

ated pure RdH MMT modified with salt A and salt C were tested. In all cases the signals are un-

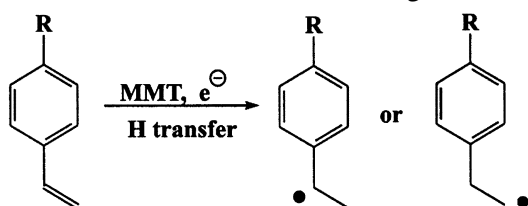


Fig.5. Possible mechanism of hydrogen abstraction.

stable and decay for several days. Spectra of radicals obtained for pure RdH MMT modified with both A and C salts strongly reveal that hydrogen

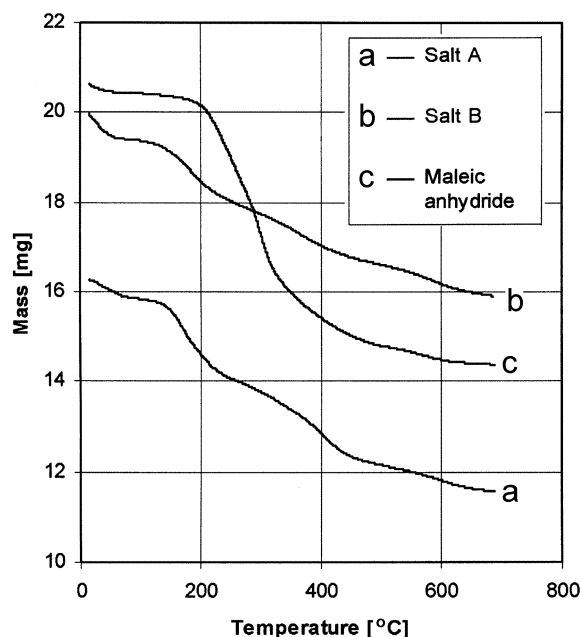


Fig.6. Thermal stability of RdH MMT modified with: a – salt A, b – salt B, c – maleic anhydride.

addition (from MMT) takes place, resulting in production of alkyl-type radical (Fig.5).

The obtained modified MMTs were used for the preparation of composites with a PP matrix. Mechanical property tests gave unexpected results: the mechanical strength of samples was poor, in contrast to former results obtained for MMT modified with maleic anhydride. For explanation of this fact, the thermal stability of the obtained modified MMT was studied using the thermogravimetric analysis (TGA) method (Fig.6).

Results of TGA measurements strongly show that the obtained ammonium salts are unstable in temperature ranges appropriate for their mixing with PP.

#### Conclusions:

- We obtained quaternary ammonium salts containing unsaturated bonds suitable for modification of MMT.
- The prepared ammonium salts undergo probably intercalation into MMT layers, as was found by wide angle X-ray scattering (WAXS) measurements.
- Mechanism of radiation-induced processes in modified MMT was proposed.
- Unfortunately, the thermal stability of modified MMT is poor, therefore such fillers cannot be used in composite based on PP. However, they are probably suitable if PE is applied as a matrix.

#### References

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## CHARACTERIZATION OF RADIATION-INDUCED GRAFTING OF ACRYLIC ACID ON VARIOUS POLYMERIC MATRICES

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The most frequently way of grafting is the procedure in which during irradiation a monomer is contacted with the surface of a polymer. The direct method requires usually much smaller doses of irradiation and, therefore, is applied for radiation sensitive polymers, e.g. polypropylene (PP). In grafting processes the radicals produced in a polymer as well as in monomers initiate covalent bonds.

Reported preliminary studies were focused on the grafting of a model vinyl monomer, acrylic acid (AAc), on three various matrices – polyethylene (PE), polypropylene (PP) and polystyrene (PS) via the gamma radiation-induced direct method. The behaviour of each individual polymer upon exposure to ionizing radiation is distinctively different. Therefore, the contribution of processes initiated by active sites situated in the matrices was estimated and compared with grafting induced by radicals generated initially in the solution. For reported in-

vestigations, Mohr's salt,  $\text{Fe}(\text{SO}_4)_x(\text{NH}_4)_2(\text{SO}_4)$ , was used as an inhibitor of homopolymerization, which was recommended by many authors, e.g. [1].

Grafting yield is determined predominantly by the level of radicals initiated both in the polymeric matrix and in solvent. The analysis of paramagnetic species performed by electron paramagnetic resonance (EPR) spectroscopy enables to estimate the ability of particular polymers to radiation-induced formation of radicals and subsequently ability to the construction of covalent bonds with monomers.

Table 1. Radiation yield of hydrogen  $\text{G}(\text{H}_2)$ .

Polymer	Radiation yield [ $\mu\text{mol}/\text{J}$ ]
PP	0.27
PS	0.036
PE	0.46

PS is considered to be the most radiation resistant polymer because of the efficient conversion of absorbed radiation energy into the heat by aromatic rings. Thus, radiation processes are very

production of alkyl radicals as well as cross-linking and the last process is the most significant in PE.

The grafting degree of AAc on PP in a function of Mohr's salt concentration (inhibitor of homopo-

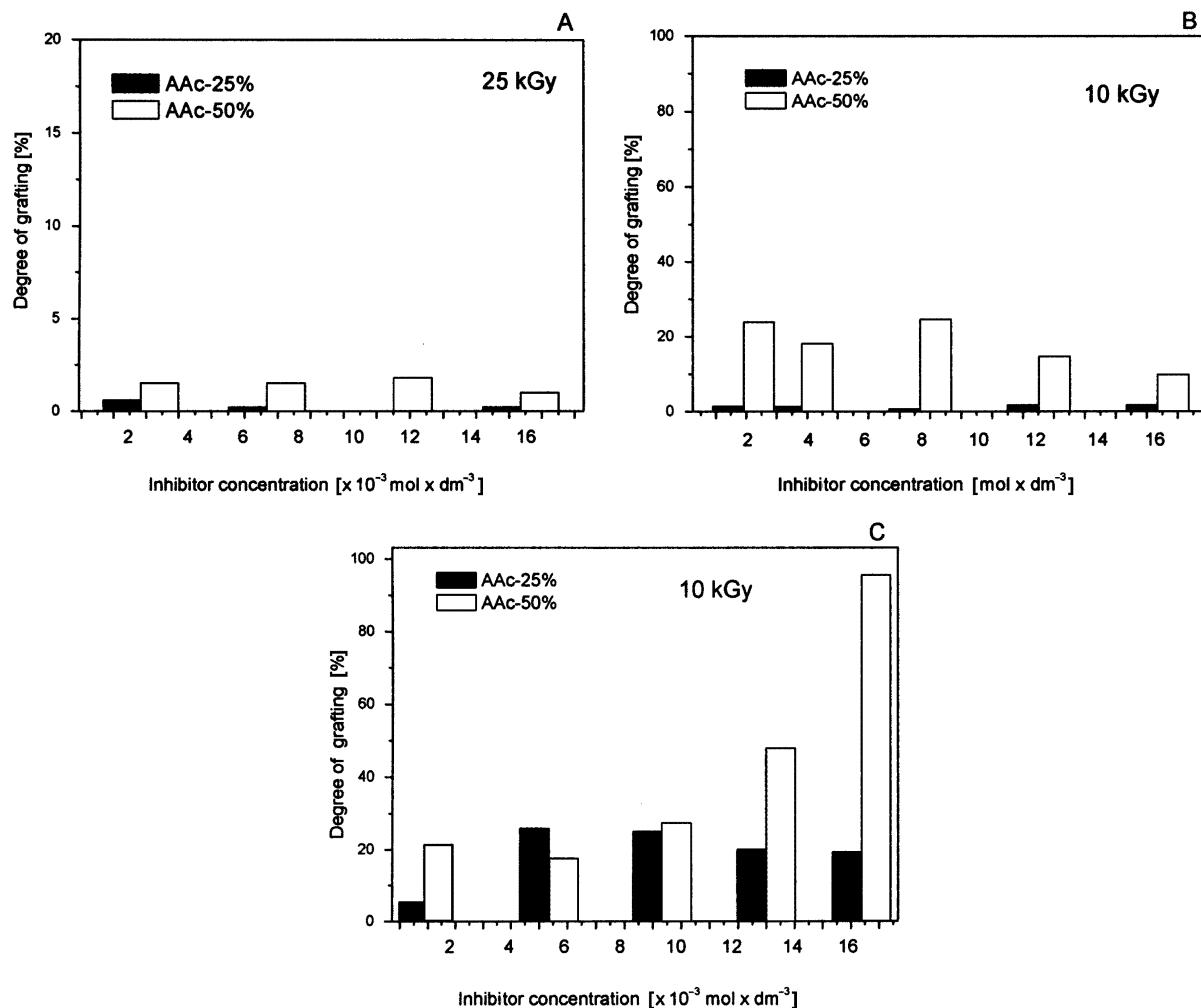


Fig. Effects of  $\text{Fe}(\text{SO}_4)_x(\text{NH}_4)_2(\text{SO}_4)_y$  concentration on the degree of grafting of AAc onto PS (A), PP (B) and PE (C).

limited and radiation yield of the radicals in PS is much lower than that found in other polymers. PE is also a radiation stable polymer, but the background of the phenomenon is different than in the case of PS. A dominant factor determining final effect of irradiation is the formation of bonds between main chains that occur in the amorphous phase. On the other hand, the population of radicals in PP is slightly smaller than in PE. A dominant product generated by ionizing radiation in PP is the third order alkyl radical that fast undergoes oxidation. The studies carried out by EPR spectroscopy confirmed that radiation yield of radicals increases in the following order  $\text{PS} < \text{PP} < \text{PE}$ .

The radicals formed in the studied polymers, PP, PS and PE, are predominantly generated upon abstraction of hydrogen. Consequently, radiation yield of hydrogen reflects indirectly the level of formed paramagnetic species. Values of  $G(\text{H}_2)$  in Table 1 reveal great discrepancies among particular polymers. The most efficient is the emission of hydrogen from PE ( $0.46 \mu\text{mol}/\text{J}$ ), smaller from PP ( $0.27 \mu\text{mol}/\text{J}$ ) and significantly minor from PS ( $0.036 \mu\text{mol}/\text{J}$ ). Dehydrogenation results in the

lymerization) is shown in Fig. The most pronounced effect of radiation-induced grafting was observed for PE. The increase in inhibitor concentration results in the gradual grow of the grafting degree. Two various tendencies support the process – high level of AAc monomers that avoid homopolymerization due to raising contents of ferrous ions and a large population of radical centres situated in the matrix. The concentration and stability of radicals generated in this backbone is higher than in irradiated PS and PP. Under experimental conditions, the degree of AAc grafting on PP reaches 25 and 95% on PE in the presence of 50% AAc, whereas for PS the yield is insignificant and does not exceed 3% even for 2.5 times higher radiation dose.

Table 2. Adsorption of ferric ions by grafted layers. Initial concentration of  $\text{Fe}^{3+}$  feed solution –  $200 \mu\text{g}/\text{ml}$ .

Sample	Average degree of grafting [%]	Average uptake [ $\mu\text{mol}/\text{g}$ ]
PE	47	65
PP	18	111

After 24 h lasting contact of grafted matrices with a feed solution containing 200  $\mu\text{g/ml}$  of  $\text{FeCl}_3$ , the adsorption yield of ferric ions by carboxyl groups was determined. The average efficiency of iron ion uptake normalized to 1 g of grafted layer is higher for PP than for PE (Table 2). It seems that the layer structure, *i.e.* grafting density and thickness, have an influence on the observed phenomenon. As was found by the EPR and gas chromatography (GC) methods, the population of radicals is higher in PE than in PP thus the distances among grafted chains for PE are shorter than for PP at the same grafting degree. The process enhances viscosity in the vicinity of grafted matrix restraining diffusion of ferric ions to carboxylic groups what results in lowering the absorption of metal ions.

The degree of radiation-induced grafting of AAc is the highest on the PE matrix, lower on PP and insignificant on PS under comparable conditions. Radiation processes in the solutions are in-

dependent of the character of immersed polymeric samples. Thus, radicals generated in the matrices have to be responsible for differences in the yields of grafting. Analyzing population of unpaired spins by EPR, it was found that concentration of radicals is consistent with increasing efficiency of grafting. The changes in radiation yield of hydrogen of PS, PP and PE also confirmed such a tendency.

However, adsorption of ferric ion by high density grafted layer (PE) is limited by increasing viscosity near the surface. Therefore, for the same degree of grafting, the process is more effective for grafted PP (layer is characterized by longer distances among grafted chains as well as longer macromolecules of PAAc) than in the case of PE matrix.

## References

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## CRYSTALLINITY AS THE BASIS FOR DISTINGUISHING THE NATURE OF RADICALS IN IRRADIATED UHMWPE

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Ultra high molecular weight polyethylene (UHMWPE) is widely applied for the production of orthopaedic prostheses (bearings in hip and knee artificial joint implantation). The influence of ionizing radiation on UHMWPE is usually considered from two points of view – as a consequence of radiation sterilization and as the effect of modification performed in order to improve some mechanical properties [e.g. 1,2]. In both cases the character of initial material is crucial. Except for radiation conditions, one of the most important factor determining final effect is the morphology of UHMWPE. Changes in the degree of crystallinity, crystal thickness and distribution involve various effects of integral radiation doses and dose rate [3]. Generally, it is accepted that UHMWPE occurs in the semicrystalline form and that ordered crys-

talline lamellae are randomly embedded in the amorphous phase of polymer. Mechanical properties and fatigue strength depend on the content of crystalline regions. The alternations in physical properties upon irradiation result from different mechanisms of free radical processes. Although second ordered alkyl radical is a dominant primary product generated upon irradiation, its fate depends strongly on the local surrounding. Irradiation induces also allyl type and polyenyl intermediates (more than three unsaturated bonds) [4].

Electron paramagnetic resonance (EPR) spectra of free radicals formed in UHMWPE of various crystallinity (85 and 50%) were detected for three days upon irradiation at fixed parameters. The examples of selected experimental spectra are shown in Fig.1. At the beginning, the signal of alkyl

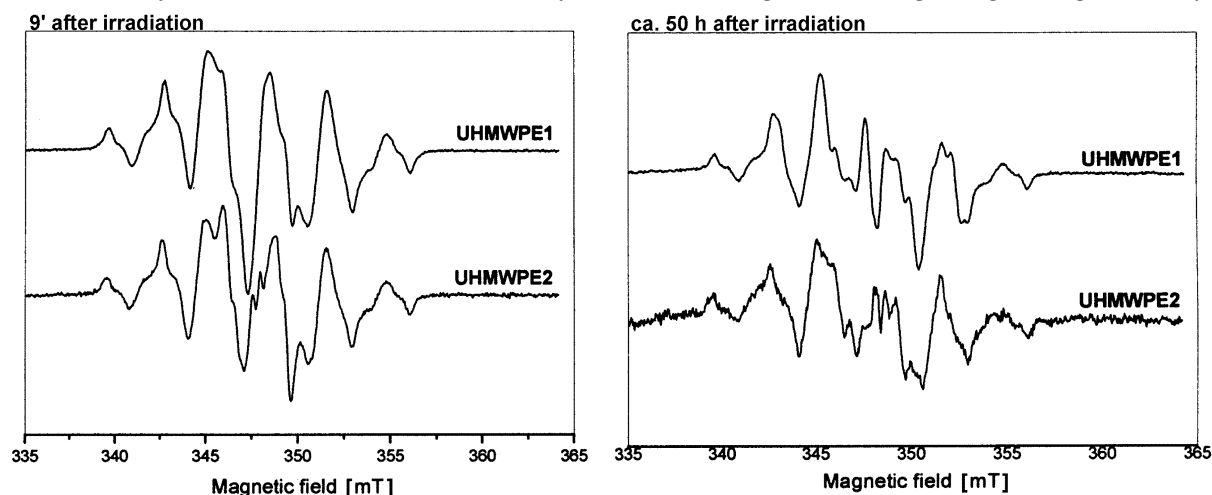


Fig.1. Left diagram – EPR spectra of irradiated UHMWPE1 and UHMWPE2 at room temperature immediately after exposure. Right diagram – EPR spectra of irradiated UHMWPE1 and UHMWPE2 at room temperature *ca.* 50 h after exposure.