

Fig. Production of radiolytic hydrogen from typical polymers in the waste in the function of absorbed dose of ionizing radiation. (Explanations in text.)

dard for the worst case anticipation of hydrogen production.

By occasion of the execution of investigations, time and again the observations were made that radiochemists do not accept fully the facts of chemical reactions generated by ionizing radiation. Therefore, the purpose of full report of investigations (*vide infra*) will mean a proposal to consider by radiochemists, especially those dealing with radioactive waste management. Relations between radiochemistry and radiation chemistry are still insufficiently close and unsatisfactory. Radiochemists do not have the access to the tools and methods of modern radiation chemistry, *i.e.* powerful sources, especially to accelerators of electrons. Hopefully, the problem of radiation-induced chemical effects connected with handling of radioactive materials, especially in the case of long time waste storage, can be solved with the help of radiation chemistry. The Department of Radiation Chemistry and Technology is ready to consult problems connected with chemical aspects of waste management, in particular of long time storage. The Department is ready to supply a full range of help, from consultation to experimental projects and computer assisted simulation of expected chemical effects.

Specific problem connected with radioactive waste management is connected with far shot analysis what can happen with salt deposits after thousands of years. The mentioned techniques are adapted to simulate what will happen if radioactive, long-lived material included in salt deposits, will be attacked by sipping water, turning the deposit into saturated NaCl brine, radiolyzed in completely different manner, in comparison to previous, initial solid state radiolysis. The system is in

fact the radiation chemistry of saturated salt solutions, bringing complications connected with direct action of radiation on the solute. Our experimental approach is prepared to overcome that complication. As a comparison and control of experiment, the simulation is done also by computer assisted simulation. In 2004, it has been done with the help of Chemsimul programme, developed in the Risø National Laboratory (Denmark) and installed in the Department. The author of the report is licensed to use the programme freely and to obtain help from the authors of the programme, if needed. The case of salty brine has been originally developed for the case of chemical changes caused by potassium-40, the β emitter in prebiotic conditions on Earth, in particular in early oceans, seas and lakes.

Precision and accuracy of measurements were under control. All reported investigations have been performed under rigorous conditions of Quality Assurance (QA), as demanded by proper basic research and/or commercial radiation processing, controlled by the ASTM/ISO standards and traced to NIST samples. Reliable results have economic importance. Proper use of the experimental approach to the questions of dangers, connected with radiolytic products of waste management and storage, can mean substantial savings. For instance, the drum containing waste can be considered of too high activity of plutonium and before storage has to be repacked at the expense of tens of thousand of USD. Our investigations have shown upper limits of permissible activity, producing hydrogen from most dangerous plastics. These data show, that the activity inside drums can be left much higher than the earlier accepted value, thus avoiding repackaging and cutting high additional costs.

During the year 2004, the work was continued, tending to formulate final conclusions to be found in a high volume INCT report.

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ALIPHATIC-AROMATIC POLYMER BLENDS AS A PROPOSAL FOR RADIATION RESISTANCE

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Several applications of polymers demand resistance towards ionizing radiation, *e.g.* for single use medical devices radiation sterilized, for nuclear medi-

cine devices, for outer space research, *etc.* Ionizing radiation can cause different effects, from positive, like crosslinking, to negative as degradation and

formation of low molecular debris of the chain. Traditional preventive approach consists in additives, mainly typical, used widely, securing resistance of the material to sunlight and increased temperature [1]. These additives can have adverse effect in applications, *e.g.* for medical purposes, therefore other proposals are looked for. Most additives of stabilizing action are aromatic compounds and their activity towards photochemical action consists in direct absorption of UV-VIS quanta and change of ionizing energy into harmless heat or to longer wavelength light not able to cause photochemical changes. However, the direct action in radiation chemistry is proportional to the participation of additives in the pool of electrons, that means it is low. However, the observed protection effect is higher than that resulting from additives percentage, what means that there must be energy transfer from the ionized main constituent of the material to the protecting additive. The best explanation is the concept of the positive hole (h^+) transfer over the chain to the energetically attractive site, like the neighborhood of aromatic additive. That effect occurs in the case of 80% of deposited energy in single ionization spurs. The remaining 20% are deposited in the multi-ionization spurs, causing serious radiation damage, chain scission and formation of low molecular weight debris [2-8].

The idea of the present investigation is the application of aromatic polymers instead of traditional low molecular weight additives. Aromatic polymers can be used in higher concentrations than additives, thus improving mechanical properties of the material and securing radiation resistance. Stabilizers and other additives will no longer introduce complications and adverse effects of mostly strange chemistry of additives. Even if the applied results will not successfully compete with conventional solutions, the basic research results will justify the research. The knowledge of energy transfer in polymers is far from perfect and the research will contribute to better basic understanding of radiation chemistry of polymers.

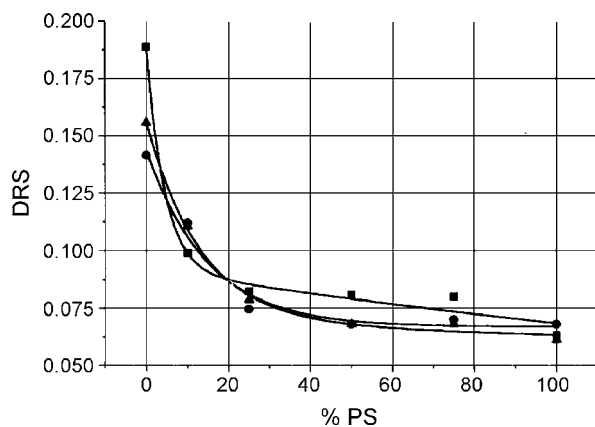


Fig. Dependence of peak intensity at $\lambda=290$ nm in the DRS spectrum from the PS content in the blend, for three media of irradiation: pure oxygen (squares), air (triangles), argon (circles).

The main constituent of polymer blends, the polypropylene (PP) has been chosen, as the most popu-

lar polymer for the application in construction of medical devices, due to the hardness and temperature resistance. Unfortunately, the virgin PP is of low resistance towards ionizing radiation, already to sterilization doses [9] and cannot be applied without additives. Following the idea expressed above, as a simple aromatic polymer, polystyrene (PS) was applied and both polymers were used as blends in different proportion and prepared in a variety of ways. Mechanical properties of blends were investigated in collaboration with the Wrocław Technical University [10,11].

Main recognition of the protection effect has been done by the diffused reflection spectroscopy (DRS), developed in the Department of Radiation Chemistry and Technology (Institute of Nuclear Chemistry and Technology) for the application to irradiated polymers [12]. The dependence of intensity of bands in the DRS spectrum, attributed to ketone groups, which are final products of oxidation, shows clearly the protection effect of PP, executed by PS (Fig.). One can assume that the contact between PP and PS chains is not intimate enough to accept all positive holes and electrons released in the primary process. Therefore, hydrogen is detached from PP, forming alkyl radicals on the chain. The PS competes successfully with oxygen for these centers, preventing the oxidation of polymers. The aromatics free PP is oxidized easily, whereas the presence of PS prevents this reaction.

It is obvious that the study of hydrogen detachment can clear these assumptions, as it has been indicated in first experiments [13]. The detachment of hydrogen is unknown in the classical chemistry of polymers. Molecular hydrogen is not released in conventional methods of crosslinking; it appears as a variety of compounds depending on the kind of crosslinking agent. Our investigations, limited by temporary access to a gas chromatograph, have shown the radiation yield connected with the participation of PP in the blend.

Results of our investigations have been compared with the measurements of mechanical properties, performed at the Wrocław Technical University, *i.e.* mass flow rate, elongation, coefficient of direct elasticity, viscosity. Results obtained, after comparison with commercial data of traditional PP compositions, indicate a possible application of our approach.

All reported investigations have been performed under rigorous conditions of Quality Assurance (QA), as demanded by proper basic research and/or commercial radiation processing, controlled by the ASTM/ISO standards and traced to NIST samples. These conditions have to be fulfilled, if the medical devices shall be permitted for application [14]. Applied radiation techniques [15-18] secure proper dosimetry, maximum to minimum dose ratio, *etc.*

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CHEMICAL CONSEQUENCES OF NUCLEAR STABILITY

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The matter around us contains chemical elements in the elemental state and in a variety of combinations. Some materials consist of two or more elements joined in chemical compounds, or are mixtures of elements or compounds or both.

Very early, in the opinion of XVIII century chemists all chemical elements should be treated as “eternal”. However, after Becquerel’s discovery of radioactivity of certain atomic nuclei such invariability became problematic and depended only on longevity of a given time scale. A chemical element can consist of different isotopes (stable or radioactive) as was firmly established by J.J. Thompson. In chemistry, atomic binding energies (*i.e.* energies of chemical bonds) are of the order of eV, whereas the level of many MeV is useful in nuclear physics. Electron structure of atom determines its chemical behaviour, and the nucleus binding energy decides about its stability. About 273 different nuclei are stable because they lack enough mass to break up into separate nucleons. The energy equivalent of the missing mass of a nucleus is called the binding energy of the nucleus. The greater its binding energy, the more energy must be supplied

to break up the nucleus. For given nucleus, the binding energy per nucleon is found by dividing the total binding energy of the nucleus by the number of nucleons, A , it contains.

The greater the binding energy per nucleon the more stable the nucleus. The graph (Fig.) illustrating the relationship between binding energy and mass number has its maximum at 8.8 MeV/nucleon when the number of nucleons is 56. The nucleus that has 56 protons and 56 neutrons is ^{56}Fe , the iron main isotope. This is the most stable nucleus, since the highest energy is needed to pull a nucleon away from the iron nucleus. All the larger nuclei are unstable and decay radioactively.

It is an empirical fact that the binding energy per nucleon is roughly the same for all stable nuclei, *i.e. ca.* 8 MeV. As the mass number increases, the binding energy per nucleon gradually decreases. This systematic trend is a consequence of the electrostatic energy repulsion of the protons within the nucleus. The binding energy curve is the key to energy production in the universe, mainly nuclear fusion leading to nucleosynthesis of heavy elements. The graph has a good claim of being the most significant in the whole science. The fact that the binding energy exists in general means that the nuclei more complex than the single proton of hydrogen ($A=1$) can be stable. This stability, in turn, accounts for the existence of the various chemical elements and, consequently, for the existence of the truly enormous amount of chemical compounds and their mixtures we see around us. For example, there are several millions of known and described chemical compounds, and even theoretically about 10^{48} of different proteins.

The semi-empirical mass formula (SEMF) was originally devised by C.F. Weizsacker [1] to represent the known nuclear masses in term of a few (five) adjustable parameters and enable useful estimates to be made of the masses of unknown nuclei. In the SEMF, the total binding energies expressed as a sum of five terms:

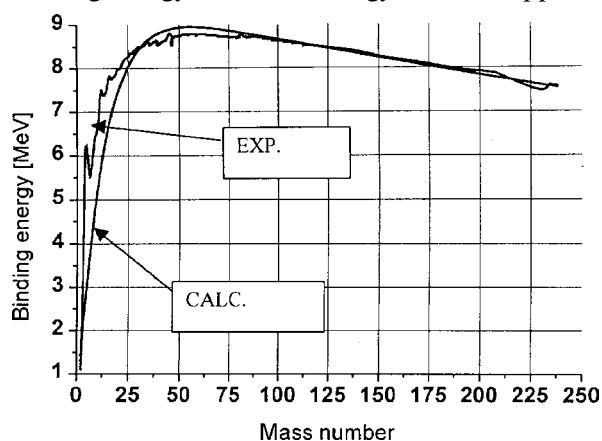


Fig. Binding energy per nucleon plotted against mass number A (experimental and calculated values, respectively).