CROSS-LINKED MACROPOROUS POLYMERS AND COPOLYMERS, THEIR SYNTHESIS AND CHARACTERIZATION

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In this work the synthesis of porous poly(methyl methacrylate) PMMA was carried out by polymerization in the suspension, while the synthesis of porous poly(methyl methacrylate-co-acrylamide) PMMA-AA copolymer was carried out by polymerization in the emulsion. Both types of polymerization were carried out in the presence of inert compounds. The morphology of the created pores was determined by SEM microscopy. The pore volume and specific surface of porous polymers were determined by mercury porosimetry. The pore volume was in the range from 0.03 to 0.64 cm³ per gram of PMMA and 3.25 cm³ per gram of PMMA-AA. The specific surface was from 9 to 17 m² per gram of PMMA and 22.7 m² per gram of PMMA-AA. The amount of residual monomers decreased for about 10 times in polymers and copolymers after boiling in water. Enzyme α-amylase was immobilized 22.9 mg per gram of the polymer on the PMMA surface and 26.4 mg of the enzyme per gram of the polymer on PMMA-AA. The hydrolysis rate of starch using the immobilized enzyme is 0.394 mg of starch/min·g of PMMA polymer and 0.507 mg starch/min·g of PMMA-AA copolymer.

Keywords: porous polymers, X-ray diffraction, SEM, mercury porosimetry, HPLC analysis, residual monomers

Introduction

Poly(methyl methacrylate) has been produced as an industrial polymer for a very long time and has a wide application. The first chemical synthesis of poly(methyl methacrylate) was done by Wilhelm Rudolph Fitting in 1877. The polymer glass called Plexiglas was patented by Otto Rohm in 1933. The first industrial synthesis was accomplished in 1936 and that was when poly(methyl methacrylate) became commercially available. During the Second World War its production experienced a great expansion.

Materials with different purposes are obtained by the synthesis of macro-porous polymer. Macro-porous polymers with closed pores give foam polymers which are used as light-weight constructional materials, as isolators or as sponge materials. Macro-porous polymers with open pores can be used to obtain different types of ion exchange resins, as adsorbents and as inert carriers of catalyst particles, enzymes or microbial cells.

Macro porous copolymer of methyl methacrylate base synthesized by the suspension copolymerization with glycidyl methacrylate (specific surface area of 12-70 m²/g and the volume of pores to 1 cm³ / g) can be used for a selective sorption of metal ions [1-3]. Also well-known is the synthesis in supercritical conditions in carbon (IV)-oxide by the sol-gel polymerization where methyl methacrylate was one of the co-monomers, which should give the hardness of the final polymer product. The specific surface area of the product was 5-328 m²/g and the average diameter of pores is 20 nm to 7.9 μm [4, 5]. The enzyme immobilization by covalent binding in poly(acrylamide) gel or in poly(methyl methacrylate) polymer is also known [6, 7]. Macro-porous cross-linked copolymers are used as starting substances for the production of different types of ion exchange resins; they are also used as inert carriers in some chromatographic procedures, as adsorbents, as catalysts, as carriers of classical catalysts or enzymes [8, 9]. Porous poly(methyl methacrylate) (PMMA) and poly(styrene) (PS), together with polyolefin, are materials which are used a lot in the polymer processing industry. However, the lack of PS and PMMA is their brittleness. On the other hand, polyolefin has sufficient toughness values but very poor optical properties.

Porous poly(methyl methacrylate) has a very significant application. In the recent times, porous polymers based on poly(methyl methacrylate) have been used to correct bone defects in humans [10]. The porous struc-
ture of the polymer is used for the controlled delivery of drugs such as antibiotics tetracycline hydrochloride [11] and gentamicin [12], as well as other medications that could be potentially used to treat osteoporosis, osteomyelitis and other bone diseases.

In order to improve the therapy, a local drug dosage is used and the drug is deposited in the poly(methyl methacrylate) implants which are implanted around the infected areas [13]. The application of polymer materials for the controlled drug distribution is conditioned by their non-toxicity and solubility in solutions of different pH values. Today, there are pharmaceutical polymeric materials that are used for the controlled release of drugs in the form of aqueous dispersion of anionic polymers of methyl acrylate, methyl methacrylate and methacrylic acid. By adjusting the molar ratios in the initial reaction mixture one can affect the solubility of the obtained polymer (poly(methyl methacrylate-co-methacrylic acid)) in aqueous solutions of different pH values. The solubility of copolymer with the monomer molar ratio 1:1 is smaller in aqueous buffer solution at pH 5, and larger in buffers the pH of which is above 6. The solubility of copolymers with 1:2 monomer ratios is smaller in buffers pH values of which are 5 and 7, and larger in the buffer solution at pH 9 [14].

On poly(methyl methacrylate) and after the chemical preparation of polymer surfaces by polymer analogous reactions the enzymes can be bonded on the surface of the porous material through the amino groups of the enzymes [6, 7, 15-17].

The aim of this study was to synthesize porous PMMA and PMMA-AA, characterize them and make the immobilization of enzymes α-amylase on them.

**Experimental**

Reagents:
Methyl methacrylate, 98 %, MMA (Merck, Darmstadt, Germany)
Acrylamide, 97 % AA (Aldrich Milwaukee, WI, USA)
Ethylene glycol dimethacrylate, 98 %, EGDM (Aldrich Milwaukee, WI, USA)
Acrylamide, 97 % AA (Aldrich Milwaukee, WI, USA)
Poly(vinylpyrrolidone) PVP (Mw=360.000, Aldrich Milwaukee, WI, USA)
Benzoil peroxid, 97 %, BP (Aldrich Milwaukee, WI, USA)
Persulfate potassium, 98 %, PP (Riedel-de Haën, Seelze, Germany)
Glycoluril, tetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dione, 98 %, GLY (Aldrich Milwaukee, WI, USA)
Formaldehyde, 37 %, (Merck, Darmstadt, Germany)
Diocyl sulfosuccinate sodium salt, 99 %, DOSS (Sigma Chemicals Co., St. Luis, USA)
Disodium hydrogen phosphate heptahydrate, 99 %, Na2HPO4·7H2O (Sigma Chemicals Co., St. Luis, USA)
Ethyl acetate, 99 %, EA (Zorka Šabac, SR)
α-Amylase (from Bacillus subtilis; Serva Feinbiochemica GmbH & Co., Heidelberg, Germany)

**The Synthesis of poly(methyl methacrylate) and poly(methyl methacrylate-co-acrylamide)**

For the synthesis of poly(methyl metacrylate) a suspension in water with 10% of organic phase was prepared (Table 1) [16, 17]. PVP is used as a protective colloid of suspension polymerization in the concentration of 1 % in water, and BP is used as the initiator of the concentration of 1.5 % compared to the mass of the monomer. EGDM is used in the synthesis of PMMA to make a network. Without networking of PMMA evaporation during the drying of inert EA would lead to the collapse of the pores. The polymerization was conducted for 4 hours at 70 °C and then the polymer was rinsed and boiled in water for 30 min to evaporate EA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water, cm³</th>
<th>MM, cm³</th>
<th>EA, cm³</th>
<th>EGDM, cm³</th>
<th>PVP, g</th>
<th>BP, mg</th>
<th>Fraction* in EA</th>
<th>Fraction* in EGDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5.29</td>
<td>4.71</td>
<td>0</td>
<td>1</td>
<td>79</td>
<td>0.471</td>
<td>0.125</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>7.32</td>
<td>1.43</td>
<td>1.25</td>
<td>1</td>
<td>129</td>
<td>0.143</td>
<td>0.125</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>6.37</td>
<td>2.86</td>
<td>0.77</td>
<td>1</td>
<td>107</td>
<td>0.286</td>
<td>0.077</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5.89</td>
<td>2.86</td>
<td>1.25</td>
<td>1</td>
<td>107</td>
<td>0.286</td>
<td>0.125</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>4.92</td>
<td>2.86</td>
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<td>107</td>
<td>0.286</td>
<td>0.222</td>
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<tr>
<td>6</td>
<td>100</td>
<td>4.04</td>
<td>4.71</td>
<td>1.25</td>
<td>1</td>
<td>79</td>
<td>0.471</td>
<td>0.125</td>
</tr>
</tbody>
</table>

* - Fraction of volume in the organic phase
For the synthesis of macroporous and cross-linked poly(methyl methacrylate-co-acrylamide) it is necessary to synthesize tetramethylol glycoluril \((1,3,4,6\)-tetrakis-hydroxymethyl-tetrahydro-imidazo \([4,5-d]\)-imidazole-2,5-dione\) starting from glycoluril and formaldehyde [16, 18]. The molar ratio of the reactants is 4:1; the synthesis is performed in the solution of disodium hydrogen phosphate with the concentration of 0.01 mol / dm\(^3\), at pH \(\approx 9.5\) and the temperature of 60 °C for 1.5 h.

The synthesis of macro porous copolymers based on methyl methacrylate and acrylamide is conducted in the emulsion the composition of which is: DOSS 0.2 % wt., PP 0.82 % wt., AA 2.28 % wt., Tetramethylol-glycoluril 0.56 % wt., water 71.64 % wt., EA 5.26 % wt., and MMA 19.24 % wt. [16, 18]. DOSS is used as an emulsifier in the process of polymerization, PP as the initiator, EA as the inert solvent for the organic phase and tetramethylol glycoluril as a crosslinking agent [18]. The reaction before the polymerization lasts for 30 min at 60 °C until the state of soft, liquid gel is obtained, and it is continued by the polymerization with the sol-gel process which lasts for another 3 hours. The obtained copolymer is cut up in small pieces and heated in water at 80 °C for 30 min until the polymerization reaction has been completed and EA has evaporated. Then the temperature is increased to 100 °C during 1 h to complete networking by the condensation of chemical groups in order to create cross-links in the polymer chain [16]. At the end, the polymer particles are exposed to dry air temperature of 120 °C to dry and to finish the condensation reaction between the reactive groups of the polymer chains [16].

Characterization of the obtained polymers

**SEM microscopy.** In the preparation phase of the macro porous polymer samples for SEM microscopy, a thin layer of gold is applied on the surface of the macro porous polymer samples using the technique of cathodes spraying with the diffuser JEOL JFC-1100E. SEM microscopy is then done using the scanning electronic microscope JEOL JSM-5300.

**Mercury porosimetry.** The cumulative distribution of the pore volume according to the pore size, a specific surface area and the total porosity of macro porous polymer samples was determined by the mercury porosimetry Carlo Erba 2000.

**Determination of the residual monomer by HPLC method.** Shredded polymer samples (50 mg) were immersed in methanol (5 cm\(^3\)) and by stirring them occasionally the residual monomer extraction was performed during 48 h. Then, the methanol solution was separated from the polymer by the filtration, while the concentration of methyl methacrylate and acrylamide in methanol was determined by HPLC chromatography under the following conditions: column: XDB ZORBAX C-18, 250 x 4.6 mm, 5 μm; eluent: methanol; flow rate: 1 cm3; column temperature: 25 °C, detector: DAD; UV detection: 210 nm.

**X-ray diffraction.** X-ray diffraction was performed on a Phillips X'Pert powder diffractometer under the following conditions: the samples were exposed to monochrome CuKα radiation and analyzed under the angle 2θ between 10 and 60° with 0.05° increment and recording time \(\tau = 5\) s. The voltage and the strength of the electric current were 40 kV and 20 mA, respectively.

Results and Discussion

Figure 1 shows SEM image of poly(methyl methacrylate), sample 1. The Figure shows that the order of the particle size of the synthesized poly(methyl methacrylate) by the suspension polymerization is about 1 mm. However, the particle is not monolithic, but is composed of many small spherical particles, the individual diameters of which were 100 to 500 μm and which were associated during the synthesis. The association was made just before the point of identity of the particles and caused by the increased viscosity of the reaction mixture dispersed in aqueous media. Figure 2 shows SEM image of poly(methyl methacrylate), also the sample 1 but with higher magnification of 200 x. The figure shows that in addition to cracks there is some porosity, but the pores are generally small and the size is smaller than 1 μm.

Figure 1. SEM image of poly(methyl methacrylate), sample 1; magnification x 50, bar = 500 μm

Figure 2. SEM image of poly(methyl methacrylate), sample 1; magnification x 1000, bar = 10 μm.
Figure 3 shows the SEM image of poly(methyl methacrylate), sample 6, where in the process of synthesis the greatest share of added substances EGDM and ethyl acetate was present. The structure of the polymer is different compared to the poly(methyl methacrylate) obtained in the synthesis of the suspension polymerization without added EGDM’s. In addition, the pore size is larger, and one can observe the pores larger than 10 μm.

Figures 4 and 5 show SEM image of poly(methyl methacrylate-co-acrylamide) with different magnification, 200x and 750x respectively. Morphologically, there is a substantial difference in the appearance of pore structure and the walls between the poly(methyl methacrylate) and poly(methyl methacrylate-co-acrylamide). Based on the images, it can be concluded that the porosity is higher in the co-polymer sample.

In addition to monitoring the morphology, a real picture of the porosity and specific surface of synthesized polymer and copolymer samples can be given by mercury porosimetry. Figures 6 and 7 show the maximum value of the pore volume and specific surface area, respectively, in the function of the volume shares of EGDM and EA applied to the synthesis of poly(methyl methacrylate). It is evident that the pore volume and specific surface area increase with the increase of the EGDM and EA share in the reaction mixture for the synthesis of poly(methyl methacrylate), but it seems that it is not enough, because it gives relatively low values of the pore volume and surface area. Thus, the highest value obtained for the pore volume of poly(methyl methacrylate) was 0.64 cm$^3$/g and for the specific surface area 17.2 m$^2$/g (sample 6). For poly(methyl methacrylate-co-acrylamide) these values were 3.25 cm$^3$/g and 22.7 m$^2$/g. Because of these, sample 6 from the series of poly(methyl methacrylate) was chosen as a representative to carry out the process of the immobilization of enzymes. Copolymer of poly(methyl methacrylate-co-acrylamide), with its values for the pore volume and specific surface area, showed that it is very favorable for immobilization.
The samples of the synthesized cross-linked copolymers were immersed in water and nonpolar organic solvents (xylene, toluene, chloroform, carbon tetrachloride), in alcohols (methanol, ethanol, n-propanol), in pyridine and tetrahydrofuran, and after the prolonged mixing (24 h) it was concluded that the copolymer and PMMA samples 2 to 6 do not dissolve and swell in the used solvents.

Figure 7 illustrates the absorption of water into the pores by the capillary forces of the sample porous poly(methyl methacrylate-co-acrylamide) together with the time of absorption. The mass of water absorbed by the polymer (W) related to the maximum mass of water that can be absorbed (Wmax) in the function of time can be represented by equation 1 (Higuchi) [19] or complex exponential equation 2:

$$\frac{W}{W_{\text{max}}} = A \cdot t^b$$  \hspace{1cm} (1)

where A = 0.34 and b = 0.21;

$$\frac{W}{W_{\text{max}}} = Y_0 + A_1 \cdot \left(1 - e^{-\frac{A_2}{t}}\right)$$  \hspace{1cm} (2)

where the coefficients are: $Y_0 = 0.0716; A_1 = 0.243; A_2 = 0.566; t_1 = 1.364; t_2 = 23.007$.

The parameters in these mathematical models of the water absorption by the porous copolymer are determined by the MATLAB software package, using the tool leastsq, fzero or fsolve, so as to minimize the sum of squared differences between the values of the experimental data and mathematical models. There is a better accordance of the experimental data and the model in equation 2, i.e. the sum of squared differences is lower, as it can be seen in Figure 8. Such analysis of the absorption of water into the pores of poly(methyl methacrylate) is not possible because the porosity is very small and some reasonable measurements in the acceptable time intervals cannot be done in order to apply the mathematical data processing.

As the experimental results do not match well with the equation 1, it shows that during the water absorption we do not have a simple diffusion through the polymer, as described by Higuchi equation. Macroporous polymer absorbs the water relatively slowly due to air bubbles in the pores, which do not allow rapid capillary penetration of the water inside the pores, and the force of thrust is insufficient to push the bubbles out of the pores. This fact does not support the use of immobilized cells or enzymes which release gaseous products whose bubbles will occupy the free space inside the polymer particles and create a permanent resistance to diffusion of the substrate from the fluid inside the polymer particles to the active centre of the enzyme or immobilized cells. However, this copolymer can be, for example, used to immobilize the enzyme of hydrolyses type that does not produce gaseous products. The rate of diffusion of the substrate to the immobilized enzyme in the pores can be a very important factor in the overall speed of the enzymatic hydrolysis.

Figure 8. Water absorption of the porous cross-linked copolymer sample and the approximation of the experimental values by mathematical models 1 and 2

In the samples PMMA and PMMA-AA the amount of residual monomers of methyl methacrylate and acrylamide were determined by HPLC method. Residual amounts of monomers are determined in order to be able to make an assessment whether these quantities could interfere with the polymer analogue reactions that will take place in PMMA and PMMA-AA and with which one can make the immobilization of enzymes on the free surface of the polymeric material. HPLC chromatogram shows a retention time of methyl methacrylate $R_t = 3.062$ min, and the UV spectrum shows the wavelength of the maximum absorbance $\lambda_{\text{max}} = 210$ nm.

For a series of solutions of methyl methacrylate in methanol HPLC chromatograms were done and for each
concentration the specific surface area of the obtained peaks was determined by using Agilent ChemStation software. The dependence of the peak (in units of internal software mAU * s) which is derived from methyl methacrylate in the function of the concentration shows that the dependence is not linear throughout the range of concentrations of methyl methacrylate monomer up to 1 mg/cm³. Linearity exists up to the concentration of 0.1 mg/cm³, i.e. the peak surface around 6500 mAU *s and for this range of the concentration the following equation can be applied:

\[ A = 906.44 + 56860.12 \cdot C \] ....................................... (3)

where \( A \) is the peak surface, mAU*s and 
\( C \) is the concentration of the monomer, mg/cm³.

From Equation 3 equation 4 can be obtained by which the concentration of the monomer from certain peak surfaces for the linear range of monomer concentration can be calculated.

\[ C = \frac{A - 906.44}{56860.12} \] ....................................... (4)

In HPLC chromatograms acrylamide the retention time was \( R_t = 2.662 \) min, and from the UV spectrum, the wavelength of the maximum absorbance is \( \lambda_{\text{max}} = 210 \) nm.

The calibration curve for acrylamide at \( \lambda = 210 \) nm shows linearity only up to 0.05 mg/cm³, and Equation 5 is applied to it:

\[ A = 992.5 + 85220 \cdot C \] .................................................. (5)

from which the concentration from the surface peaks can be determined by the equation 6:

\[ C = \frac{A - 992.5}{85220} \] .......................................................... (6)

Figure 9 shows a chromatogram of the poly(methyl methacrylate-co-acrylamide) extract. From the chromatograms it can be seen that there is no overlapping of peaks arising from acrylamide \( (R_t = 2.662 \) min) and methyl methacrylate \( (R_t = 3.064 \) min) so that their surfaces can be easily used to determine their concentrations by using calibration curves. From the concentration of the residual monomer in the extracts, the mass of the unreacted monomers per gram of polymer is calculated and these results are shown in Tables 2 and 3. Table 2 shows the mass of the residual monomers for poly(methyl methacrylate) and Table 3 for poly(methyl methacrylate-co-acrylamide). Generally, it can be concluded that after the polymer has been processed by heating it in boiling water, the concentrations of residual monomers are lowered for about 10 times and the values of 0.62 to 2.21 mg/g are reached. It is estimated that the mass of the residual monomers would not significantly affect the performance of polymer-analogous reactions on the surface of polymers and copolymers, so no other treatment of polymers is needed.

![Figure 9. HPLC chromatogram of acrylamide and methyl methacrylate from the copolymer extract](image)

Table 2. The mass of residual monomers in the samples of poly(methyl methacrylate)

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM¹, mg/g</td>
<td>8.32 ± 0.11</td>
<td>10.02 ± 0.10</td>
<td>9.68 ± 0.11</td>
<td>7.55 ± 0.10</td>
<td>7.12 ± 0.09</td>
<td>8.26 ± 0.12</td>
</tr>
<tr>
<td>MM², mg/g</td>
<td>0.89 ± 0.03</td>
<td>1.11 ± 0.03</td>
<td>0.95 ± 0.03</td>
<td>0.62 ± 0.02</td>
<td>0.60 ± 0.02</td>
<td>0.78 ± 0.03</td>
</tr>
</tbody>
</table>

¹ After the synthesis
² After the boiling process
Figures 10 and 11 show the x-ray diffraction pattern on the samples 6 PMMA and PMMA-AA, before and after the immobilization of enzymes α-amylase. The immobilization was performed by the chemical transformation of methyl ester and amide groups with 1% solution of hydrazine to the acyl-hydrazine group. This is further converted into acyl-amide group that easily condenses with the free amino group from the enzyme molecule [6, 7, 18]. The pictures of x-ray diffraction show that there are no crystalline zones in the synthesized samples of PMMA and PMMA-AA and that it does not change after the process of chemical polymer preparation as well as after the immobilization of enzymes.

Figures 12 and 13 show the SEM micrographs of the sample 6 PMMA and PMMA-AA after the immobilization of enzymes α-amylase. From the pictures the deposits on the surface of the polymer which can be assumed to originate from the immobilized enzyme can be seen. From the difference between the concentration of the enzyme before and after the process of immobilization of enzymes on polymer, the amount of immobilized enzyme is determined. The most appropriate sample from the series of samples of poly(methyl methacrylate) is sample 6 where 22.9 mg of the enzyme α-amylase are immobilized per gram of the polymer. Enzyme 26.4 mg per gram of the polymer were immobilized on poly(methyl methacrylate-co-acrylamide).

Check-up of the enzymatic activity of the immobilized enzyme is made by starch digestion in 2% solution to the glucose, the concentration of which is measured spectrophotometrically by using the picric acid in the solution of sodium carbonate. By monitoring the concentration of glucose in the allocated time, the speed of the hydrolysis of starch is determined, which is 0.394 mg starch/min·g polymer for the immobilization on poly(methyl methacrylate) and 0.507 mg starch/min·g polymer for the immobilization on poly(methyl methacrylate-co-acrylamide).

Table 3. The mass of residual monomers in the sample of poly(methyl methacrylate-co-acrylamide)

<table>
<thead>
<tr>
<th></th>
<th>MM', mg/g</th>
<th>MM'', mg/g</th>
<th>AA', mg/g</th>
<th>AA'', mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28.39 ± 1.84</td>
<td>2.21 ± 0.45</td>
<td>5.17 ± 0.28</td>
<td>0.45 ± 0.03</td>
</tr>
</tbody>
</table>

1 After the synthesis
2 After the boiling process

Figure 10. The X-ray analysis of the sample 6 of poly(methyl methacrylate) without (1) and with the enzyme (2)

Figure 11. The X-ray analysis of the sample of poly(methyl methacrylate-co-acrylamide) without (1) and with the enzyme (2)

Figure 12. SEM image of the sample 6 of poly(methyl methacrylate) with the immobilized enzyme; magnification x 3500, bar 5 μm.
The synthesis of the samples of poly(methyl methacrylate) with the suspension polymerization and the samples of poly(methyl methacrylate-co-acrylamide) with the emulsion polymerization at the beginning of the process and in later stages with the sol-gel process was conducted. SEM analysis showed that during the suspension polymerization of poly(methyl methacrylate) the association of initial spherical shapes and agglutination during the polymerization process appears. By using the mercury porosimetry it was found that the pore volume and specific surface area increased with the increase of the EGDM and EA share in the reaction mixture for the synthesis of poly(methyl methacrylate). The largest value obtained for the PMMA pore volume was 0.64 cm$^3$/g, and the specific surface area was 17.2 m$^2$/g. For PMMA-AA the corresponding values were 3.25 cm$^3$/g and 22.7 m$^2$/g.

The analysis of the residual monomer by HPLC showed that the values of methyl methacrylate in the PMMA samples range from 7.12 to 10.02 mg/g, and methyl methacrylate and acrylamide in the copolymer range from 5.17 and 26.39 mg/g. After processing the polymers by boiling them in water at the boiling temperature, the concentration of residual monomers is about lower 10 times.

X-ray diffraction of the synthesized polymers PMMA and PMMA-AA showed that there are no crystal zones in polymers.

Sample 6 from the series of poly(methyl methacrylate) was elected as a representative to carry out the process of immobilization of enzymes. Copolymer poly(methyl methacrylate-co-acrylamide) with its values of pore volume and specific surface area showed that it is very favorable for immobilization.

$\alpha$-Amylase enzyme, 22.9 mg per gram of the polymer were immobilized on PMMA and 26.4 mg of the enzyme per gram of the polymer were immobilized on PMMA-AA. The speed of the hydrolysis of starch by the immobilized enzyme is 0.394 mg of starch / min·g of the polymer for PMMA, and 0.507 mg of starch / min·g of the polymer for the immobilization of the PMMA-AA.

Acknowledgements

This paper is a part of the MNTR TR-33034 project financed by the Ministry of Education and Science of the Republic of Serbia.

Abbreviations and symbols

- MMA - Methyl methacrylate
- EGDM - Ethylene glycol dimethacrylate
- AA - Acrylamide
- PVP - Poly(vinylpyrrolidone)
- BP - Benzoyl peroxid
- PP - Persulfate potassium
- GLY - Glycoluril, tetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dione
- DOSS - Dioctyl sulfosuccinate sodium salt
- EA - Ethyl acetate
- PMMA - Poly(methyl methacrylate)
- PMMA-AA - Poly(methyl methacrylate-co-acrylamide)

References

Izvod

UMREŽENI MAKROPOROZNI POLIMERI I KOPOLIMERI, NJIHOVA SINTEZA I KARAKTERIZACIJA

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U ovom radu izvršena je sinteza poroznog poli(metilmetakrilat) PMMA polimerizacijom u suspenziji i sinteza poroznog kopolimera poli(metilmetakrilat-ko-akrilamid) PMMA-AA polimerizacijom u emulziji. Obe vrste polimerizacija su vodene u prisustvu inertnih jedinjenja. Morfologija stvorenih pora je određena pomoću SEM mikroskopije. Zapremina pora i specifična površina poroznih polymera je određena pomoću živine porozimetrije. Zapremine pora PMMA su u opsegu 0,03 do 0,64 cm³/g, a za PMMA-AA je 3,25 cm³/g. Specifična površina za PMMA je od 9 do 17 m²/g a za PMMA-AA je 22,7 m²/g. Sadržaj rezidualnih monomera u PMMA polimerima i kopolimerima nakon ključanja u vodi se smanjuje oko 10 puta. Na površini PMMA je imobilisano 22,9 mg enzima α-amilaze po gramu polimera a na PMMA-AA 26,4 mg enzima po gramu polimera. Brzina hidrolize skroba imobilisanim enzima α-amilaze iznosi 0,394 mg skroba/min·g polimera za PMMA i 0,507 mg skroba/min·g polimera za PMMA-AA.

Ključne reči: porozni polimeri, rasipanje X-zraka, SEM, živina porozimetrija, HPLC analiza, rezidualni monomeri