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Role of the polymer degradation processes in environmental pollution and waste treatment

Summary — The effect of various processes of environmental degradation of polymers (under atmospheric conditions, in water, soil, living organisms) on the pollution of the environment has been characterized. Activities concerning utilization of plastics wastes have been described. Some problems concerning the use of photo- and biodegradable polymers have been discussed. The results of author's research works on the course of degradation of polyolefins (PE, *i*-PP) or epoxy resin (ER) with addition of various amounts of lignin modified with epoxy groups are presented as well as the effect of such blends on the plants growth. Except the positive influence on vegetative mass also significant detrimental effects occurring during blossom period have been observed.

Key words: environmental degradation, environment pollution, biodegradation, polyolefins, epoxy resin, plants growth.

GENERAL INFORMATION

Polymer degradation as a factor of environment pollution

All materials of organic origin including natural polymers show an inherent tendency to degradation. For many decades this property has been regarded as a major disadvantage, especially when the materials were used for long-life products. The efforts were developing materials characterized with nearly infinite durability or at least improved durability in comparison with the existing materials. Traditionally, the synthetic polymers have been designed to be environmentally resistant, so most of them were inert or undergoing bio-, photo- or environmental degradation very slowly. Now the industry produces daily many tons of indestructible packings and other short-term use products, which influence negatively on the environment.

Scientists started searching for compromising solutions to reduce the durability of the products to a controlled duration. Generally, the natural polymers are very efficient from ecological point of view. Consequently, the role of the natural polymers was re-assigned when they are modified or used in mixture with synthetic polymers. In such mixtures the synthetic polymer retards microbiological attack due to the hydrophobic nature, while the biodegradable component shows accelerating effect.

As a rule, the environment causes *via* various degrading agents (light, mainly UV light, heat, water, ultrasounds, high energy radiations, oxygen, chemicals, enzymes, very high or very low temperatures) the deterioration/degradation (or aging), decomposition and disintegration (or even mineralization) of materials, so they become wastes polluting the environment. Various kinds of environmental effects surround us, so environmental deterioration may be slow or rapid but always occurs, its type depends on the prevalent factor or degrading agent (photochemical, thermal, chemical, hydrolysis, oxidation, biodegradation). In the materials' ageing, several factors are coupled and their combination may create more serious damage of a material than each one separately. Degradation of polymers participates in a continuously rising pollution of the environment (soil, water or atmosphere), depletion of ozone layer, increase of the intensity of solar radiation and of radioactivity, increase in the concentration of the pollutants such as sulphur or nitrogen oxides, dust and other toxic agents along with the appearance of other specific toxic substances (dioxins, benzofurans, *etc.*) [1]. Mechanisms of degradation in various environments are specific and differ for separate agents and coupled ones. For example, in natural terrestrial environments such as garden soil, marine floating or coastal sediment, biodegradation occurs in aerobic conditions being accompanied by photo-degradation, oxidative degradation and hydrolysis, while in man-made environments (landfills, digesters, composting wastes) the conditions are usually anaerobic, photo- and oxidative processes rather do not occur.

The changes in the polymers properties accompanying the degradation process may or may not be desirable, depending on the application considered. For example the light-induced embrittlement of polyolefins may be considered as a desirable or not desirable result in the case of photodegradable materials used as short-term products (*e.g.*, packings) and as respectively the long-term products. In case of short-term products an accumulation of photo- or bio-degradation products occurs while in the long-term ones an accumulation of wastes takes place; the impact on the environment always exists but it is probably less important in the first case.

When the service-life is overpassed, the degraded polymer products become wastes which finally pollute soil, but also air and water by release their ingredients and degradation products. Independently on polymer application, finally it becomes waste material, which must be either disposed or utilized [2]. One may conclude that the "status" of polymers as pollutants of the environment has drastically changed last years. Until 1985 polymers were considered as serious macro-pollutants with low toxicity but with many side effects. Recently a sudden change has been observed. Essentially this is due to the rapid development of the polymeric materials in the packaging industry and consumption, followed by a large accumulation of plastic wastes.

Most people consider that the fast food packaging (mainly PS foam) and disposable diapers are major constituents of garbage. It is not true; they constitute only 0.3—0.5 percent. It is also believed that plastics as constituents of solid wastes, by their non-biodegradability create serious problems and must be considered as dangerous "hazardous" wastes. The plastics industry has generally agreed that plastics are not easily biodegradable, but explained that this in an advantage, citing the problems arising from the by-products of biodegradation, which are known as "greenhouse gases".

Role of degradation in polymer waste treatment

Rapid degradation of materials is often preferred for environment protection. The so-called "5R" objectives of solid waste management imply: reduction, reuse, recycling, recovery and research. In each direction proposed for wastes treatment, degradation of polymer material plays a key role. Its preventing is important for the reduction, reuse and recycling. Its controlling is important for recovery and for the development of photo- and biodegradable materials. Recyclability of plastics and also of paper is limited because of deterioration of their quality and physical characteristics in a "cascade effect".

Induced degradation (photo- and biodegradable plastics) is a new solution but it is still a subject of discussion. It is thought that in the depth of a typical municipal landfill an intense chemical and biological fermentation occurs that transform the organic matter, except common plastics, into a sort of rich moist brown humus converting the wastes at least to "the nature".

It is also believed that paper biodegrades easily. The dynamics of a modern landfill is very close, opposite of what most people think. Landfill is very much more static biologically and chemically than it is commonly supposed. Biodegradation of some materials go on for a while and then slows down to a steady state; for other materials biodegradation does not proceed at all. Up to 10—15 years old paper is easily identified. Therefore it is not true that paper biodegrades and plastics not: oxidized plastics degrade in the environment. Coexisting with biodegradation is also a leachate, a toxic complex mixture of chemicals that diffuse into surrounding contaminating it.

The treatment (recovery) procedures are mostly destructive such as oxidation, bacterial conversion, solvolysis, hydrolysis, pyrolysis and combustion [2].

Some problems connected the use of the bio- and photo-degradable polymer materials

It is thought that biodegradable polymers degrade with a rate which match or exceed that of naturally occurring polymers and should have no detrimental effect on human health or environment; they should eventually be incorporated into natural cycles, being non-accumulative in the environment. Photo- and biodegradable materials are developed by synthesis of copolymers, by mixing of synthetic polymers with natural ones, by adding of some additives, by microbial synthesis or are obtained from renewable resources, as biomass [3]. Actually biodegradable plastics must totally converse to carbon dioxide + water and compost. Occasionally, intermediate products of biodegradation cause pollution of the environment if they are released in a short period of time and a narrow space. Their big quantity affect vegetation and probably some living organisms. Landfills are fascinating microbial environments, so that under anaerobic conditions, ninety percent of the natural polymers and part of the synthetic ones are transformed by biodegradation into methane, carbon dioxide, nitrogen or ammonia. It is well-known that the increase of CO_2 concentration in atmosphere causes the greenhouse effect with direct consequences for climate and the growth of plants.

Therefore, only apparently photo- and biodegradable polymers are environmentally friendly materials. On the other hand, introducing of degradable plastics into the recycling stream may create problems in the quality of plastic articles contaminated with biodegradable material.

All these considerations show that bio- and photodegradation is not a magic solution for solid waste disposal problem. Photo-fragmentation of polymers, abiotic and biodegradation can be proposed as ultimate solutions for un-collectable plastic wastes treatment.

Controversial aspects and problems for discussion appear concerning the fate of the fragments of polyethylene (PE) resulted by bio-disintegration of PE-based materials. These materials persist in finished compost and accumulate in soil so could hinder microbial and plant growth; the metal salts as those of Co, Mn, Cu, added to increase the rate of disintegration and the degree of fragmentation, contaminate the compost. Inserting PE even in infinitesimal quantities but every day is altering the fundamental property of soil [4].

The unanswered questions for research and society are:

a) does the fast biodegradation of dissolved organic matter in water consume oxygen and may be accompanied by reduction of oxygen content and whether this would affect aquatic life?

b) how to protect the climate through the reduction of carbon dioxide released by biodegradation and to prevent the greenhouse effect?

c) which is the effect of intermediate products of biodegradation on the vegetation and other living organisms?

This paper presents a summary of the studies on the use of lignin in polymer blends and composites directed mainly to recovery of lignin, which is a by-product in pulp and paper industry, to improve some properties of synthetic polymers and also to increase the degradation rate of the materials. Next to cellulose, lignin is the most abundant renewable resource on the earth. Lignin is now a very attractive raw material for industry because it is renowable and natural resource, is also available locally, and it can reach very interesting price levels that are very competitive to oil derivatives [5].

EXPERIMENTAL

Polymer blends consisting of synthetic polymers — epoxy resins (ER), and polyolefins (PO) such as polyethylene (PE) or isotactic polypropylene (IPP) — in the mixtures with various amounts of epoxy modified lignin [LER, with low molecular weight (dynamic viscosity 8000—20 000 cP), epoxy equivalent of 0.06—0.17%, water soluble] have been studied by investigation their morphology (visually and by optical and electronic microscopy), and estimation the changes in the mechanical, dielectric, thermal and superficial properties in comparison with those of the base synthetic polymers. The ER/LER blends have been prepared by mixing the liquid components in various ratios followed by curing in presence of the maleic anhydride, phtalic anhydride or diaminodiphenylmethane while PE or PP/LER blends have been obtained by open-roll/pressing method; for details see [6]. Samples were buried in soil and pH of the soil was monitored. The samples were also exposed to a microorganisms' culture, which was an mixture consisting of standardized and special fungi (*Aspergillus niger, Paecilomyces varioti, Penicillium funiculosum, Caetonium globosum, Trichoderma viride, etc.*) active in natural polymers biodegradation. Active growth on surface was examined with a stereomicroscope and by weight loss of polymer blends.

Terrestrial plant growth test was used to assess the influence of the degradation products on vegetation. The studied plants were *Vicia X Hybrida hort, Lathyrus Sativus L, Pisum Sativum L, Amorpha Fruticosa L* and *Myosotis Alpestris*

Two series of experiments have been made to investigate the influence of the degradation products, released to the soil, on the vegetation and effect of the gaseous degradation products educed to the atmosphere. Dynamics of plants growth was monitored during several vegetation cycles by following germination, plant height, blooming, number of buds and seeds, vegetable crude and dried mass after cropping, chlorophyll (A and B) pigments, carotenoidic pigments, lignin (Klasson-Komarov), mineral content — ash and microelements (by atomic absorption spectroscopy). All determinations have been made comparatively with reference plants cultivated in the same conditions but without polymer samples (degradation products) close to their constitutive elements (roots, leaves, *etc.*). Details on such studies can be found in [6—10].

Pollution caused by pyrolysis or incineration products appears mainly by accidents or when they leave the installations as exhaust gases. Average composition of gaseous pyrolysis products (obtained from municipal plastics pyrolysis, at atmospheric pressure, at temperature 400—500°C, autogenerated atmosphere) was: 1.6% H_2, 16.4% CH_4, 5.3% ethane and ethene, 11.4% propane and propene, and 61.85% C_4 hydrocarbons and CO and CO_2. Pyrolysis gas was trapped in a reservoire equipped with pressure gauge and flowmeter and than passed over *Myosotis Alpestris* plants in a constant time interval (each 3 days) and in a constant amount.

RESULTS AND DISCUSSION

Environmental degradation of polymer blends containing epoxy-modified lignin

In composite material as wood, lignin there is a polymer matrix in which cellulose fibres are embedded. It is obviously designed as a high-impact strength, thermally resistant material, thermoset, which performs in combination with highly crystalline cellulosic fibres.

Lignin is considered to be a non-biodegradable material, but naturally it is transformed into humus at a slow rate in a carbon-oxygen cycle helped by catabolitic activities of microorganisms. Ligninase acts by cleavage of the bonds and finally humus, small phenolic fragments, carbon dioxide and water are formed.

Industrial and commercial lignins are different, they have low molecular weight and different functionalities with random distribution and they are soluble in water. These kinds of lignins are more easily degradable in environmental conditions and more compatible with other polymers [5].

The incorporation of epoxy-modified lignin into all above mentioned synthetic polymers leads to [6]:

— a significant increase of the dielectric properties (2—4 orders of magnitude),

— increase of Charpy impact strength (2—5 times),

— significant improvement of adhesive properties.

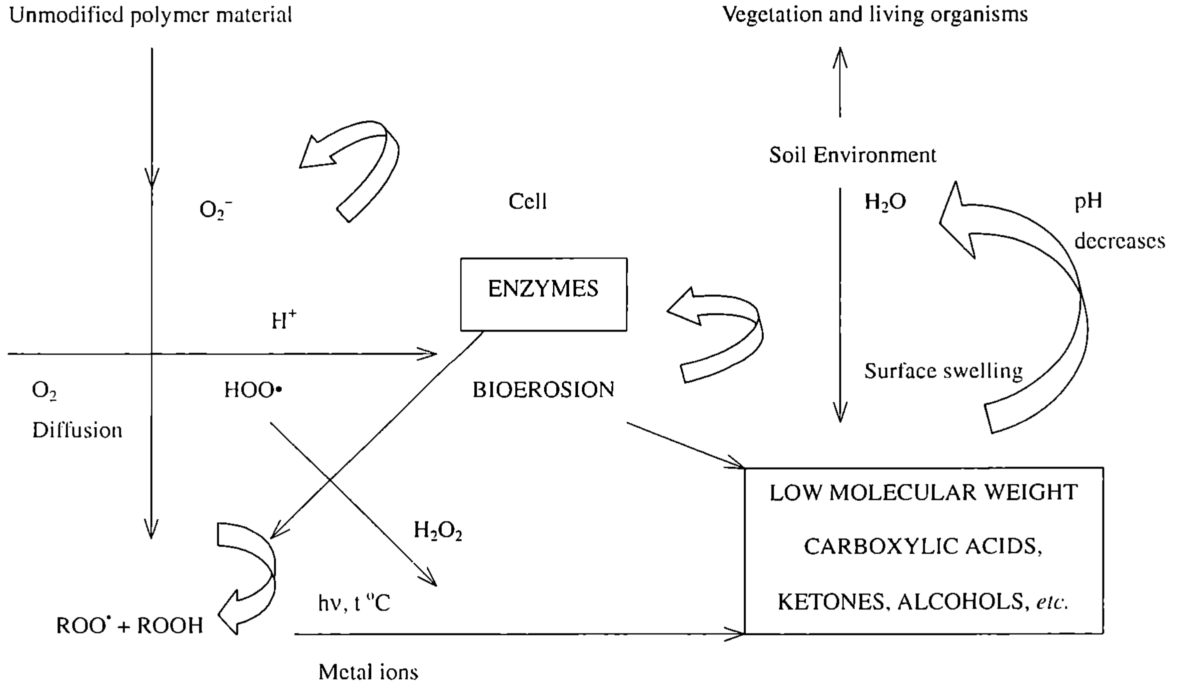
Due to its phenol propanoidic structure lignin acts as antioxidant (concentration < 5%, the decomposition temperatures increased about 10—20°C), and surface properties improves by increasing of the hydrophilic character of compounds (polar components of the free surface energy increase of 3—4 times, mainly electron donor component due to the presence of oxygen-containing groups). In the case of higher incorporated amount of LER, a clear tendency to environmental degradation was observed. After at least seven months of soil burial the change in ER/LER or PO/LER blends starts at surface by formation of cracks, cavities loss of physico-mechanical properties, water absorption (at beginning), weight loss, presence of the micro-organisms which were observed on the surface, *etc.*

The weight loss was 75—90% for ER/LER blends containing more than 30% LER, while the weight loss of the blends containing less than 30% LER was only 2—3%, similar to the samples containing PO.

PO/LER blends containing 10—15% LER, photo-oxidized and plasma or electron beam exposed, exhibited a significant weight loss: more than 20 wt. %. Naturally, the weight loss is explained either by leaching of water-soluble natural polymer from the surface or by evolution of some products of degradation. Migration of water in, out or through the samples favours degradability starting with leachable components, leaving matrix brittle and more susceptible to further degradation. According to the literature data and our results [6, 11], the degradation of the blends leads to a series of compounds such as hydrocarbons, acids, phenols, aldehydes, ketones, esters which effect is the decrease of pH, the increase of acidity of soil and consequently the anabolism and enzymatic activity will be perturbed.

The effect of polymer blends and pyrolysis gases on the plants growth

Microbial environment is also affected *e.g.* if some bacteria prefer retaining on the surface, the activity of some enzymes is inhibited so equilibrium is disturbed. The intermediate products of photo-, thermo- and bio-oxidation are biodegradable low molecular weight carboxylic acids and alcohols (Scheme A) formed primarly in the surface layers of polymers. They migrate into soil so the roots plants are in close contact with them; in



Scheme A. Schematic representation of environmental degradation of a polymer material and influence of intermediate product of degradation on soil and enzymatic activity some cases a negative influence on the plants' growth is observed.

Positive and negative influences of the buried samples on the plants' growth are observed. Positive influence is assessed for the plants being higher what results in greater accumulation of crude and dried vegetable mass in comparison with reference plant. The negative influence appears during blooming period (Tables 1 and 2) and is much significant when the LER content is higher than 10 wt. % and for weight loss higher than 20 wt. %.

When the degradation was fast and high amount of degradation products was evolved the germination was affected, the content of pigments in the leaves of the plants decreased and the content of microelements was changed.

Table 1. Data of the plants' growth test in the presence of ER/LER and ER/LER/Fe_2O_3 blends

Samples (crosslinked with diamino-diphenyl-methane)	Blooming period		Total Chloro-phyll, %		Carotenoidic pigments, %		Lig-nin %
	Height of the plant, cm	No. buds	I	II	I	II	
Reference plant (without polymer samples buried in soil)	52	50	0.0342	0.6041	0.0012	0.0317	20.3
ER	30	31	0.0160	0.9558	0.0005	0.0739	22,5
86% ER/ 14% LER	22	21	0.0204	0.7866	0.0013	0.0408	20.9
75% ER/ 25% LER	14	8	0.0164	0.7202	0.0009	0.0459	22.8
LER	17	28	0.0316	0.4807	0.0011	0.0442	15.6
ER/5% Fe_2O_3	17	14	0.0202	0.6031	0.0011	0.0503	20.5
81.4% ER/ 13.5% LER/ 5% Fe_2O_3	26	33	0.0200	0.8220	0.0019	0.0503	21.8
71% ER/ 24% LER/ 5% Fe_2O_3	18	21	0.0201	0.5939	0.0047	0.0307	20.5
LER/5% Fe_2O_3	28	41	0.0239	0.4526	0.0011	0.0359	17.6

I — the first vegetation cycle, 4 months during autumn, winter period; II — the second vegetation cycle, two months, summer period.

It is well-known that biodegradation processes of the lignin and its derivatives results with substances of aromatic structure and carboxylic groups of phenoxy-acetic type which skeletal structure is also found in phyto hormones, auxines with stimulating effect on the plants' growth. On the other hand, by processes of demethylation, oxidation and by microorganisms' attack, the humus is formed which is an important constituent for maintaining of favorable conditions in soil for vegetation growth. Humus influences the structure and texture of soil increasing aeration and moisture holding capacity. It is also able to store and gradually release nutrients to the surrounding environment by simulation of plant enzyme system. This is explanation for apparent positive effect.

A decrease of chlorophyll and carotenoidic pigments as well as microelements' content is evident from Tables 1 and 2. It is due to the change of soil environment. The intermediate products decrease the pH of the soil and therefore physiological state of the plant and also its ability of microelements assimilation are affected.

Table 2. Data of the plants' growth test in the presence of PO/LER blends (greenhouse conditions, summer period)

Samples*)	Blooming period		Content of micro-elements (mg/100 g dried mass)				Lig-nin %
	Height of the plant cm	No. buds	Fe	Mn	Cu	Zn	
Reference plant (without polymer samples buried in soil)	52	50	0.28	0.38	0.37	1.73	20.3
IPP	33	36	2.04	2.71	1.05	2.72	21.3
91% IPP/9% LER (PP-*g*-GMA)	42	34	0.41	1.34	0.59	2.34	19.8
87% IPP/13% LER (PP-*g*-GMA)	40	21	1.09	1.54	1.21	2.43	19.3
PE	35	26	0.41	1.28	0.78	0.97	21.0
PE/20% LS-NH_4 (EVA)	46	38	0.30	1.83	0.25	0.15	20.5
PE/30% LS-NH_4 (EVA)	44	42	0.16	0.45	0.14	0.52	19.7

*) In the brackets, the compatibilizing agents are given: PP-*g*-GMA — polypropylene grafted with glycidyl methacrylate, EVA — ethylene/vinyl acetate copolymer, LS-NH_4 — ammonium lignosulfonate.

Test of incubation with one micro-organism or colonies of micro-organisms showed that micro-organisms in soil act similarly to the wood-degrading micro-organisms. The hyphae growth on the sample surface were more abundant. The longer exposure time was, the surface covered by micro-organisms increased starting from micro-domains of natural polymer. From the complex microbial population only certain fungi were accumulated on the surface namely: *Penicillium funiculosum, Stachybotrias atara, Myrothecium verrucaria,* and have acted the tested polymers. The results indicate no significant differences between the behaviour of the lignin-filled polymers and starch-filled PO [11, 12].

The maximum height of the *Myosotis Alpestris* plant unexposed to the pyrolysis gas was 9.5 cm and 11—12 cm for exposed plants, therefore the same greater accumulation of vegetative mass in exposed samples has been observed as in those grown in the presence of polymers buried in soil. The content of the pigments in the leaves of the plant exposed to the pyrolysis gases is smaller than that of reference plant: 3.84 mg/g in com-

Table 3. **Content of assimilatory pigments in *Myosotis Alpestris* exposed to gaseous pyrolysis products**

Plants	Chlorophyll		Total Chlorophyll	Carotenoidic Pigments	Total available pigments	Chlorophyll A/B Ratio
	A	B				
REFERENCE	1.32	0.46	1.78	4.83	6.62	2.87
EXPOSED	0.72	0.27	0.98	2.49	3.84	2.67

parison with 6.62 mg/g (Table 3). The cartenoidic pigments content was higher in unexposed leaves, the ratio chlorophyll A/B was also higher. The physiological data obtained by biochemical analyses of photosynthetic potential of the leaves confirm the decrease of the carotenoidic pigments content and of both chlorophylls content. The pH of soil slightly decreases, so diminishing of the photosynthetic capacity of these phytotaxoms in presence of the degradation products has been shown.

CONCLUSIONS

The degradation processes are essential in polymer waste management. Each method of degradation presents both advantages and disadvantages in respect with environment protection.

The intermediate degradation products influence the plants' growth. Both positive and negative influences of the buried samples are observed. The plants grown in presence of polymer samples or degradation products are higher and show greater accumulation of crude and dried vegetable mass in comparison with reference plant. Negative influence appears in blooming stage and is much significant when the degradation was fast and high amount of degradation products was evolved. In such case pH of the soil decreased, the germination was affected and the content of pigments in the leaves of the plants decreased.

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