Struktura 2005 - Postery

P1

SAXS AND WAXS STUDY OF UHMWPE AFTER IRRADIATION

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Ultra-high molecular weight polyethylene (UHMWPE) is used in arthroplasty as a part of total joint replacements (TJR) due to its excellent friction properties. Nevertheless, one of the main causes of TJR failures is the wear of UHMWPE, which is believed to induce osteolysis. In recent years, wear resistance of UHMWPE was enhanced by crosslinking with ionizing radiation such as accelerated electrons (-irradiation) or gamma rays (-irradiation).

In this study, both - and -irradiation were used to crosslink UHMWPE. Samples were irradiated with various doses from 0 to 200kGy. After that the specimens were remelted, i.e. heated above the melting temperature, in order to deactivate free radicals formed during irradiation, whose presence leads to oxidative degradation of material. Several remelting procedures were tested and the results were compared from the point of view of oxidation damage and macroradicals content.

Both irradiation and thermal treatment result in considerable changes in both molecular and supermolecular structure of the polymer, which influences not only its wear resistance, but also other mechanical properties. We followed the structural changes by small- and wide-angle X-ray scattering (SAXS and WAXS). As supplementary methods we used scanning electron microscopy (SEM), infrared spectroscopy (IR), electron paramagnetic resonance (EPR) and solubility tests. Combination of all above mentioned techniques allowed (i) to propose a model of structural changes during irradiation and thermal treatment and (ii) to draw some conclusions concerning optimal thermal treatment of UHMWPE.

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P2

STRUCTURE OF MONTMORILLONITE CO-INTERCALATED WITH OCTADECYLAMINE AND STEARIC ACID

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One way to find new suitable precursors for nanocomposite materials based on polymer/clay is modifying the interlayer space of clays, especially silicates like montmorillonite, with different types of organic molecules. In this work stearic acid and octadecylamine species were used for intercalation of Na-montmorillonite. Na-montmorillonite was co-intercalated by two different ways. The first one three powder substances: octadecylamine (ODA), stearic acid (STA) and Na-montmorillonite (MMT) were mixed with molar ratio 1:1:2, carefully homogenized and heated at 80 °C for one hour. The second one Na-MMT was firstly intercalated with ODA to the stage with basal spacing 33 Å and subsequently the powder mixture of ODA-MMT intercalate and STA was heated at 80°C for one hour. The molar ratio of the individual components was the same. Stearic acid itself does not intercalate into Na-montmorillonite.

Structure analysis was carried out using combination of experimental methods like X-ray powder diffraction and IR spectroscopy with molecular modeling (force field calculations) in *Cerius*^{2} modeling environment. Results of structure analysis revealed the chemical reaction of guest compounds leading to the formation of octadecylammonium stearate (ODST). This reaction may occur even before the intercalation out of the interlayer space of montmorillonite. The presence of ODST in the samples was clearly confirmed by IR spectroscopy and X-ray diffraction.

Present result showed that both ways of co-intercalation leads to the similar result. In the interlayer space of montmorillonite the formation of ODST salt is created. This structure of Na-montmorillonite intercalated with ODST does not create a stable arrangement in the interlayer space. Intercalated Na-MMT exhibits highly disordered structure with a maximum basal spacing within the range 27-39 Å. This structure is very unstable and exposure to ambient conditions has two consequences. First of all intercalate is gradually decomposed, that means part of ODST escapes from the interlayer space and the second this deintercalation is accompanied by the rearrangement of the interlayer guest structure and probable formation of the Na-stearate and octadecylammonium cations in the interlayer space. Molecular modeling showed that STA has stronger interaction with Na-cations, than with octadecylammonium cations and formation of Na-stearate in the interlayer space is highly probable. The formation of Na-stearate in the interlayer space is accompanied with rising of octadecylammonium cations compensating the layer charge. The consequence of these changes is the rearrangement of polar head-groups and gradual rearrangement of the guest structure in the interlayer space. As a result of the deintercalation we obtain a mixture of ODST salt, which escapes from the interlayer space, and the intercalated Na-MMT, where the guests are: ODST salt, Na-stearate and octadecylammonium cations. This structure of intercalate is characterized by powder diffraction pattern after 4 days in ambient conditions, where one can see the small peak at 48 Å corresponding to the ODST salt, and peak at 28 Å corresponding to the liquid like arrangement of the ODST and Na-stearate and peak at 18 Å corresponding to the MMT intercalated with octadecylammonium. Anyway the character of the interlayer structure, i.e. the monolayer liquid like arrangement of the chains does not promise the easy exfoliation required for polymer-clay nanocomposite precursor.

P3

SOLVATOMORFIE VYBRANÝCH PŘÍRODNÍCH A SEMISYNTETICKÝCH ERGOPEPTINŮ

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Námelové alkaloidy jsou produkty parazitické houby paličkovice nachové - *Claviceps purpurea*. Jedná se o látky farmaceuticky aktivní. Známá je jejich neselektivní afinita k různým dopaminovým, serotoninovým a -adreno receptorům. Jak přírodní, tak zejména chemicky modifikované – semisyntetické formy námelových alkaloidů nacházejí široké terapeutické uplatnění v medicíně, např. při léčbě migrény, kognitivních poruch a mnoha dalších chorob [1].

Zkoumání polymorfie a solvatomorfie farmaceuticky aktivních látek je velmi důležité, nebo jednotlivé polymorfy (solvatomorfy) se od sebe mohou lišit farmakokinetickým profilem a biodostupností.

Byly připraveny krystalické formy přírodních námelových alkaloidů ergocristinu a ergotaminu, a to ve formě bis(benzen) soldátů. Jejich struktura byla stanovena pomocí RTG difrakce na monokrystalu. Prostorové uspořádání a konformace molekul přírodních námelových alkaloidů byly porovnávány s jejich solvatomorfy nalezenými v CSD – ergotaminem tartarátem ethanol solvátem [2] a ergocristinem aceton solvátem [3]. Provedeno bylo také porovnání s jejich semisyntetickými deriváty. Navzdory jejich chemické podobnosti se obě struktury liší nejen svými mřížkovými parametry, ale také velikostí a tvarem dutin, v nichž jsou umístěny molekuly solventu.

Dále byla připravena řada solvatomorfů námelového alkaloidu ergocorninu (monohydrát acetonitril solvát, monohydrát bis (nitromethan) solvát, bis (ethanol) solvát, hemihydrát bis (i-propanol) solvát, monohydrát bis (n-propanol) solvát a monohydrát hydrát bis (methanol) solvát), jejichž struktura byla rovněž stanovena pomocí RTG difrakce na monokrystalu. I u těchto molekul bylo provedeno vzájemné porovnání prostorového uspořádání. Všechny solvatomorfy krystalují ve stejné prostorové grupě, v mřížkových parametrech se však navzájem liší.

Tato práce byla podpořena v rámci výzkumného projektu CEZ: MSM 223100002 Ministerstva školství, mládeže a tělovýchovy České republiky a projekty Č. 203/00/D095, Č. 203/02/0436 and Č. 203/99/M037 Grantové agentury České republiky.

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P4

EXSOLVED PYROXENES FROM SEDLICE ULTRAMAFITE BODY, EASTERN SLOVAKIA

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Pyroxenes are important rock-forming minerals. They are common in ultramafite bodies, in Western Carpathians in *Ol – Spl – Opx – Cpx* assemblage.

Typical feature of pyroxene-group minerals is presence of silicon tetrahedrons in the crystal structures arranged to so-called „pyroxene chains“, parallel to *Z* coordinate axis, and the chains must have the *c* glide plane symmetry [1]. The same symmetry have two octahedral chains, containing two non-equivalent cation positions designated as *M*(1) and *M*(2). There are two principal pyroxene groups: orthorhombic (*Opx*) and monoclinic (*Cpx*). *Opx* belong to the unique space group *Pbca*. In the class of *Cpx* the situation is more complicated. Ionic radii of cations in *M*(2) versus *M*(1) positions are decisive for different space-group symmetry. If $M(2)^{VIII} > M(1)^{VI}$, then space group $C2/c$ arises. Whereas $\mathrm{M}(2)^{VI}$ $M(1)^{VI}$, pyroxenes with $P2_1/c$ space-group occur. Extreme is the case if $\mathrm{M}(2)^{VI} < M(1)^{VI}$, then *C*2 symmetry appears [1].

At elevated temperatures all pyroxenes have $C2/c$ symmetry. During cooling of rock systems following phase transitions become possible: $C2/c$ *Pbca*, $C2/c$ $P2_1/c$, originally $C2/c$ symmetry remains unchanged. The mentioned phase transitions are realized in solid state. As a consequence of this process, exsolution phenomena give rise, having the form of exsolution lamellae and/or granular exsolutions (fig. 1 and 2).

Orientational relationship between host and exsolved phase depends on symmetry of both phases and they can occur as $Pbca_{host}$ - $C2/c_{lam}$ parallel to $(100)_{host}$, $C2/c_{host}$ - $P2_1/c_{lam}$ parallel to $(100)_{host}$ and $(001)_{host}$ and $Pbca_{host}$ - $P2_1/c_{lam}$ parallel to $(100)_{host}$. The orientations correspond to exsolution events, but at present time, the real orientations must be slightly different from the idealized due to non-equal thermal contractions of both – host and exsolved phases.

Not so frequent are exsolutions of euhedrally shaped spinels in *Opx* (fig. 3, 4).

We made preliminary works about these phenomena using samples from the only one low serpentinised ultramafic (spinel lherzolite) body near Sedlice village, Eastern Slovakia. All the samples pictures are taken from this locality.

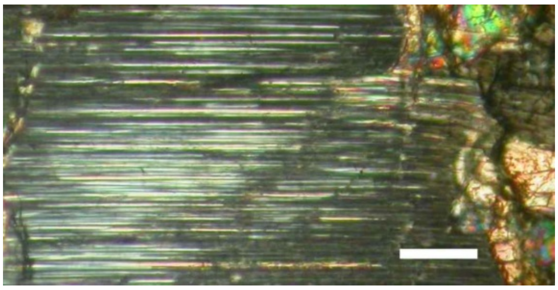

Fig. 1. Microphotograph of exsolution lamellae of *Cpx* in *Opx*, crossed polars, scale bar 100 m.

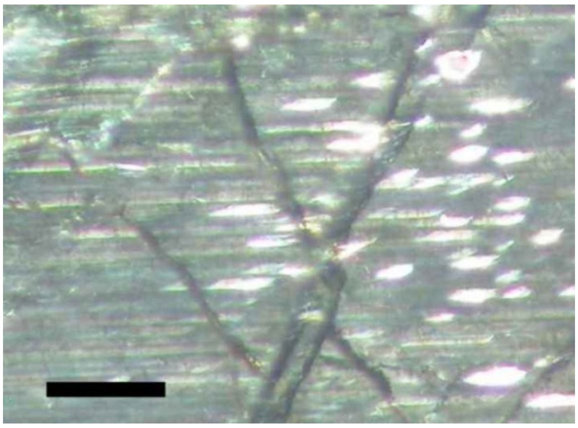

Fig. 2: Microphotograph of lamellar and granular exsolutions of *Cpx* in *Opx*, Crossed polars scale bar 100 m.

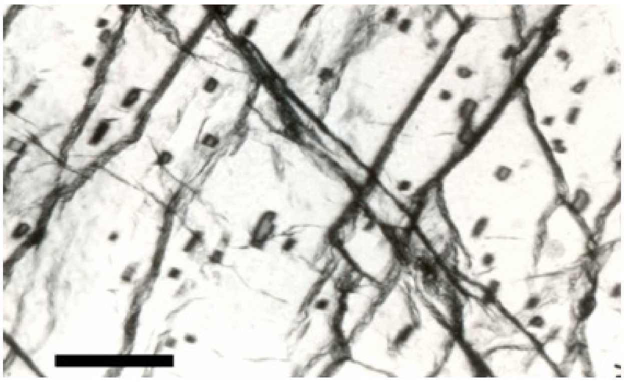

Fig. 3: Microphotograph of exsolved spinel (view down approximately $[100]_{Spl}$) in *Opx*, parallel polars, scale bar 200 m.

Petrological experimental studies were based on CMS (CaO – MgO – SiO_2), CMAS (CaO – MgO – Al_2O_3 – SiO_2), CFMS (CaO – FeO – MgO – SiO_2) systems. Results were obtained for *Opx – Cpx*, *Opx – Cpx – Spl*, *Cpx* – Ol – *Spl, Opx – Ol – Spl* and *Ol – Spl* phase equilibria.

Presented results are based on petrological works published in70’s and 80’s [2]. Interpretation of the follows:

1. crystallization of *Opx* from melt at 1297° C and 51 kbar pressure,
2. exsolution of *Cpx* lamellae and subsequent reequilibration of *Opx* – Cpx_{lam} assemblage at 1098° C and 19 kbar,
3. corrosion of *Opx* by matrix mineral phases *Cpx– Ol,*
4. reequilibration of *Opx* – Cpx_{matrix} at 966° C and 11 kbar,

5. reached equilibrium of *Opx* – matrix minerals at 944° C and 11 kbar,
6. last event was equilibration of *Ol* – *Spl* in solid state at 812° C.

Suggestions for future work are: detailed studies of exsolution phenomena with TEM experiments (SAED and CBED) [3], study of real phase boundaries between host and exsolved phases. Treatment of fluid inclusions, and application of recent experimental petrologic works will also be done.

The study was supported by grant # 1/2030/05, of the Grant Agency of Slovak republik (VEGA).

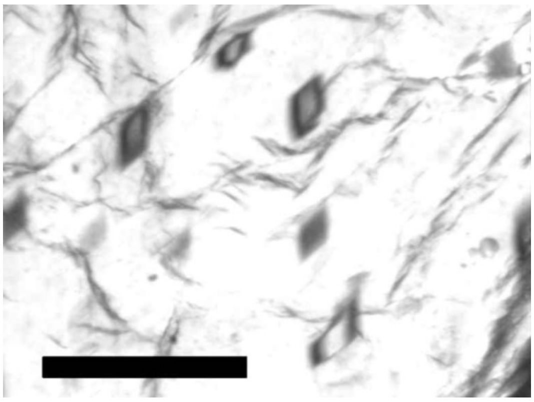

Fig. 4: Microphotograph of exsolved spinel (view down approximately $[110]_{Spl}$) in *Opx*, parallel polars, scale bar 200 m.

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P5

PREPARATION AND CHARACTERISATION OF ANALCIME BY X-RAY AND SEM.

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Leucite($KAlSi_2O_6$) based materials having high fracture toughness and being useful for making ceramic-fused-to-metal restorations [1] represent a very promising composite material for dental applications. For its extensive use is, however, necessary to develop a suitable and reproducible technology of its preparation. This can be achieved either by the direct hydrothermal synthesis of leucite or by the ion-exchange of analcime ($NaAlSi_2O_6 \cdot H_2O$) as a precursor. The purpose of this study was to investigate the synthesis of analcime and the effect of principal factors influencing its crystallisation. Analcime powders were prepared by hydrothermal synthesis in a Teflon lined stainless steel autoclave. The role of the composition of the reaction mixture (source materials, silica/alumina ratio, OH^- concentration, and water concentration), reaction temperature and time was studied.

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P6

NANO-MECHANICAL PROPERTIES OF CARBON AND SILICON FILMS

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A short paper will be published in next issue.

P7

MDFT PROGRAM: CALCULATION OF 2D AND 1D DIFFRACTION PATTERNS FROM ELECTRON MICROGRAPHS

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