

Radiation effects in polypropylene/polystyrene blends as the model of aromatic protection effects

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Abstract. A technically useful composition containing polypropylene (PP) as a principal constituent, expected to be working or to be processed in ionizing radiation field, e.g. for sterilization, has to be protected from undesired radiolysis resulting in radiation damage. Usually, conventional additives are used which are generally effective, especially when containing aromatic groups. They can be sometimes unacceptable, e.g. in medical applications. Polystyrene (PS) has been investigated as a protective component, in analogy to the classical case of cyclohexane/benzene system. Mechanical mixing of both polymers showed to be of modest effect, but two other procedures, of soaking polypropylene powder with polystyrene dissolved in styrene, or soaking with styrene and γ preirradiation with resulting grafting ($G = 12000$ effects/100 eV), resulted in the composition of improved resistance towards radiation. The energy transfer, which explains the effect, is extended at a distance of 8–12 mers of polypropylene. The investigations have been made by gas chromatography and diffuse light reflection spectrophotometry (DRS), after 10 MeV electron beam irradiations.

Key words: energy transfer • polypropylene • polystyrene • protection effect • radiation grafting

Introduction

Several applications of polymers demand their resistance towards ionizing radiation, e.g. those for disposable medical devices sterilized by radiation, for devices to be located in outer space applications in nuclear industry and in nuclear reactors etc. Depending on the nature and extent of radiation damage, solution of the problem consists in application of additives, produced for general application of polymers. They work often very well also as a protection from radiation damage, especially when they contain aromatic groups which act as energy sink via energy transfer mechanism. Some additives are not acceptable, especially in medical applications and one of the aims of the present investigation was to answer the question if an aromatic polymer as an additive can limit the extent of radiation damage. However, the main topic of the project is basic research on classic aliphatic/aromatic energy transfer, this time extended from small molecules to polymers.

Freeman [4] has first found that in irradiated simple system of cyclohexane/benzene, radiolytic hydrogen was not formed in proportion to the composition, i.e. benzene was reducing the hydrogen yield in a higher degree than was expected. The effect was investigated later in several laboratories and was called “deviation from the mixture law”. It was investigated also in a frozen system, revealing interesting facts connected with solid crystalline state. It became obvious that crystals

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of both constituents must have nanosize dimensions to reach the energy transfer. It is obtained by freezing the mixture from the gas phase. Classical case of previously investigated protection phenomena, i.e. benzene/cyclohexane, was effective only in liquid state [5] or frozen from the gas phase [3]. Shock freezing of liquid mixture is not sufficient to form close assemblies of crystal of both compounds.

The deviation from the mixture law in the field of radiation chemistry of polymers was never investigated systematically. Albano *et al.* investigated the (PP/PS) 20/80% blends, at low doses [1] and high doses [2] (70–400 kGy) with resulting full protection of PP, as expected.

As in the case of cyclohexane/benzene system, the hydrogen production was used as a basic indication of radiolysis extent, but in the PP/PS system. In addition, formation of CH₄ and CO (after oxidative experiments) in the function of dose and composition was studied. In addition, unusual experiments were done consisting in oxidation of a just irradiated sample, in the same vial after removing hydrogen, all on line, during the chromatographic experiment. Air was injected into the vial and the kinetics of oxygen consumption was recorded in function of elapsed time.

Further stages of oxidative degradation of polypropylene were studied by diffuse reflection spectrophotometry (DRS). That is the only possible technique, due to the opacity of the polymer samples.

Introduction of small molecule additives into a polymer composition is simple, but preparation of aliphatic/aromatic polymer blends is more complicated and demands the development of new procedures. The case of polypropylene/polystyrene, i.e. of a semicrystalline, nonpolar thermoplastic polymer and a polar, amorphous polymer is known to be immiscible. Mechanical mixing proved formation of unsatisfactory blend from the point of view of energy transfer, but other approaches described here resulted in a proper mixture.

Materials

Sample A was prepared by mixing commercial polymers: polypropylene (PP) Malen P J-400Z*1632/01 from Basell-Orlen and polystyrene (PS) from Owispoldwory. Proportions were 0, 10, 25, 50, 75, 100 wt.% of PS. In spite of most thorough blending injection and pressing in a mechanical way, the surface area of contact between both polymers has not been expected to be most favourable for energy transfer and therefore two other procedures of sample preparation have been developed. Sample B was prepared from a virgin polypropylene (F 401) powder, collected from the Orlen-Olefins production line, without additives. It was impregnated with polystyrene dissolved in styrene monomer (fresh distilled, free of stabilizers) to get the proportion of PP/PS as above. Afterward the styrene was removed by evaporation during gentle heating. The sample C was prepared by soaking polypropylene powder with stabilizer-free styrene and polymerization/grafting processed in the gamma field from cobalt-60 at a dose rate of 1.5 kGy/h to the a of 3 kGy. All added styrene has polymerized totally, its percentage was checked gravi-

metrically. Polymerization grafting of styrene proceeds in a chain mechanism in the presence of polypropylene, with high radiation yield (12000 effects/100 eV), due to the generous supply of free radicals by irradiated PP. The styrene alone (the same batch), γ or electron beam irradiated, polymerizes very slowly and the progress of reaction can be followed by the increase of viscosity only. All proportions of both polymers were checked by weighing the final preparations.

Irradiations

All irradiations, except gamma exposure mentioned above, were done with an electron linacs, Elektronika 10/10 (10 MeV, 9 kW) or LAE 13/9 (up to 13 MeV, 9 kW straight beam, or 6 kW bent beam of improved monoenergetic spectrum) [6].

Product analysis

Determinations of H₂, CH₄, and the secondary product CO, as well as of O₂ consumption were done by gas chromatography (Shimadzu GC 2040 and GC 2010, molecular sieves 5 Å), in carrier gas Ar resp. He. Samples were irradiated in 3.5 ml vessels closed with rubber septa, shielded by a thick lead hood, if irradiated on the conveyor. When irradiated by a narrow electron beam, no shields were needed because the beam was centred on the sample at the bottom of the vial. Hydrogen was released immediately from samples of any shape, whereas determination of methane demanded gentle heating of the vessel in the case of thick films of the material, before sampling from the gas phase of the vessel was done. Carbon oxide was determined after aeration during subsequent lapses of time.

Ketone and peroxy groups were determined by diffuse reflection spectrophotometry using a Perkin Elmer Lambda 7 spectrophotometer with an integrating sphere. That technique has been applied earlier in the investigation of radiation chemistry of neat polypropylene [8]. The DRS method is by two orders of magnitude more sensitive than IR spectroscopy because of much higher molar extinction values of absorbing groups. Therefore, that sort of spectroscopy is able to show the effects even of sterilization doses. FTIR spectra recorder after sterilization doses usually indicates no chemical changes in polymers, because of low sensitivity. Maxima on DRS absorption spectra were identified (210 nm – peroxy; 245, 295 nm – ketone groups) [7].

Results and discussion

Figure 1 shows the production of hydrogen in classical coordinates vs. composition of the aliphatic/aromatic polymer. Curve A refers to mechanically mixed polypropylene and polystyrene. Almost linear dependence of hydrogen release, in the function of composition resembles the classical case of a shock frozen benzene/cyclohexane mixture, where crystals of both compounds were too big to reach sufficient area of contact. In our case, the macromolecules of both polymers were

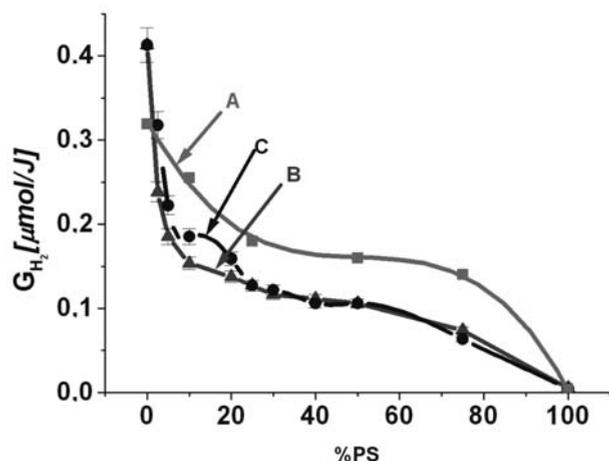


Fig. 1. Radiation yield of hydrogen in the function of PP/PS composition. The A curve (■) does not start at the same point as curves B (●) and C (▲), because a commercial PP was used in this case, already containing additives. Curves B and C start from virgin PP. Radiation yields are constant in the full range of applied doses 25–100 kGy. Curves were graphed by Origin program.

also in poor contact and radiolysis proceeded almost independently in each of them. The classical benzene/cyclohexane crystalline mixture has shown a proper, expected behaviour almost like in the liquid state, when frozen from the gas phase. Samples B and C were really tightly packed polymers, and the protection effect could appear, as it is visible from concave shape of the curve. A rough estimate shows that protection extends at the distance of 9–12 mers of the polypropylene. This is connected with the energy transfer of single ionization spurs [5], which have some freedom of movement along the chains.

A limited volume of the paper submitted for publication does not allow to present details of the fate of multi-ionization spurs, formed at the expense of ca. 20% absorbed energy, at low LET radiation used in the present study. It should be mentioned that radiation yield (Fig. 2) of methane as one of the debris is connected with multi-ionization spurs, which are localized in the

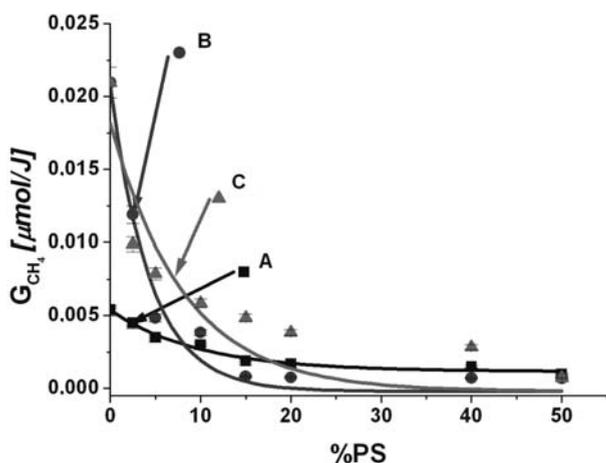


Fig. 2. Radiation yield of methane in the function of PP/PS composition. The A curve (■) does not start at the same point as curves B (●) and C (▲), because a commercial PP was used in this case, already containing additives. Curves B and C start from virgin PP. Doses 25–100 kGy.

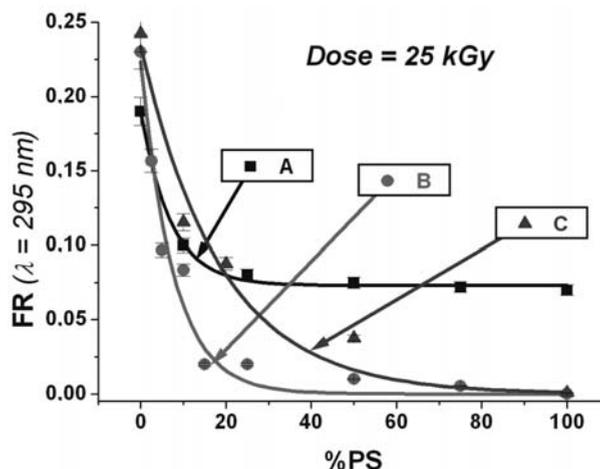


Fig. 3. Formation of oxidation products on PP chain ($\lambda = 295$ nm) in the function of composition of the PP/PS blend. Dose 25 kGy.

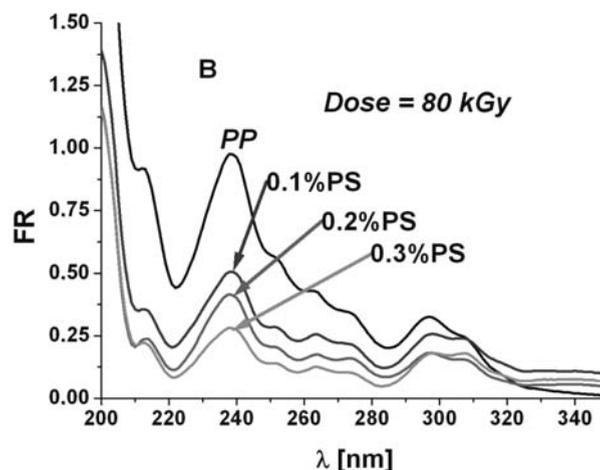


Fig. 4. DRS spectra of blend B irradiated in oxygen to the dose of 80 kGy. The maximum of absorption is due to oxidation products. FR – light absorption in Kubelka-Munk function [7].

site of deposition of comparatively high amount of energy (> 100 eV). They cannot change the location and are unable to participate directly in energy transfer.

DRS results are connected with oxidation phenomena, described in Refs. [9, 10]. As preliminary information Fig. 3 shows the oxidation phenomena in preparation A. A more pronounced PS effect, in comparison to that of hydrogen production, is explained by the influence of surface phenomena and kinetics of diffusion of oxygen – Fig. 4 shows DRS spectra of blend A after the dose of 25 kGy.

Conclusions

As concerns the applied methods of analysis and investigation: gas chromatography together with diffuse reflection spectrophotometry have shown to be effective in recognition of protection effects in aliphatic/aromatic blends of polymers. Key intermediates and final products of radiolysis have been determined, i.e. hydrogen, methane and CO.

As concerns preparation of blends and mixtures of aliphatic/aromatic polymers: three methods have been proposed. Conventional blending of polypropylene (PP) and polystyrene (PS) in the Brabender processing and/or by injection does not give desired results of protection of radiolysis of PP by PS. Mechanical methods cannot secure sufficiently large interphase for energy transfer. Application of grafting of styrene on polypropylene by two slightly different procedures resulted in the expected protection effect. It extended, according to vague estimate, at the distance of 9–12 mers of the polypropylene. Thus, the classical case of radiation protection effect in the benzene/cyclohexane system has been extended into the field of polymers. Solid state system benzene/cyclohexane shows the energy transfer only if it is crystallized from the gas phase to secure close contact of the constituents. In the case of the polymeric system of polypropylene/polystyrene, the mechanical mixing is not sufficient and the effect of energy transfer occurs only in impregnated and grafted samples. Chains of both polymers, aliphatic and aromatic must have sufficient area of contacting, or exhibit short distance sites for energy transfer to the aromatic structure, which is the sink of energy.

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