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Accelerated Degradation of Polymers

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Application of photochemical processes for the environment protection against plastic waste has been shown in this communication. The ways of acceleration of decomposition of high molecular compounds including the effect of UV-radiation, metal salts and hydrogen peroxide are shown. The results of photo-oxidative degradation of selected commercial polymers using IR, UV-Vis spectroscopy, viscometry, gel permeation chromatography and optical microscopy has been presented.

Keywords: photooxidative degradation of polymers; accelerated degradation; environment protection

INTRODUCTION

In recent years, there is a growing awareness caused by fast increase of pollution by plastics. Recycling and incineration of plastic waste have many, serious limitations, thus, the production of new materials with enhanced degradation - plastics friendly for environment - seems to be solution of this problem. Accelerated decay of macromolecules can be

achieved during their exposure to UV light. This paper presents our results concerning acceleration of polymer photodegradation in the presence of low-molecular inorganic compounds ^[1-12].

EXPERIMENTAL PART

Thin polymer films were obtained by solution casting onto glass plates. After solvent evaporation samples were dried in vacuum at room temperature. Some experiments were conducted in polymer solutions.

Low-pressure mercury vapour lamp (TUV 30W, Philips, Holland) was used for UV irradiation of polymers.

Average molecular weights and polydispersity of polymers was estimated by viscometry (using Ubbelohde viscometer) and by gel permeation chromatography (Shimadzu C-R4A). Infrared spectra were obtained by Perkin Elmer spectrometer (1650). Absorption spectra were recorded with Shimadzu (UV-160) or Beckman (7500UV/Vis) spectrometer.

Optical microscopy (Nikon, Japan) and scanning electron microscopy (Jeol JSM-820) was applied to observe the crystallinity of PEO and changes in morphology induced in samples by UV-irradiation.

RESULTS AND DISCUSSION

The course of photooxidative degradation of polymers depends not only on their chemical structure but also on other factors such as presence of defects in chains, external impurities, degree of crystallinity, physical state and morphology of sample, atmosphere as well as temperature.

We studied photooxidative degradation of different commercial polymers

such as PS, PMMA, PPO, PB, PVP, PEO and PAA*. We found that some of them are very susceptible to UV-irradiation (PB, PVP, PEO) but others are more photoresistant (PS, PMMA, PPO).

We accelerate photochemical processes in these polymers by introducing small amount (1-5% wt) of inorganic low-molecular compounds (transition metal salts ^[1-6] or hydrogen peroxide ^[7-12]).

It was proved by gel permeation chromatography, viscometry and spectroscopic methods (FT-IR, UV-Vis) that metal salts such as CuCl₂, or FeCl₃ cause acceleration of main chain scission and oxidation in UV-irradiated PEO ($\lambda=254$ nm). Moreover, PEO with addition of CuCl₂ was very unstable upon visible light ($\lambda>400$ nm). Besides of photochemical reactions fast destruction of crystalline phase of PEO caused by UV-irradiation in the presence of metal salts was observed. Iron (III) chloride was also tested in mixture with PS and PMMA. In these inhomogeneous systems photoreactions were much faster and more efficient than in pure PS or PMMA. Chlorine radicals (Cl \cdot) and ionradicals (Cl₂ \cdot^-) formed during photolysis of these salts are the main initiators influencing the efficiency of polymer decay.

Hydrogen peroxide was an effective accelerating agent in case of water-soluble polymers (PAA, PEO, PVP). It was estimated that these polymers undergo efficient chain scission, when they were UV-irradiated in more or less diluted H₂O₂ solutions. Moreover, hydrogen peroxide also enhances degradation of non-soluble in water polymers (PPO, PB). In this case, photoreactions occurring on the phase boundary are enough effective for initiation of macromolecule destruction inside the polymeric phase. Hydrogen peroxide is a source of hydroxy (HO \cdot) and hydroperoxy (HO₂ \cdot)

* look abbreviations

radicals, which accelerate polymer degradation. This indicates that migration of these active, mobile radicals in polymer take places. During UV-irradiation of above polymers in the presence of hydrogen peroxide also effective oxidation was observed. In case of polymers, showing tendency to photocrosslinking (PPO, PB), the amount of insoluble gel was much less in the presence of H_2O_2 than in pure polymers. It indicates that recombination of macroradicals with small radicals formed during photolysis of H_2O_2 is dominant process in termination. Moreover, the photodeformation of polymer surfaces (microcrazes formation and increase of roughness) is also accelerated by hydrogen peroxide.

It was also proved that the course of photooxidative degradation of polymers strongly depends on the sample composition and morphology.

CONCLUSIONS

During UV irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack of bacteria and fungi in natural environment. It is also well known that the efficient main chain scission in irradiated polymers causes their mechanical deterioration and breaking onto small pieces. Thus, the access of oxygen and microorganisms is facilitated to the bulk of such destroyed products. In this way polymers become biodegradable.

Obtained results suggest that those non toxic metal salts as $CuCl_2$, $FeCl_3$ can be used as accelerating agents in utilisation of plastic wastes.

Hydrogen peroxide can be applied during sewage treatment of sewers containing water-soluble polymers.

Abbreviations:

PMMA – poly(methyl methacrylate)

PS – polystyrene

PPO – poly(2,6-dimethyl-1,4-phenylene oxide)

PB – polybutadiene

PEO – poly(ethylene oxide)

PAA – poly(acrylic acid)

PVP – poly(vinyl pyrrolidone)

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