants Meeting to that specific question [16].

The concept is very clear: it may be justified to make moderate radiation degradation onto the targeted polymer, if on the resulting initiation site we start a new polymerization by this. Radiation offers a productive way of forming polymer bridges to bond together very different polymeric and non polymeric element of an engineering structure. That is all similar to the original meaning of *grafting* in the gardening (agriculture) or in the medicine (transplantation). We make a *wound* (on the body, on the plant), than we *heal* it by inserting something healthy, proliferating, growing stuff, to achieve a higher, better quality.

A parallel lecture treats all these processes from the point of view of compatibilization [16]. Here we cite some of our earlier results using recycled wood waste, talc and calcium carbonate to bond together all these components by a modest dose of radiation, in presence of a limited amount of reactive additive [17].

TABLE I. EB-PROCESSED MINERAL REINFORCED POLYMER COMPOSITES



Composition (weight part)					
PP homopolymer	100	70	70	70	70
Talc	–	30	30	–	–
Calcium-carbonate	–	–	–	30	30
Reactive additive	–	–	1	–	1
EB dose [kGy]	–	–	8	–	8
Properties					
Tensile strength [MPa]	32.1	32.9	35.3	30.6	36.9
Flexural strength [MPa]	36.8	47.0	53.8	40.4	45.0
Flexural modulus [GPa]	1.20	2.70	2.88	1.95	1.94
Impact strength [J/m]	15.6	19.5	19.3	18.6	23.9
Heat tolerance at 1 GPa [°C]	51	104	105	82	82
MFI 230°C/2.16 kg, g/10 min	19.2	10.2	40.4	18.0	31.5

By evaluating the WF-PP procedure from the point of view of the dose, we have to note, that even a 9 kGy (low) dose is causing a substantial degradation to the unprotected polypropylene. This is reflected in the Melt-Flow Index (MFI), changing from 2.8 to 16.8 g/600s at 230 °C and 2.16 kp load. Consequently, all the improvements in mechanical properties, heat tolerance and flow capability as benefits of the procedure should be evaluated in view of the degradation-causing initiation. This process begins with a slight degradation, followed by a strong improvement [18].

The radiation initiated compatibilization makes in principle all synthetic and natural polymers radiation cross-linkable, including those considered radiation-degradable in earlier studies.

Conclusions

(1) The protection of polymers against high doses (20 – 1000 kGy) requires efficient additives preventing and/or stopping *chain reaction* type oxidative degradation. Primary and secondary antioxidants work well here in synergy. Commercial raw materials are available for radiation-sterilizable medical devices made of polyolefins and other thermoplastics. Similarly, polymer compounds of suitable formulae are offered commercially for high-dose applications in nuclear installations.

(2) The controlled degradation of polymers of large molecular mass - or even of cross-linked molecular structures – is a promising field of radiation application. One area here is related to recycling non-accessible polymers as fluorinated plastics or cross-linked rubber products. Another large possible area is the controlled radiation degradation of natural polymer systems. Radiation may facilitate the access to cross-linked natural polymer systems, such as wood, plant cellulose and biomass in general, decreasing to use of aggressive chemicals. The result is energetically favorable, environmentally friendly new possible procedures and raw materials of natural origin.

(3) A limited dose applied to polymers although may cause some degradation, however afterwards, may initiate new bonds on the "wounded" chain. The popular graft-copolymerization technique can be applied in new, up-coming polymer processing technologies such as alloying, composite processing and reconstitutive recycling. By this way, even those polymers described earlier as radiation-degrading types, can be cross-linked by radiation in presence of reactive additives.

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