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Novel phosphorus-containing polymers – synthesis, properties and applications

This dissertation provides the description of syntheses, properties and application potential of novel phosphorus-containing polymeric materials.

The dissertation consists of the description of synthesis procedures and characterization of four groups of materials:

1. Hydrogels/superabsorbent polymers (SAPs) obtained using acrylic acid (AAc), 2-(methacryloyloxy)ethyl phosphate (MEP) or bis[2-(methacryloyloxy)ethyl] phosphate (BMEP).
2. Interpenetrating polymer networks (full-IPNs), where P(MEP) was applied as a first component network, whereas selected AAc/BMEP copolymer (point 1) acted as a second component network.
3. Phosphorylated polyether polyols based on sucrose and glycerin (Rokopol® GS364, Rokopol® GS484), which can be further applied in the preparation of full-IPN type hydrogels as a first component network. For the second component network AAc/BMEP copolymer (point 1) was repeatedly chosen.
4. Interpenetrating polymer networks (full-IPNs), where N-vinylformamide (NVFAm) crosslinked with pentaerythritol triacrylate (PETA) was applied as a first component network and, similarly to cases presented in points 2 and 3, AAc/MEP copolymer acted as a second component network.

The aforementioned polymers were synthesized by free radical polymerization employing bulk polymerization technique. The choice of monomers and synthesis technique are crucial factors that circumstantiate the aim of this work, especially when future application purpose of obtained polymers is considered.

Organophosphates exhibit limited hydrolytic stability. According to literature reports, MEP may undergo hydrolysis in water by two possible mechanisms. One of them leads to the creation of phosphoric acid and 2-hydroxyethyl methacrylate (HEMA). This feature was employed within present work as the possibility of using this monomer in the role of phosphorus source, which can be released from hydrogel in the course of hydrolysis. Phosphates, e.g. potassium salt of phosphoric acid, are one of the most important fertilizers

used in agriculture. Phosphorus, alongside potassium and nitrogen, is one of the primary macroelements, however plants often suffer from its deficiency in soil. Phosphorus scarcity leads to negative physiological and metabiological effects, what in due course may result in crops depletion and, at the same time, serious economic losses. Phosphorus resources are finite and non-renewable, therefore its sustainable usage is of crucial importance, all the more since excessive use of this element causes negative effects in aquatic ecosystems, such as eutrophication.

In the course of research involving the first group of described materials, low hydrolytic stability of MEP and BMEP was confirmed, which allowed to use aforementioned polymers for phosphorus release purposes. Because of this feature, hydrogel beside its primary role as water reservoir is also an instrument for controlled release of elements necessary for plants optimal growth (slow release device – SRD, slow release fertilizer – SRF, slow release fertilizer hydrogel – SRFH). Furthermore, the presence of tetrafunctional BMEP monomer in commercial MEP was confirmed and made use of – to the best of my knowledge, MEP monomer was used in hydrogels synthesis as a crosslinking agent for the first time. Due to the fact that both compounds undergo hydrolysis and BMEP hydrolysis is tantamount to the decrease of crosslinking degree, hydrogels change their properties as the time passes – the release of phosphates is followed by the increase of the ability to absorb water. This property is, however, possible to observe only for materials with certain nominal crosslinking degree. It is also worth to mention that BMEP was first used in agricultural hydrogels synthesis not sooner than in 2016. By this time, the research considering hydrogels described herein was already being conducted.

Many of the commercial hydrogels applied in agriculture are produced employing acrylamide (AAm). In recent years this approach is rather controversial, especially when toxic and carcinogenic properties of AAm are taken into consideration and, at the same time, the consequences to which applying this monomer in the production of agrogels may lead. The AAm and its derivatives replacement with organophosphorus compounds, which are not only less toxic, but also may provide additional functions while being the part of hydrogels structure, seems to be completely justified.

The dissertation provides new information about enumerated organophosphorus monomers and polymers. Materials presented herein are novel and exhibit most of all a very good ability to absorb water. The presence of acidic functional groups determines the ability of changing the properties due to environmental conditions, simultaneously promoting those

polymers as smart materials. It was proven that manipulation of such properties is possible not only by the choice of components and their mutual ratios, but also with the polymerization technique.

Ultimately, properties of presented hydrogels should fulfill the needs of agricultural sector, so its characterization was performed with respect to this particular application. The characterization involves the ability to absorb water, properties under different pH, ionic strength and simulated conditions, hydrolytic stability, spectroscopic analyses. The properties of obtained materials were collected and compared with those of chosen commercial agricultural hydrogels which contain acrylamide or its derivatives' units within their structure.