10.17951/aa.2019.74.2.101-113

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA

VOL. LXXIV, 2 SECTIO AA 2019

Implantation of superabsorbent polymer by magnetic iron oxide particles

Maciej Grzesiak* and Łukasz Szajnecki

Department of Polymer Chemistry, Faculty of Chemistry
Institute of Chemical Sciences,
Maria Curie-Skłodowska University in Lublin,
Gliniana 33, 20-614 Lublin, Poland,
**e-mail: maciej.grzesiak@poczta.onet.pl*

The aim of this research was to optimise methods of magnetic particles of iron oxides implantation into superabsorbent polymer based on partially neutralized acrylic acid (SAc/AAc) crosslinked with ethylene glycol dimethacrylate (EGDMA). The structure of the obtained materials was confirmed by infrared spectroscopic analysis (FT-IR/ATR). The quality of implantation process was evaluated on the basis of microscopy images. Swelling properties of the obtained implanted materials were also determined.

Keywords: superabsorbents, hydrogels, magnetic particles, swelling properties.

1. INTRODUCTION

Superabsorbent polymers (SAP) are widely used substances in various industries, from personal hygiene products (disposable diapers, sanitary pads) to water storage beads for plants watering [1-4]. Those materials can absorb a large amount of liquids such as water, urine or blood up to several hundred times of their mass [5-7]. Such swelling properties come from their polymeric structure

which is based on monomers that contain hydrophilic groups like carboxyl, hydroxyl, amine, imide and so on [8-9]. Without special treatment those polymers can dissolve in water solutions thus they are crosslinked in small degree [10]. Too high degree of crosslinking can transform those materials into completely insoluble in water solutions.

Materials called magnetic particles (MP) are used in wide range of disciplines, e.g. catalysis, MRI (magnetic resonance image), drug delivery, data storage, bioseparation [11-13]. Most common magnetic particles are based on iron oxides like magnetite (Fe_3O_4) which is ferrimagnetic or ferromagnetic maghemite (γ-Fe_2O_3). Both of the oxides are relatively easy to obtain [11, 14] and they have been proven to be biocompatible. Various methods of obtaining MP have already been developed allowing to prepare them as nano-sized particles which gives them additional properties e.g. superparamagnetism if Fe_3O_4 particles are lesser than 15 nm). To prepare stable suspension of nano-sized MP it is required to stabilise them by coating with various surfactants, polymers, or grafting them with polymers [15-16].

Combination of those two materials gives very promising hybrid material which opens new application possibilities. Some reports show the use of the magnetic superabsorbents as organic dyes absorbent [17]. The addition of magnetic substance into SAP provides additional ability to manipulate such hybrid material by magnetic field. The ability to move such materials with magnetic field gives the opportunity to do a research on targeted drug delivery system [18-19], targeted cancer treatment [20] or separation of sorbent after absorption of contaminant [17].

2. EXPERIMENTAL

2.1. Materials

Acrylic acid (AAc), potassium peroxodisulfate (KPS), α,α′-azo-isobutyronitrile (AIBN), SPAN® 80 were obtained from Fluka (Germany). Sodium hydroxide, hexane, methanol, were obtained from Avantor Performance Materials (Poland). Ethylene glycol dimethacrylate (EGDMA), iron(II) chloride, iron(III) chloride were obtained from Sigma-Aldrich (USA). Ammonium hydroxide was

obtained from Chempur, whereas Gamma iron(III) oxide was obtained from Alfa Aesar (Germany).

2.2. Superabsorbent synthesis

To minimize negative effect of water on the synthesized polymer an inverse phase suspension polymerisation was used. Monomers used in this synthesis were sodium acrylate (SAc\AAc) (obtained through partial neutralization (85 %) of acrylic acid (AAc) – (10 g) with sodium hydroxide), and ethylene glycol dimethacrylate (EGDMA) as crosslinking agent. Potassium peroxo-disulfate (KPS) was used as radical polymerization initiator. Hexane was used as reaction phase, and SPAN® 80 was used as suspension stabiliser. Neutralization of AAc was carried out slowly in ice bath with constant stirring to prevent an uncontrolled polymerization of monomer.

Partially neutralized acrylic acid was mixed with specific quantity of crosslinker (0.12 g) and initiator (0.3 g). Reaction mixture was transferred to three-necked flask which contained hexane and SPAN® 80. The flask was equipped with a reflux condenser and a mechanical stirrer. Whole mixture was kept under constant stirring and heated up to hexane boiling point. Reaction was carried out for 2 hours, then azeotropic distillation was used to remove water. After distillation, dispersion of the obtained polymer was left for sedimentation.

Hexane was removed and polymer particles were then poured with methanol and dried in the inert atmosphere. Dried product was kept in sealed containers. Chemical structures of used monomers are shown in Fig. 1.

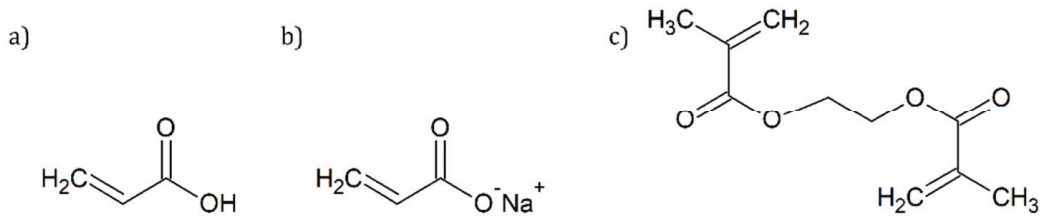

Fig. 1. Monomers used in synthesis of superabsorbent polymer: acrylic acid (AAc) (a), sodium acrylate (SAc) (b), ethylene glycol dimethacrylate (EGDMA) (c).

2.3. Co-precipitation synthesis of magnetic iron(II,III) oxide particles

Iron(II,III) oxide (Fe_3O_4) particles were obtained in wet co-precipitation method. As a precursors iron(II) chloride and iron(III) chloride anhydrous salts were used. Ammonium hydroxide was used as a precipitation reagent. The synthesis began with weighing 2.000 g of $FeCl_3$ and 0.869 g $FeCl_2$ to separate beakers. 50 cm^3 of distilled water was added to both beakers and mixed until both salts dissolved.

Solutions of iron salts were mixed and transferred to two-necked flask equipped with mechanical stirrer and dropping funnel. The mixture of iron salts was left under constant stirring for 30 minutes. 20 cm^3 of ammonium hydroxide was poured into dropping funnel and then dropwise into the salt mixture. Obtained black precipitate (Fe_3O_4) was stirred for 30 minutes and then content of flask was transferred to beaker for sedimentation. Liquid above the sediment was removed and the precipitate was then poured few times with distilled water to remove unreacted substances and water-soluble products. Afterwards the precipitate was dried in 70°C until constant mass was achieved. The dried product was then stored in sealed containers to prevent oxidation.

2.4. Post-implantation of MP on SAP surface

This method is based on implantation of the MP on SAP surface during controlled swelling of the polymer. Pre-synthesized SAP was used as an implantation matrix while iron(II,III) oxide and γ-iron(III) oxide were used as implanted materials. SAP, methanol, and MP (γ-Fe_2O_3 or Fe_3O_4) were weighed into 6 Eppendorf tubes. Into each tube specific quantity of distilled water was added. Tubes were tightly closed and left in an auto-shaker for 15 minutes. Next day content of tubes was centrifuged, and the liquid was decanted. Swollen SAP particles were left to dry. Parameters of this method are shown in Table 1.

Table 1. Parameters of post-implantation method.

Sample name*	Methanol [cm³]	SAP [g]	Type of MP	MP [g]	Distilled water [cm³]
SAP-P-MP-1	1.0	0.20	Fe_3O_4	0.02	0.5
SAP-P-MP-2					1.0
SAP-P-MP-3					1.5
SAP-P-MP-4			———		0.5
SAP-P-MP-5			γ-Fe_2O_3		1.0
SAP-P-MP-6					1.5

*unlike the names of sorbents implanted during synthesis, the abbreviations of post-implanted polymers contain the letter p.

2.5. Implantation of MP during SAP synthesis

This method involves adding MP into monomers solution and then polymerization as explained in chapter 2.2. Each material obtained by this method was synthesized under different conditions (Table 2, Table 3). Syntheses 1 and 2 were different in the reference to the implanted MP type (Fe_3O_4 or γ-Fe_2O_3). In third synthesis an initiator was added before MP into monomer solution. Next syntheses (4-6) exploited different homogenisation method that caused large bulk of MP to be lost before adding them into reaction flask. During these syntheses there were problems with KPS when using Fe_3O_4 as implant supposedly because Fe^{3+} ions with combination of KPS make redox polymerization initiator system which initiates polymerization during preparation of reagents solution. For this reason, KPS was replaced by AIBN. The results were not satisfactory so during next syntheses KPS was used again. Re-use of KPS was possible thanks to minor modifications of the synthesis conditions. The fifth synthesis was conducted using higher speed of mixing (500 rpm) leading to smaller polymer spheres. The last synthesis of SAP was implanted with Fe_3O_4 made directly before implantation process. The obtained Fe_3O_4 was stabilized by glycerine, and some amount of prepared suspension was added to monomer solution. In this case exact mass of MP added to reaction flask was unknown.

Table 2. Quantities of used substances during syntheses of SAP-MP materials.

Sample name	Mass of substance [g]				
	AAc	NaOH	EGDMA	MP	Initiator
SAP-MP-1	10.0201	4.4548	0.1212		
SAP-MP-2	10.0144	4.4509	0.1209	0.50	0.3
SAP-MP-3	10.0703	4.4678	0.1265		
SAP-MP-4	10.0952	4.4894	0.1270	1.01*	0.4
SAP-MP-5	10.0060	3.3420	0.1312	1.51*	0.3
SAP-MP-6	10.0256	3.3927	0.1322	–**	

* large bulk of used MP was lost during homogenization process.
** exact mass is unknown cause of used method of adding MP into monomer solution.

Table 3 Parameters of syntheses of SAP-MP.

Synthesis parameters	Sample name: SAP					
	MP-1	MP-2	MP-3	MP-4	MP-5	MP-6
Desired degree of neutralization of AAc [%]	80	80	80	80	60	60
Real degree of neutralization of AAc [%]	80.03	80.00	79.86	80.05	60.12	60.91
Desired degree of crosslinking EGDMA:AAC [mol/mol]	1:200					
Real degree of crosslinking EGDMA:AAC [mol/mol]	1:227	1:228	1:219	1:219	1:210	1:209
Type of MP	γ-Fe_2O_3	Fe_3O_4	Fe_3O_4	Fe_3O_4	Fe_3O_4	Fe_3O_4
Initiator type	KPS	KPS	KPS	AIBN	KPS	KPS

2.6. Measurement methods

Infrared spectroscopy analysis was carried in FTIR TENSOR 27 (Bruker, Germany) spectrophotometer using attenuated total reflectance (ATR) – Fourier transform infrared (FT-IR) technique. The spectra were recorded in the range of 4000 to 700 cm^{-1} averaging 32 scans with resolution of 4 cm^{-1}.

Microscopic analysis was carried out using MORPHOLOGI G3 (Malvern, United Kingdom). This analysis was used to check morphology of obtained products and quality of implantation process. All images were obtained using z-stacking technique that involves taking series of pictures of the same area but with different focus on z-axis. All images are then processed and presented as one image with focus on all parts of the object. Size distribution of synthesized Fe_3O_4 particles was measured using laser diffraction technique (MASTERSIZER 2000, Malvern, United Kingdom). During measurement refractive index of samples was set to 1.544, and absorption index to 0.0001. Fe_3O_4 particles were dispersed in distilled water.

Swelling properties of implanted superabsorbents were analysed to examine impact of the synthesis parameters. 0.1 g of implanted SAP was placed into Falcon tubes (45 cm^3), then 25 cm^3 of 0.9% solution of NaCl was added and tube was sealed and shaken. After 30 minutes their content was centrifuged and decanted. The tube with swollen SAP was weighed and emptied from SAP gel. Empty tube was rinsed, dried, and weighed. Swelling ratio (Sw) was calculated from following equation [3]:

$$Sw\ [\%] = \left(\frac{m_s - m_d}{m_d}\right) \cdot 100\% \tag{1}$$

where m_s is the mass of swollen SAP, m_d is the mass of dry SAP (Superabsorbent polymers are highly hygroscopic thus they relatively easy absorb water from atmospheric air. That way SAP materials are always wet in small degree, but for convenience non-swollen polymer we call as dry).

3. RESULTS AND DISCUSSION

3.1. Results of an infrared spectroscopy analysis

The FT-IR spectra of monomers (AAc, SAc/AAc, EGDMA) are shown in Fig. 2.

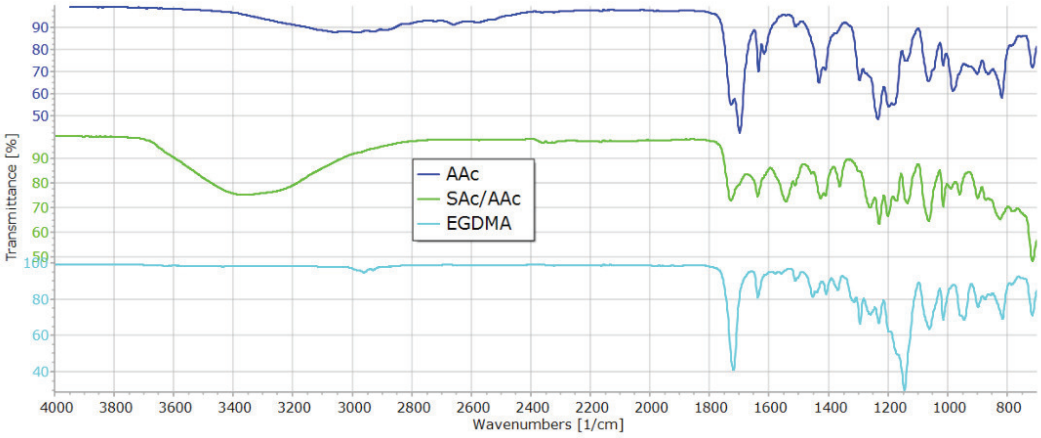

Fig. 2. FT-IR spectra of the used monomers.

Comparing spectra of acrylic acid (AAc) and partially neutralized acrylic acid (SAc/AAc) one can see decrease of stretching vibration band of carbonyl group ν(C=O) at about 1698 cm^{-1} and appearance of carboxyl anion group vibrations as two bands at 1543 and 1362 cm^{-1}. Wide band observed at about 3700-2800 cm^{-1} comes from stretching vibrations of OH group from H_2O created during AAc neutralization process. In the EGDMA spectrum band at 1720 cm^{-1} comes from ester carbonyl group stretching vibrations is visible. Strong band at about 1145 cm^{-1} comes from ester C-O-C stretching vibrations. Band at 1636 cm^{-1} observed in all spectra comes from vinyl groups stretching vibrations.

In Fig. 3 spectra for the obtained SAP-MP materials are shown.

All spectra are similar with exception of SAP-MP-6 at which at about 1100 and 1046 cm^{-1} peaks of hydroxyl groups coming from glycerine used in the synthesis are visible. Peaks at 3000-2850 cm^{-1} come from asymmetric and symmetric stretching vibrations of CH_3 and CH_2 groups. Absence of band of vinyl group at 1636 cm^{-1} and appearance of CH_2 vibration peaks confirm polymerization process. Two bands at 1556 and 1362 cm^{-1} come from carboxylic anion of

SAc blocks of polymer. Peak at 1720 cm^{-1} comes from carbonyl group stretching either from AAc or EGDMA.

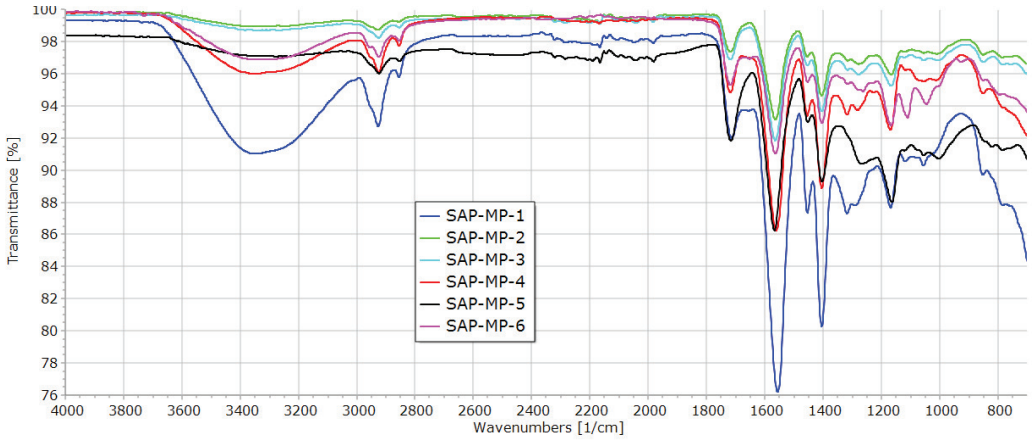

Fig. 3. FT-IR spectra of the obtained SAP-MP materials.

3.2. Morphology of the obtained polymers

Exemplary microscopic images of implanted superabsorbents are shown in Fig. 4.

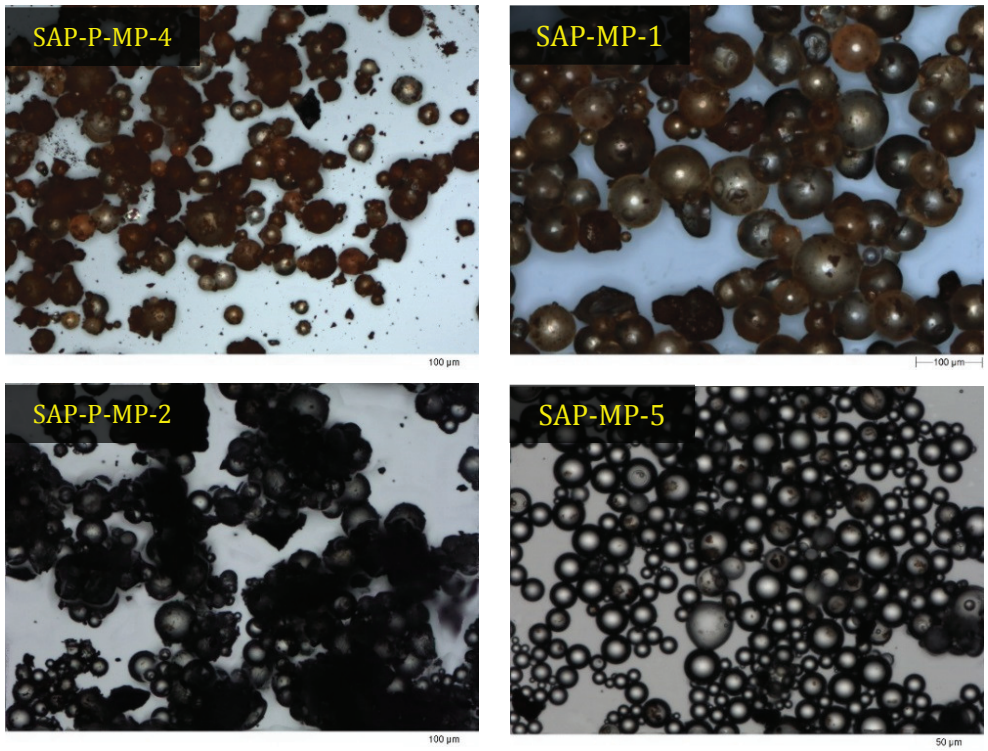

Fig. 4. Microscopy images of SAPs implanted with MP: SAP post-implanted (left), SAP implanted during synthesis (right).

The degree of the implantation of microspheres with magnetic particles can be estimated on the basis of the analysis of microscopic images. SAPs obtained in post-implantation method (Fig. 4, left) are not uniformly implanted. SAP particles obtained without MP were smaller in diameter than the used MP which led to low efficiency of implantation whereas implantation during SAP synthesis gave better result (Fig. 4, right). In both methods, the degree of sphere coverage varies greatly. It is observable that there are SAP particles that have no MP on their surface nor in their matrix.

3.3. Size distribution of obtained Fe_3O_4 particles

Due to the agglomeration of Fe_3O_4 particles in the solid phase, it is not possible to determine the size of the individual particles. Particle size analysis was carried out in water dispersion by laser diffraction technique. The results are shown in Fig. 5. Statistics of size distribution analysis are shown in Table 4.

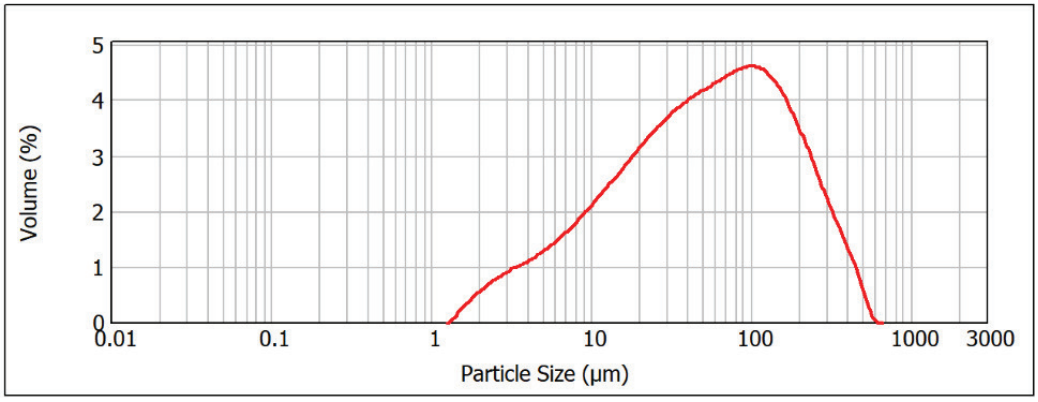

Fig. 5. Size distribution of particles of synthesized Fe_3O_4.

Table 4. Characteristic data of size distribution of Fe_3O_4.

Sample name	d(0.1)* [µm]	d(0.5) [µm]	d(0.9) [µm]	Span**
Fe_3O_4	7.359	54.389	228.972	4.075

*D(0.1), d(0.5) and d(0.9) defines the size below which respectively 10%, 50%, 90% of the sample is contained.

**Span describes the width of the distribution. Lower number means narrower distribution.

As shown in Fig. 5 the obtained particles cannot be qualified as nanoparticles directly. Majority of the particles (90%) are over 7.359 μm in diameter. Fe_3O_4 particles have large particle size dispersion.

3.4. Swelling properties of the obtained polymers

Swelling properties analysis was carried out for 4 of 6 samples (SAP-MP-1-3, 5). These data are presented in Table 5.

Table 5. Results of swelling properties of the obtained SAP-MP.

Sample name	Dry sorbent m_d [g]	Tube with swollen sorbent [g]	Dry tube [g]	Swollen sorbent m_s [g]	Absorbed solution [g]	Sw [%]
SAP-MP-1	0.1065	18.4714	12.4006	6.0708	5.9643	5600
SAP-MP-2	0.1040	16.7248	12.4225	4.3023	4.1983	4037
SAP-MP-3	0.1056	17.3601	12.3429	5.0172	4.9116	4651
SAP-MP-5	0.1067	–	–	–	–	–

Swelling of SAP-MP-5 could not be determined because of agglomeration that appeared after introducing water into tube containing sample. The best swelling properties was obtained by SAP-MP-1. In this case the mass of the absorbed water solution was 56 g/ 1 g SAP. The additional analysis of swelling properties was made on microscope by measuring diameter of dry and swollen SAP-MP-1 sphere as can be seen in Fig. 6. One can observe that the target sphere after introducing water into it changed its diameter from 69 μm (Fig. 6, left) to 530 μm (Fig. 6, right), expanding its volume about 450 times. (Volume was calculated assuming the spherical shape of the particle).

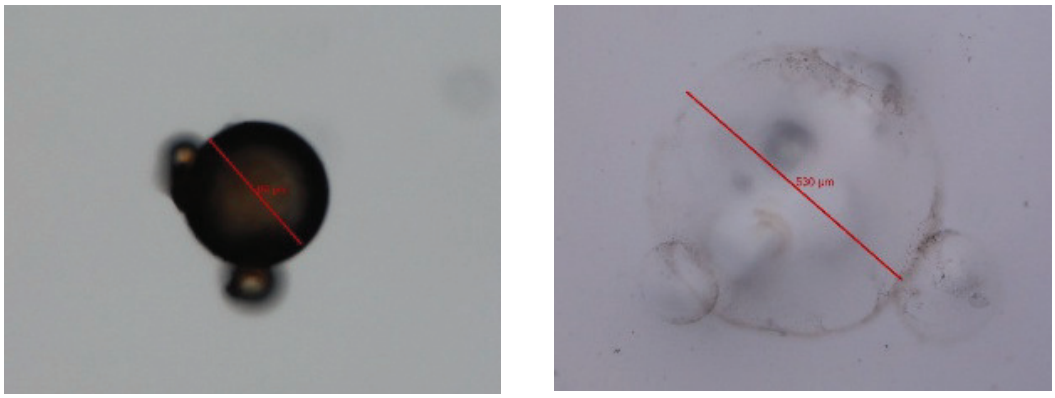

Fig. 6. Microscopy images of dry (left) and swollen (right) SAP-MP-1 particle.

4. CONCLUSIONS

Two series of superabsorbent polymers implanted in two ways were obtained. FT-IR analysis confirmed the polymerization reaction occurrence and the presence of carboxylic anions in the structure of the obtained SAP. Microscopy images successfully proved implantation of SAP materials in both methods. Swelling properties analysis showed that the obtained materials have good liquid absorption properties. Better results were obtained for the samples prepared when implantation took place during synthesis of SAP materials.

REFERENCES

[1] L. Mingzhu, G. Tianhua, *Journal of Applied Polymer Science*, **82**, 1515, (2001).
[2] S. Kiatkamjornwong, *Sci. Asia.*, **33**, 39, (2009).
[3] N. Bharti Shukla, G. Madras, *Journal of Applied Polymer Science*, **125**, 630, (2012).
[4] Z. Jian, S. Min-Wei, Z. Le, X. Xu-Ming, *Journal of Applied Polymer Science*, **90**, 1851, (2003).
[5] H. Fengjun, Q. Mengping, *Journal of Materials Science*, **36**, 731, (2001).
[6] L. Xingli, L. Xiaolan, L. Zhiyong, M. Xinping, *Journal of Polymer Research*, **18**, 897, (2011).
[7] C. Jun, P. Haesun, P. Kinam, *Journal of Biomedical Materials Research*, **44**, 53, (1999).

[8] A. B. Argade, N. A. Peppas, *Journal of Applied Polymer Science*, **70**, 817, (1998).
[9] E. Karadag, D. Saraydin, *Turkish Journal of Chemistry*, **26**, 863, (2002).
[10] J. Maitra, V. Kumar Shukla, *American Journal of Polymer Science*, **4**, 25, (2014).
[11] W. Wei, H. Quanguo, *Nanoscale Research Letters*, **3**, 397, (2008).
[12] P. Yue, D. Xuewen, Z. Fan, X. Bing, *Chemical Society Reviews*, **41**, 2912, (2012).
[13] J. Estelrich, E. Escribano, J. Queralt, M. A. Busquets, *International journal of molecular sciences*, **16**, 8070, (2015).
[14] S. Ansari, E. Ficiarà, F. Ruffinatti, A., I. Stura, M. Argenziano, O. Abollino, R. Cavalli, C. Guiot, F. D'Agata, *Materials,* **12**, 465, (2019).
[15] T. Swaddle, P. Oltmann, *Canadian Journal of Chemistry*, **58**, 1763, (1980).
[16] S. Ghosh, W. Jiang, J. D. McClements, B. Xing, *Langmuir*, **27**, 8036, (2011).
[17] H. Hosseinzadeh, A. Javadi, *Polymers Advanced Technologies*, **27**, 1609, (2016).
[18] Y. Li, G. Huang, X. Zhang, B. Li, Y. Chen, T. Lu, T.J. Lu, F. Xu., *Adv. Funct. Mater*, **23**, 660, (2013).
[19] G. R. Bardajee, Z. Hooshyar, *Carbohydrate Polymers*, **101**, 741, (2014).
[20] R. Hernandez, C. Mijangos, *Macromolecular Rapid Communications*, **30**, 176, (2009).