Hybrid polymer containing ferric oxides obtained using a redox polymer
Part I. Synthesis and characterization

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Abstract: A hybrid polymer containing hydrated iron oxide was obtained in a one-step redox process. Macroporous S/DVB copolymer containing *N*-chlorosulfonamide groups in Na^+ form ([P]–SO_2NClNa) was used as a macromolecular oxidant for Fe(II) ions which in the form of iron oxide were deposited within a polymer matrix. The final product ([P]–$SO_2NH_2\#5Fe_2O_3\cdot 9H_2O$) contained 12 % Fe(III) in the form of ferrihydrite which presence was confirmed by FT-IR and Mössbauer spectroscopic studies. The deposition of iron oxide caused reduction in BET surface and porosity of the host material.

Keywords: hybrid polymers, iron oxides, redox polymers, nanocomposites.

Polimer hybrydowy zawierający tlenki żelaza otrzymany z wykorzystaniem polimeru redoksowego. Cz. I. Synteza i charakterystyka

Streszczenie: Polimery hybrydowe typu polimer/tlenki żelaza stanowią grupę materiałów o doskonałych właściwościach adsorpcyjnych. W pracy przedstawiono syntezę tego typu polimeru hybrydowego opartą na reakcji utleniania jonów Fe(II) za pomocą makroporowatego, redoksowego kopolimeru S/DVB z *N*-chlorosulfonamidowymi grupami funkcyjnymi w postaci soli sodowej ([P]–SO_2NClNa). Otrzymany materiał ([P]–$SO_2NH_2\#5Fe_2O_3\cdot 9H_2O$) zawierał 12 % Fe(III) w postaci ferrihydrytu. Z przeprowadzonej analizy zdjęć SEM produktu wynika, że depozyt żelazowy był zdyspergowany w matrycy polimeru równomiernie, a jego wprowadzenie nie spowodowało degradacji struktury polimeru (rys. 1a i 1b). Wykazano jednocześnie, że w odniesieniu do wartości odpowiadającej polimerowi wyjściowemu, zmniejszeniu uległa powierzchnia BET (tabela 1). W widmach IR stwierdzono obecność pasm charakterystycznych dla struktury ferrihydrytu (rys. 2). Obecność ferrihydrytu potwierdziły również widma Mössbauera (rys. 3). Otrzymany polimer hybrydowy wykazywał cechy paramagnetyczne oraz amorficzne.

Słowa kluczowe: polimery hybrydowe, tlenki żelaza, polimery redoksowe, nanokompozyty.

Composite materials with incorporated inorganic nanoparticles (dispersed or doped) within the structure of organic or inorganic polymers found many applications in catalysis, separation technology, optics, electronics, protective coatings and medicine [1—4]. The examples of such materials are hybrid products obtained by incorporation of iron oxide into the matrix of porous organic polymers *e.g.* ion exchangers [5—8].

Ferric oxides are inexpensive, readily available, harmless and stable reagents, which have long been used in catalysis as well as in separation processes [9—11]. Along with development of the nanotechnology, reports on various ferric oxide nanoparticles, of heterogeneous size and morphology, *i.e.* amorphous nanoparticles as well as nanocrystalline polymorphs in the form of powders, composites, layers, thin films or coated particles, have been published [12]. These fine materials, having an extremely high surface area to volume ratio of the particles, offer very favorable sorption, redox and magnetic properties. Isolated structures of nano- and microparticles tend to aggregate into bigger clusters, which reduces the active surface. It also causes difficulties with application in fixed-bed unit flow systems due to a drop in hydraulic pressure resulting in clogging up of the bed.

In several studies it has been shown that dispersed ferric oxide particles included in structures of high molecular weight materials (insoluble but swelling in water), combine favorable sorption properties of the inorganic nanoparticles with the excellent hydraulic characteristics of ion exchanger spherical beads. One way to obtain hybrid polymers involves taking advantage of the reactivity of ion exchange resins: highly crosslinked, high molecular weight materials, which show high physical, chemical and thermal strength. The characteristic feature of these materials is their geometric porosity, high surface area, as well as the presence of functional groups with cationic or

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anionic properties, which enable iron oxide to be deposited within a polymer matrix.

In many works sulfonated styrene-divinylbenzene copolymers (gel-typed, macroporous, mesoporous) were used as three-dimensional carriers of iron oxide nanoparticles. Incorporation of these nanoparticles into the inner construction of the cation exchange resins was possible using two main synthesis routes: (a) alkaline oxidation of ferrous ions sorbed by functional groups of the resin [5, 6, 13], and (b) forced hydrolysis of ferric ions sorbed by functional groups of the resin [7, 8, 14—17]. In other publications, strong base type macroporous anion exchangers having quaternary ammonium functional groups and styrene/divinylbenzene matrix were used to embed iron oxide nanoparticles [18—22]. Dispersing hydrated ferric oxide nanoparticles within a resin structure is scientifically challenging because the ferric ion and quaternary ammonium group are both positively charged. The essence of this multi-step process was the oxidation of ferrous ions by OCl^-, MnO_4^- or $Cr_2O_7^{2-}$ ions adsorbed by functional groups of the parent resin.

In many papers it has been reported that the polymeric matrix is not only a carrier of the dispersed inorganic phase, but also has a large influence on the formation of its structure, both crystalline (such as hematite, maghemite, goethite or magnetite) and amorphous. The chemical route of synthesis, the nature of the polymer matrix and the polymer morphology strongly affect the composition of the end product [13, 23, 24].

The hybrid polymers described to date were obtained using cation or anion exchangers as supporting material in several-stage processes. We obtained a hybrid polymer by a different method. A copolymer of our own production, which containing functional groups with oxidizing properties (not ion exchange properties), was used as a high molecular weight starting material, whereas an aqueous solution of $FeSO_4$ was used as the reducer:

$$\begin{gathered}[P]\text{-}SO_2NClNa + 2\ FeSO_4 + 6\ H_2O \rightarrow \\ [P]\text{-}SO_2NH_2\ \#2\ Fe(OH)_3 + NaCl + 2\ H_2SO_4\end{gathered} \tag{1}$$

[P] — signifies the copolymer styrene/divinylbenzene macroporous structure, # — within polymer matrix.

The used copolymer is a high-molecular weight analogue of the well-known low molecular oxidants, such as chloramine-T. This polymeric material shows strong oxidizing properties and has been used already many times to remove toxic admixtures (having the character of reducers) from diluted aqueous solutions [25—30]. The deironing of water (from trace amounts of Fe(II)) is one of the redox processes where such water-insoluble oxidants can be applied. As a consequence of this study, we found that it was possible to obtain specific polymer materials, which include dispersed iron oxide/hydroxide particles in their internal structure, using suitable conditions [31, 32]. In the present study, instrumental methods were used to characterize the iron oxide precipitated in a matrix of a macroporous styrene-divinylbenzene sulfonamide copolymer (S/DVB).

EXPERIMENTAL PART

Materials

A crosslinked S/DVB copolymer containing 2.30 mmol/g of $-SO_2NClNa$ groups (*i.e.* 4.60 meq/g of active chlorine of the resin) was used as a heterogeneous oxidant. The quoted content of active halogen in the copolymer refers to the constant mass of air-dried product. The redox copolymer also contained a small quantity of sulfonic groups (less than 0.50 mmol/g) as a result of hydrolysis which occurs as a side reaction during the sulfonamide preparation.

The copolymer was prepared by chemical modification of a sulfonic cation exchanger using methods published elsewhere [32]. As a starting material was used Amberlyst 15 (produced by Rohm and Haas Co.), a commercially available sulfonic cation exchanger. This is a macroporous poly(S/20 % DVB) resin which in the air-dried state contained 4.7 mmol of $-SO_3H$/g; surface area 45 m^2/g; average pore diameter 25 nm; uniformity coefficient < 1.70; harmonic mean size 600 to 850 μm. We transformed its initial functional groups to chlorosulfonyl, and then to sulfonamide groups, which joined the active chlorine atoms as a result of the sodium hypochlorite reaction:

$$[P]\text{-}SO_3H \rightarrow [P]\text{-}SO_2Cl \rightarrow [P]\text{-}SO_2NH_2 \tag{2}$$

$$[P]\text{-}SO_2NH_2 + NaOCl \rightarrow [P]\text{-}SO_2NClNa + H_2O \tag{3}$$

All the reagents were of analytical grade. For the preparation of hybrid polymer 0.075 M $FeSO_4$ aqueous solution was used as the reducing agent.

Preparation of the hybrid polymer

The synthesis was carried out in batch regime: ~ a 5 g dried sample of the resin was placed in a flask and treated with 0.075 M of $FeSO_4$ solution (650 cm^3) providing *ca.* 2:1 molar excess of Fe(II) in relation to the amount required by stoichiometry. The flask was airtight closed and shaken at the temperature 22 °C in the dark for 24 hours. Subsequently the resulting suspension was filtered and the resin was thoroughly washed with water and 200 cm^3 of aqueous ethanol (1:1). The resulting product was dried at 60 °C for 24 hours.

Methods of testing

— In order to determine the Fe(II) and Fe(III) content in the polymer matrix, 0.5 g hybrid polymer samples were treated with 25 cm^3 of 2 M H_2SO_4 solution for 24 hours. The obtained solution was analyzed for the content of both ions with spectrophotometric methods. The concentrations of Fe(II) and Fe(III) were measured using a Spekol 1200 spectrophotometer (Analytik Jena, Germany). Fe(II) and Fe(III) were determined with respectively 1,10-phenanthroline and potassium thiocyanate. Absorbance measurements were taken at 510 and 480 nm, respectively [34].

— Microscopic examinations were performed with a HITACHI S-3400N scanning microscope equipped with an EDS microanalyzer (4 nm, BSE detector).

— The porous characteristics of the polymeric supports and hybrid polymers were determined from the adsorption isotherms for liquid nitrogen at 77 K using Accelerated Surface Area and Porosimetry Analyzer ASAP 2020, 2007, Micrometrics.

— X-ray powder diffraction (XRD) patterns were recorded with an ULTIMA IV/Rigaku/2008 instrument operated at 40 kV and 40 mA with Cu Kα radiation at the wavelength of 0.15406 nm.

— Far infrared spectra in the range 50—700 cm^{-1} were recorded in a Nujol mull using the 2000 FT-IR Perkin-Elmer Spectrometer.

— Mössbauer spectrum was measured using a POLON spectrometer with a conventional constant acceleration drive system. During the measurements the source $^{57}Co/Rh$ and the samples remained at the room temperature. Isomer shift δ is given with respect to α-Fe. The Mössbauer parameters were obtained from the experimental data by means of the MOSSFIT-96 fitting program.

RESULTS AND DISCUSSION

Reaction of *N*-chlorosulfonamide S/DVB copolymers with iron(II) sulfate aqueous solutions at different acidity was described in the previous study [31]. Our method of preparing hybrid polymers has several special, favorable features: (i) products are prepared in a very simple way — in a single-stage process at the room temperature (22 °C); (ii) there is a high content of active chlorine (over 4.0 meq/g) in the resin, which allows one to obtain hybrid polymers with a very high content of iron oxides; (iii) the hybrid polymers contain desirable ferric oxide particles, but they do not contain ion exchange functional groups (this can be favorable in some cases). In order to obtain hybrid material containing the highest possible iron deposit, the reaction was conducted in a solution without pH adjustment (pH = 3.0). Taking into account properties of ferrous and ferrite solutions, both acidic and alkaline conditions were disadvantageous [dissolution of iron oxide in the acidic environment and low persistence of Fe(II) ions in the alkaline environment]. The reaction was carried out in a batch regime so as to obtain a product, whose beads were homogeneous. Synthesized hybrid material had the appearance of grayish-brown beads and contained 12 % of Fe(III) and 0.39 % of Fe(II) in the form of iron oxide. The characteristics of the polymeric support and hybrid polymer are presented in Table 1.

The morphology of the obtained hybrid polymer is presented in the SEM images shown in Fig. 1. As can be seen, the method of iron oxide deposition did not cause degradation of the polymer matrix and the beads kept their previous shape. Although no aggregates of iron oxide deposited on the polymer surface were observed, the EDS analysis confirmed the presence of iron within the outer and inner surface of the beads, whose content at different points of the surface was the same order of magnitude, from several percent to a dozen percent. These results showed that iron oxide particles were well-dispersed throughout the polymer matrix. The porosity characteristics of the starting polymer and the hybrid polymer are listed in Table 1. Both raw material and product exhibited relatively high BET surface area (as S/DVB reactive

Table 1. Characteristics of polymeric materials — raw materials and product

	Sulfonamide copolymer	*N*-chloro-sulfonamide copolymer	Sulfonamide copolymer containing iron oxide
Sample code	R/S	R/ClNa	R/S/Fe
Polymer matrix	S/DVB[1)]	S/DVB[1)]	S/DVB[1)]
Chemical constitution	$-SO_2NH_2$	$-SO_2NClNa$	$-SO_2NH_2\#5Fe_2O_3\cdot 9H_2O$
Main functional group, mmol/g	3.9	2.3	2.3[2)]
Retained $-SO_3^-$ group, mmol/g	0.5	0.3	0.3[2)]
Fe(III) content, %	–	–	12
Fe(II) content, %	–	–	0.39
BET surface area, m^2/g	50.98	36.86	34.25
Total pore volume, cm^3/g	0.3532	0.2832	0.1944
Micropore volume, cm^3/g	0.0000	0.0001	0.0003
BJH desorption average pore diameter, nm	31.2	31.5	17.6
Average pore diameter, nm	27.7	30.7	22.7

[1)] Macroporous styrene-divinylbenzene copolymer; [2)] Assessment based on mass comparison before and after reaction of Fe(II) oxidation (constant mass).

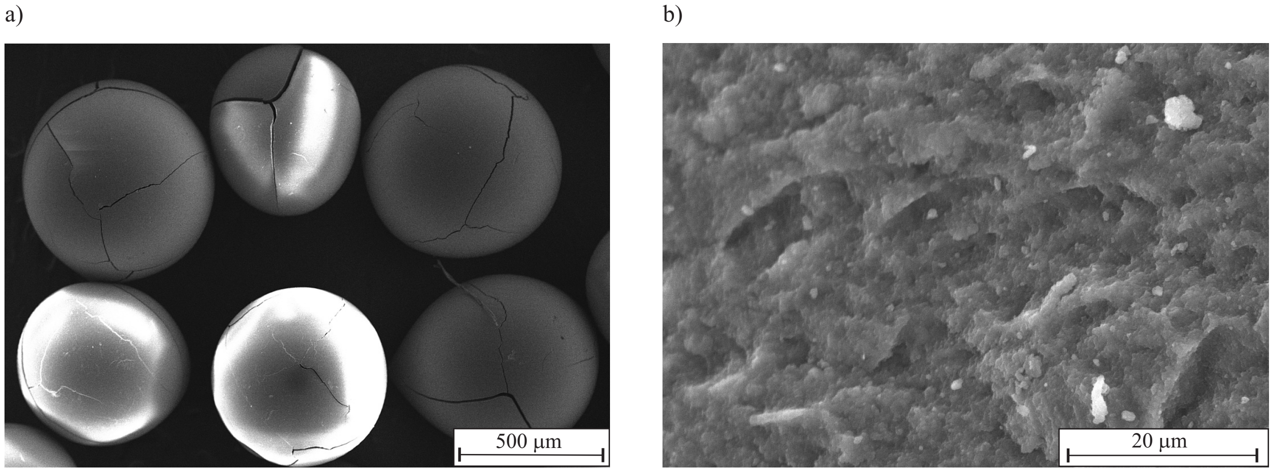

Fig. 1. SEM images of hybrid polymer containing iron oxide

polymers) and mesoporous structure. Analysis of the N_2 adsorption-desorption isotherms and shape of the hysteresis showed adsorption of type III, indicating bottle-shaped pores. From the comparison of S_{BET}, pore volumes and average pore diameter, it is evident that the textural structure of the hybrid polymer (R/S/Fe) is different from that of the host material (R/S). Incorporation of iron oxide within the polymer matrix caused a reduction of its porous structure. These results suggest that the surface of the supporting polymer was covered with a thick film of iron oxide.

The results of X-ray diffraction analyses presented in the literature [7, 13] revealed that some methods of iron oxide incorporation into an amorphous polymer matrix led to deposition of its crystalline polymorphs (reflections characteristic for maghemite and magnetite were observed). Therefore, in this study, XRD analysis of obtained hybrid polymer was also performed. The measured XRD pattern was characteristic for amorphous materials, which indicates that iron oxide encapsulated within the polymer matrix was probably also of amorphous nature.

The IR analyses were performed in the far-infrared region, since the characteristic absorption bands, due to Fe-O lattice vibrations, are at lower wavenumber. The IR spectra shown in Fig. 2 were measured for sulfonamide S/DVB copolymer, hybrid polymer containing iron oxide and iron oxide obtained by oxidation of Fe^{2+} with NaOCl. The spectrum of obtained hybrid polymer showed evident changes as a result of iron oxide deposition within the polymer matrix and presented absorption bands characteristic for both organic and inorganic components. The bands observed at 695—755 cm^{-1} are assigned to CH out-of-plane bending in aromatic ring and the features at 683, 563, 520, 623 may be assigned to respectively $\omega(NH_2)$, $\omega(SO_2)$, $\delta(SO_2)$ vibrations of the $-SO_2NH_2$ group in the polymer matrix. The bands observed in the range 660—695 cm^{-1} and at 420 cm^{-1} and 278 cm^{-1} indicate the presence of iron oxide and correspond respectively to Fe-OH-bending and Fe-O-bonds [35]. The obtained IR spectra can be assigned to both δ-FeOOH and ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$). Therefore the exact nature of the inorganic deposit could not be determined.

The Mössbauer spectrum of the obtained hybrid material measured at the room temperature included a cen-

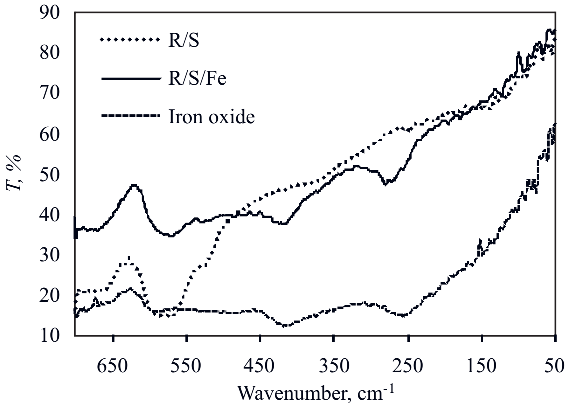

Fig. 2. Far infrared spectra of polymer matrix — sulfonamide S/DVB copolymer — R/S, hybrid polymer containing iron oxide — R/S/Fe and iron oxide obtained by oxidation of Fe(II) with NaOCl

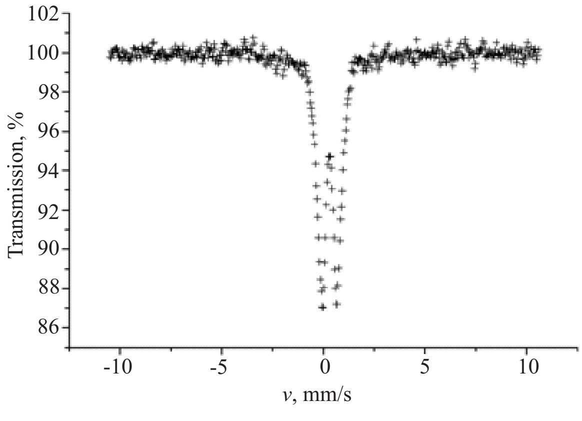

Fig. 3. Mössbauer spectrum of hybrid polymer R/S/Fe recorded at 25 °C

tral paramagnetic doublet assigned to high-spin Fe(III) (Fig. 3). The value of isomer shift of the doublet was 0.28 mm/s and its quadrupole splitting was 0.78 mm/s. The doublet parameters were indicative of the presence of ferrihydrite and confirmed the results of infrared spectroscopy.

The spectroscopic results explained the lack of reflections in the XRD pattern because ferrihydrite low-intensity and broad reflections were masked by a high background of amorphous structures such as polymer matrix. Presence of ferrihydrite in the hybrid material is advantageous since amorphous iron oxides are known to be especially effective adsorbents compared to crystalline forms [9].

CONCLUSIONS

In the present study a hybrid material containing iron oxide deposited in the polymer matrix was obtained. Using as a starting material S/DVB copolymer with functional groups with oxidizing properties enabled us to produce in a one-step process a hybrid polymer containing 12 % Fe(III). The analyses revealed that iron oxide was in the form of ferrihydrite, and its deposition reduced the porous structure of the polymer matrix, whose outer and inner surface was covered with a thick film of iron oxide.

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