NIȚĂ TUDORACHI, AURICA P. CHIRIAC*)

"Petru Poni" Institute of Macromolecular Chemistry
Grigore Ghica Voda Alley No. 41 A, 700487 Jassy, Romania
*) Corresponding author; e-mail: achiriac1@yahoo.com

Biodegradable polymeric template and magnetic composites on its base

Summary — Modified starch and sodium polyaspartate blend was used as a polymeric template for the preparation of a magnetic composites. Their structural and magnetic properties (by SEM, magnetometry, IR), as well as thermal stability and particle size distributions were characterized. The dependence between the magnetite content and magnetic susceptibility values is stressed. The study confirms the possibility to obtain magnetic composites from magnetite (Fe_3O_4) and the polymeric composite template based on carboxymethyl starch and sodium polyaspartate. The importance of these magnetic composites derives from the biodegradability of the template as well as the possibilities given by functional groups able to couple both magnetite and further bioactive substances.

Key words: carboxymethyl starch, sodium polyaspartate, magnetite, magnetic composite, structure, properties.

BIODEGRADOWALNA MATRYCA POLIMEROWA I MAGNETYCZNE KOMPOZYTY NA JEJ PODSTAWIE

Streszczenie — Otrzymano skrobię modyfikowaną kwasem monochlorooctowym (CMS) oraz sól sodową poli(kwasu asparaginowego) (PSI-Na), których mieszaninę (1:1) użyto w charakterze biodegradowalnej matrycy polimerowej w kompozytach magnetycznych. Wytworzono też nanocząstki magnetytu (Fe_3O_4) z mieszaniny $FeCl_3$+$FeCl_2$. Na podstawie wspomnianej matrycy i magnetytu sporządzono kompozyty magnetyczne zawierające 2,5 %, 5 % lub 25 % Fe_3O_4. Metodą IR scharakteryzowano budowę otrzymanej matrycy i jej składników a także magnetycznego kompozytu (rys. 1—3, tabela 1 i 2). Zbadano strukturę wytworzonych produktów (SEM, rys. 5), ich termostabilność (TG i DTG, rys. 4, tabela 3) i podatność magnetyczną (rys. 6); określono także rozkład wymiarów cząstek biodegradowalnej matrycy, magnetytu oraz kompozytów magnetycznych o różnym udziale Fe_3O_4 (rys. 7). Podkreślono wzajemną zależność pomiędzy zawartością cząstek magnetytu a wartością podatności magnetycznej kompozytów. Wyniki przedstawionych badań potwierdzają możliwość uzyskania kompozytów CMS/PSI-Na/Fe_3O_4. Znaczenie takich materiałów wynika zarówno z biodegradowalności matrycy polimerowej, jak i ze zdolności obecnych w matrycy grup funkcyjnych do wiązania nie tylko magnetytu, ale i innych substancji bioaktywnych.

Słowa kluczowe: skrobia karboksymetylowana, poliasparaginian sodu, magnetyt, kompozyt magnetyczny, struktura, właściwości.

The interest and use of the nanostructured materials with magnetic properties in biomedical and biotechnological applications, including drug delivery, biosensors, chemical and biochemical separation and concentration of trace amounts of specific targets, such as bacteria or leukocytes, enzymes encapsulation, and contrast enhancement in magnetic resonance imaging are well known [1—3]. In most applications, spherical nanoparticles have been used. However, spherical magnetic nanoparticles still need to be improved for better controlling of particle sizes, surface functionalizations, and their environmental compatibility, due to the structural limitations of spherical particles when multifunctionality of their surfaces is required [4—7].

Magnetic composites can be produced by a large diversity of methods and starting substances. The specific type of interactions between template and magnetic particles depend on the composition and shape of the matrix as well as its surface functionality accessibility. Thus, magnetic composites can be prepared for example by coating of magnetic susceptible particles with synthetic polymers with suitable functional groups for the future supplementary attachments, or addition at the appropriate templates of the magnetic ferrofluids without any loss of subsequent binding activity. The preparation of a ferrofluid as stable colloidal dispersion necessitates the very good dispersion of the superparamagnetic iron oxide nanoparticles. Thus, there is necessary the presence of suitable matrix to maintain the colloidal suspension stability. Also, for the use of the magnetic carriers in biochemical processes it is essential that these matrices should be biocompatible as for example natural and biodegradable polymers [8—11]. The literature mentions the use of starch as cheap and "green" dispersant for medical and environmental applications. Thus, starch provides dispersion of silver nanoparticles in water without agglomeration [12—14].

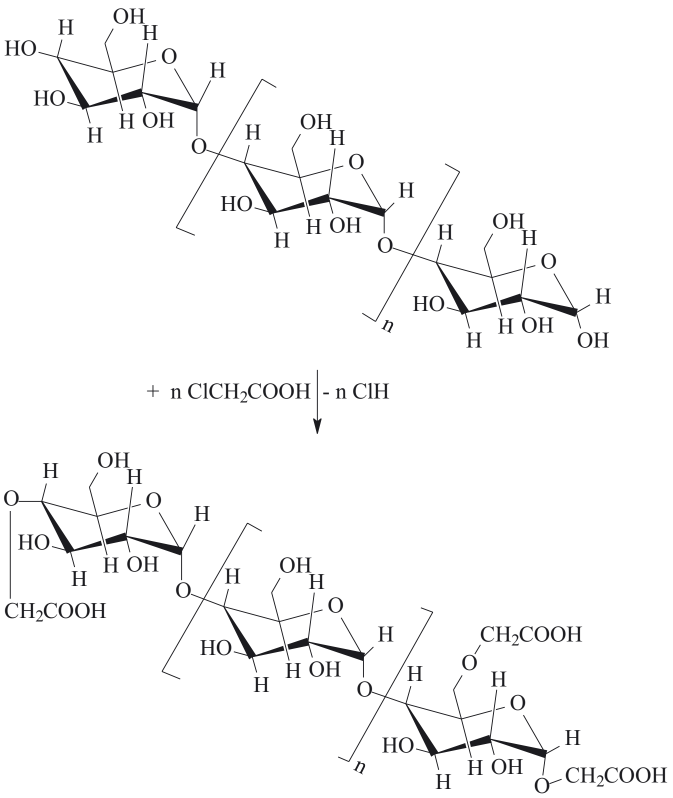
In our study a mixture composed from poly(aspartic acid) salt and modified starch was chosen as polymeric template for the preparation of the magnetic ferrofluids. Such template is water soluble, non toxic and biodegradable and, additionally, modified starch contains functional groups, which are both able to secure an increased coupling capacity and stability of the ferrofluid.

EXPERIMENTAL

Carboxymethyl starch (CMS) preparation

Corn starch ($C_6H_{10}O_n$, Merck) was modified with monochloroacetic acid according to the following reaction [Scheme A] and procedure.

In a three-necked flask equipped with a reflux condenser, 30 g of starch dissolved in 400 ml of isopropyl alcohol was stirred very carefully with an anchor type stirrer at ~ 400 rpm (Heidolph RZR 2020 equipment). The process was performed at room temperature for one hour to reach the homogeneous solution. Having stirred for one hour (also at room temperature) 80 ml of about 30 % NaOH solution was added; than monochloroacetic acid (36 g) was added step by step. The reaction is performed for 4 hours at 55—60 °C. The reaction product — white crystals — was decanted and mixed together with about 70 % methanol till reaching neutral pH. Again the liquid phase was decanted and the solid product of modified starch was washed several times with absolute methanol and dried under vacuum at 60 °C.

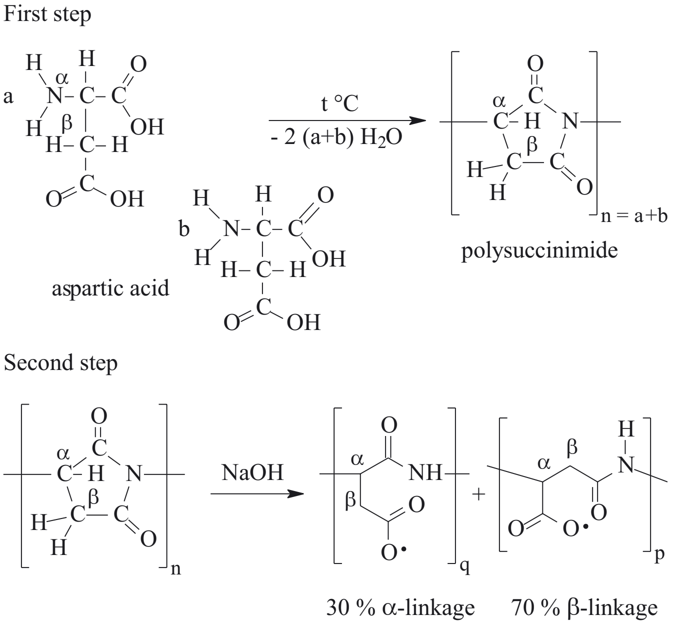


Scheme A. Starch modifying reaction with monochloroacetic acid

It is known that the degree of substitution (*DS*) of starch during the modification reaction depends on the composition of the reaction mixture, reaction time and temperature [14]. For determination of *DS* value of CMS obtained in the condition described, the product was extracted in methanol during 72 h and dried at 60 °C in vacuum. After that pH of carboxymethyl starch (0.5 g) disperion in deionized water (50 ml) was adjusted to 3.5 with 1N HCl and the dispersion was stirred for 20 min to convert the ionized carboxyl groups to free acid form. Carboxymethyl groups were titrated with standardized 0.1N NaOH solution in the presence of phenolphthalein as indicator [15]. *DS* of CMS was 0.6 and the yield corresponding to the reaction between starch and monochloroacetic acid was about 92 %.

Sodium polyaspartate (PSINa) preparation

Polysuccinimide (PSI) synthesized by the acid-catalyzed thermal polycondensation of *L*-aspartic acid was prepared as described previously in the literature [16] and then prewashed polysuccinimide was used for the preparation of linear form of sodium polyaspartate [17—24] as described below. The course of this two-stage synthesis of PSINa is presented in Scheme B.



Scheme B. The reaction mechanism of poly(aspartic acid) synthesis

Preparation of poly(succinimide) (PSI)

A 250 mL glass reactor equipped with a stirrer, heating jacket, thermometer and condenser is charged with 24 mL of dodecane (Fluka) and 12.45 g of *D*,*L*-aspartic acid (Sigma). The acid and alkane slurry is mixed well and heated to about 175 °C. Than 6.3 g of 85 % ortho-phosphoric acid (Chemical Company) as an aqueous solution is added semi-continuously to the agitated reactor contents while the temperature of reacting mixture was maintained at about 175 °C *via* the heating jacket. Also, the solids in the reactor are well dispersed by the agitation throughout the organic reaction medium during the thermal polycondensation reaction of aspartic acid to poly(succinimide). Water formed during the reaction is condensed and collected continuously. The reaction is discontinued (catalyst charge stopped) when condensing water accumulation stops. Total reaction time at about 175 °C is about 6 h. The reactor content is cooled to temp. about 20 °C. Conversion based on H_2O recovered is 93.6 %.

In situ hydrolysis of PSI using anhydrous NaOH

After formation of the PSI, the reactor content is filtered and 14 g of PSI and 66 g of dodecane are recharged into the reactor. 5 g of anhydrous sodium hydroxide (Fluka) is milled into fine powder form and added to the dodecane PSI slurry with agitation for about 7 hours at 20—24 °C. The sodium polyaspartate reaction product present as a slurry in dodecane is centrifuged to remove the organic reaction medium and dried in the vacuum oven at 80 °C overnight to remove organic residuals. Complete dissolution of the solids in water demonstrates successful hydrolysis.

Sodium poly(aspartate) received according to the described procedure was used for the preparation of the magnetic composites. The salt can be further converted to poly(aspartic acid) by reaction with a strong acid (HCl).

Magnetic composite preparation

The magnetite nanoparticles were prepared by a conventional coprecipitation from a solution containing $FeCl_2$ (0.033 M) and $FeCl_3$ (0.067 M) which was poured into a base solution of NaOH (200 mM) under stirring at 60 °C. The ferrofluid suspension of Fe_3O_4 was cooled at room temperature. The black solid was settled over a magnet, leaving a clear supernatant liquid that was decanted. The black solid of Fe_3O_4 was washed several times with acetone and MeOH, and the precipitates were isolated from the solvent by magnetic decantation. This washing-decantation procedure was repeated 3 times.

The synthesized biodegradable polymeric structures were utilized templates for the magnetic composites preparation. Three variants of magnetite concentration were used, namely of 2.5 %, 5 % or 25 %.

For the magnetic composite with 2.5 % magnetite concentration the following procedure was performed: CMS and PSINa (ratio 1:1) were mixed together in water at 40—45 °C till a homogeneous clear solution was obtained. The prepared solution was added drop wise to coat the prepared magnetite particles (0.05 g) well dispersed in distilled water (20 ml) before sonication (30 sec). The process takes at least 1 h at 55—60 °C. During this time, the dispersion medium was stirred at 500—1000 rpm. For better dispersion and stabilization of the magnetic composite 10 ml of NaOH solution (12.5 %) was added, the mixture was stirred at 500—1000 rpm and maintained for about 3 h at 40—45 °C. Finally, the prepared magnetic composites were collected using a magnet and washed consecutively with petroleum ether and acetone. The microspheres were dried in an oven at 40 °C for 2 days.

The same procedure was used for two other variants of composites, based on magnetite concentration equal to 5 % and 25 %.

Methods of testing

— IR absorption spectra have been recorded using a Perkin Elmer 577 spectrophotometer (state resolution 8 cm^{-1}, in an air, thermoelement with vacuum as detector, and ATR accessories) — the frequency range 400— 4000 cm^{-1} for equal quantities of ~0.1 mg films made of polymers prepared.

— TG and derivative thermogravimetric (DTG) curves were recorded using a MOM Budapest derivatograph under the following operational conditions: sample weight 50 mg, heating rate 12 °C /min, in an air flow of 30 mL/min and with reference material α-Al_2O_3.

— The structure of the magnetic composite was evaluated from the images obtained by means of a scanning electron microscope BS 340 TESLA type (SEM, 20 kV accelerating voltage, 15 mm working distance, 0.5 nm spot size). The samples were covered with pure metallic silver. The laying down of silver was carried out using evaporation of the metal under a high vacuum, to give a thickness of around 15—20 Å.

— The prepared composites were characterized from the view point of their magnetic susceptibilities; the measurements were realized using own construction device [25].

— Particle size and particle size distributions of polymeric template and the prepared magnetic composites were characterized using a Mastersizer 2000 analyzer scheduled with a Hydro S sample dispersion unit; 0.1 mg samples and redistilled water were used for the preparation of the dispersions.

RESULTS AND DISCUSSION

Carboxymethyl starch

The synthesized carboxymethyl starch was characterized by IR spectroscopy (Fig. 1) and the bands corresponding to the functional groups are mentioned in Table 1.

Table 1. Bands and corresponding functional groups of CMS and starch [26]

Frequency range, cm^{-1}	Bond and Compound Type	
Modified starch	1710 cm^{-1}, stretch	C=O specific for COOH
	1420 cm^{-1} and 1610 cm^{-1}	C=O specific for COO$^-$
	3400 cm^{-1}	OH from CMS and water absorbed
	1020—1160 cm^{-1}	C–O from glycoside ring C–O–C and C–OH
Starch	1650 cm^{-1}	OH from the water absorption
	3400 cm^{-1}	OH from starch and water absorbed
	980—1190 cm^{-1}	C–O from glycoside ring C–O–C and C–OH

The presence of some very wide absorption bands at 3400 cm^{-1} characteristic to OH group and to water absorbed is observed in CMS spectrum as well as in starch one. In IR spectrum of modified starch the appearance of some vibration absorption bands C=O at 1710 cm^{-1} characteristic to –COOH groups is noticed. Also, at 1420 cm^{-1} and 1610 cm^{-1} high intensity vibrations of the absorption bands C=O characteristic to COO– groups appear.

The absorption bands at 980—1190 cm^{-1} in starch are specific to C–O linkages present in glicosidic rings C–O–C and in C–OH groups. These bands are representative for starch. The bands are discovered also in CMS but a narrower interval 1020—1160 cm^{-1} emphasize the presence of the glicosidic structural unity in the structure of the synthesized modified starch. The more important differences in the spectra are those at 1650 cm^{-1} which corresponds to the unmodified starch and water adsorption and also at 1710 cm^{-1}and 1610 cm^{-1} related to the carboxylic groups present in modified starch.

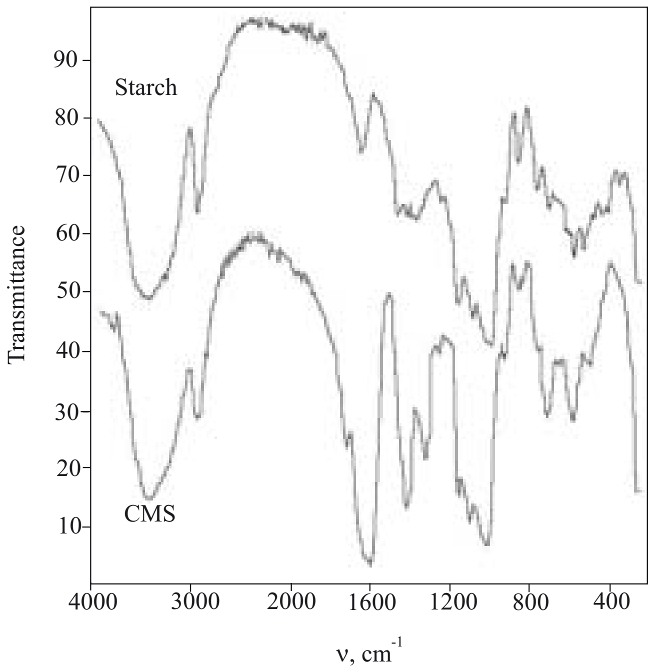


Fig. 1. IR spectra of starch and carboxymethyl starch

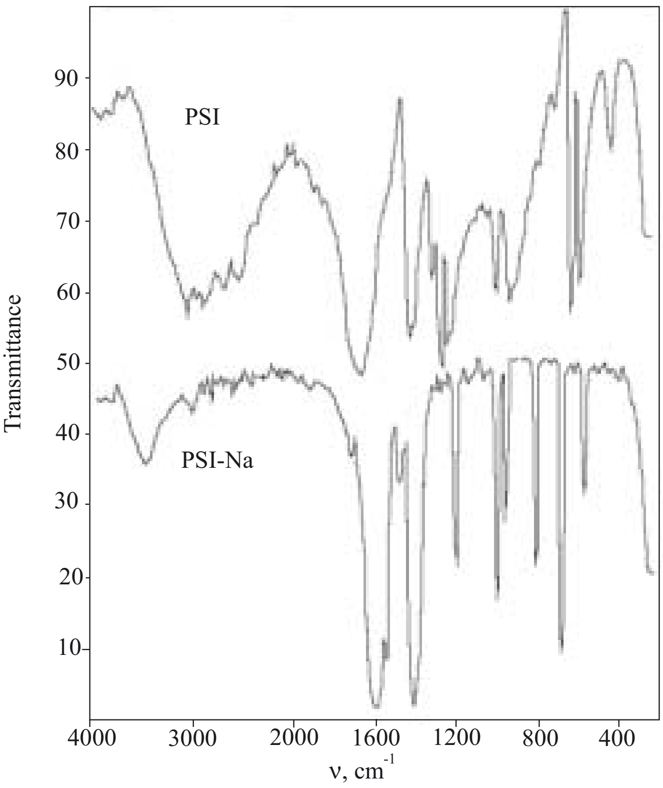


Fig. 2. IR spectra of PSI and PSI-Na

Sodium salt of poly(aspartic acid)

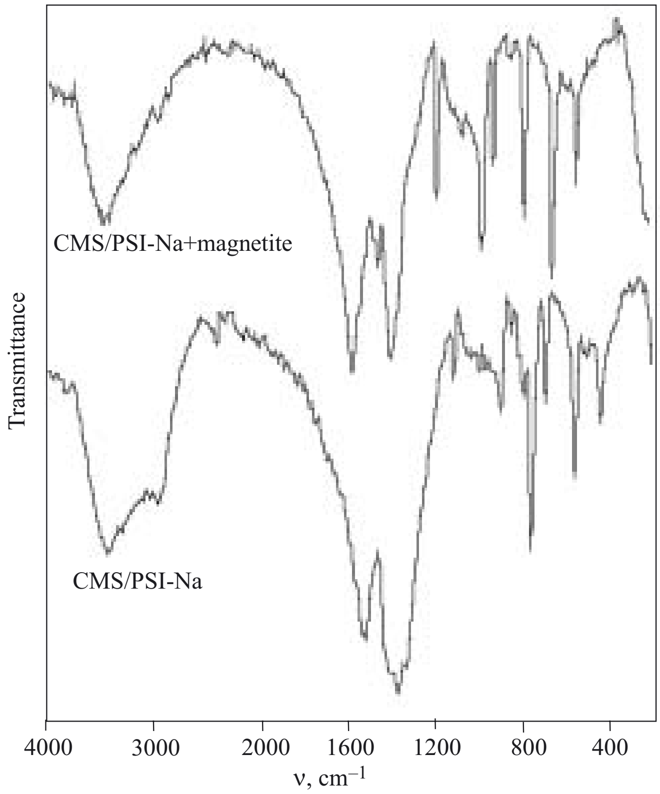
IR spectra of poly(succinimide) (PSI) and sodium salt of poly(aspartic acid) (PSI-Na) are presented in Fig. 2.

Magnetic composite

Figure 3 presents IR spectra of the biodegradable template (CMS/PSI-Na) and magnetic composite (CMS/PSI-Na-magnetite) (Fig. 3a), as well as of the magnetite (Fig. 3b).

IR spectra of the polymeric matrices used for the preparation of the magnetic composites present the specific absorption bands corresponding to CMS as well as to PSI. The IR spectrum of the prepared magnetic composite comprises again the particular bands of the specific functional groups and they are mentioned in Table 2.

All specified groups evidenced in the IR spectra are capable for coupling of magnetite through coordinative links [27—29]. The polymeric composite matrix covers the magnetic particles and holds them apart through repulsive forces against attracting forces by surface tension. Moreover, the formation of a polymer layers on the



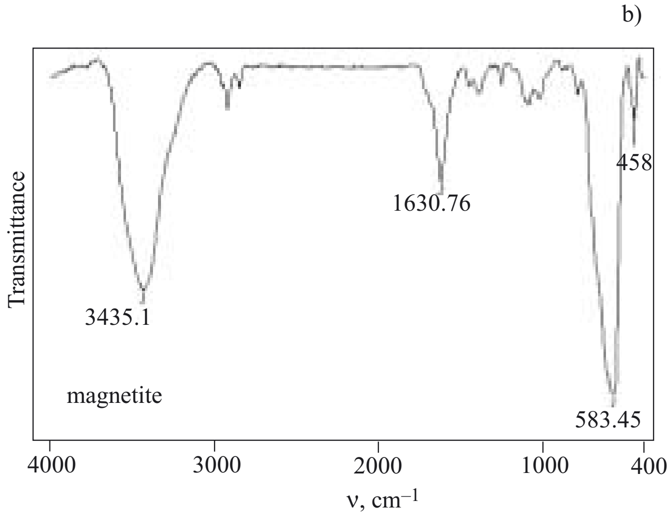


Fig. 3. IR spectra of the polymeric template CMS/PSI-Na and magnetic composite CMS/PSI-Na-magnetite (a) and the magnetite prepared (b)

surfaces of the magnetite nanoparticles — as can be observed from SEM micrographs — maintains the stability of the magnetic particles dispersion preventing the coalescence. Thus, the stability of the dispersion against forces due to thermal motion, repulsion, *etc.*, which in the ferrofluid must be stronger than the attraction forces is assured. It is well known that the stability of ferrofluids composed of magnetic particles is not only affected by inhomogeneous particle size distribution, but also by the surface charge of the particles in the solution [1, 30]. The polymeric template gives the stabilization of the ferrofluid by the electrostatic repulsion of similarly charged surfaces.

Table 2. Bands in the IR spectra of polymeric template and magnetic composite corresponding to specific functional groups [26]

Frequency range, cm^{-1}		Bond – Functional Group Type
Polymeric template and magnetic composite	980-1190 cm^{-1}	C–O from glycoside ring C–O–C and C–OH
	1550 cm^{-1} and 3400—3500 cm^{-1}	NH_2 from alkyl - NH_2
	1610 cm^{-1} stretch	C=O specific for COO^-
	980—1160 cm^{-1}, 1020—1160 cm^{-1}	C–O from glycoside ring C–O–C and C–OH

Thermal behavior of the prepared magnetic composites is presented in Fig. 4 (as weight loss during thermal decomposition reaction).

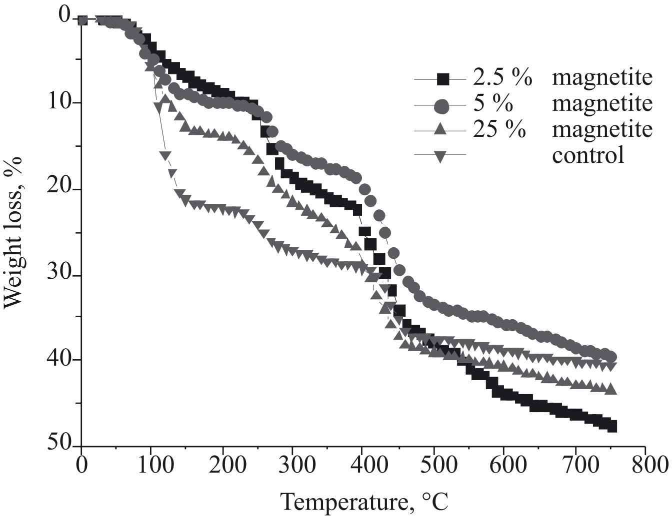


Fig. 4. TG curves of the magnetic composites CMS/PSI-Na/magnetite and polymeric template CMS/PSI-Na (as control sample)

Table 3. Data concerning thermal behavior of samples studied[*)]

Magnetite, %	T_{10}, °C	W_{750}, %	T_i, °C	T_f, °C
0	120	41	200	370
2.5	235	48	215	375
5	240	39	210	375
25	140	44	205	340

[*)] T_{10} — temperature corresponding 10 % weight loss.

T_i, T_f — initial and final temperature of the main thermal decomposition process.

W_{750} — weight loss at 750 °C.

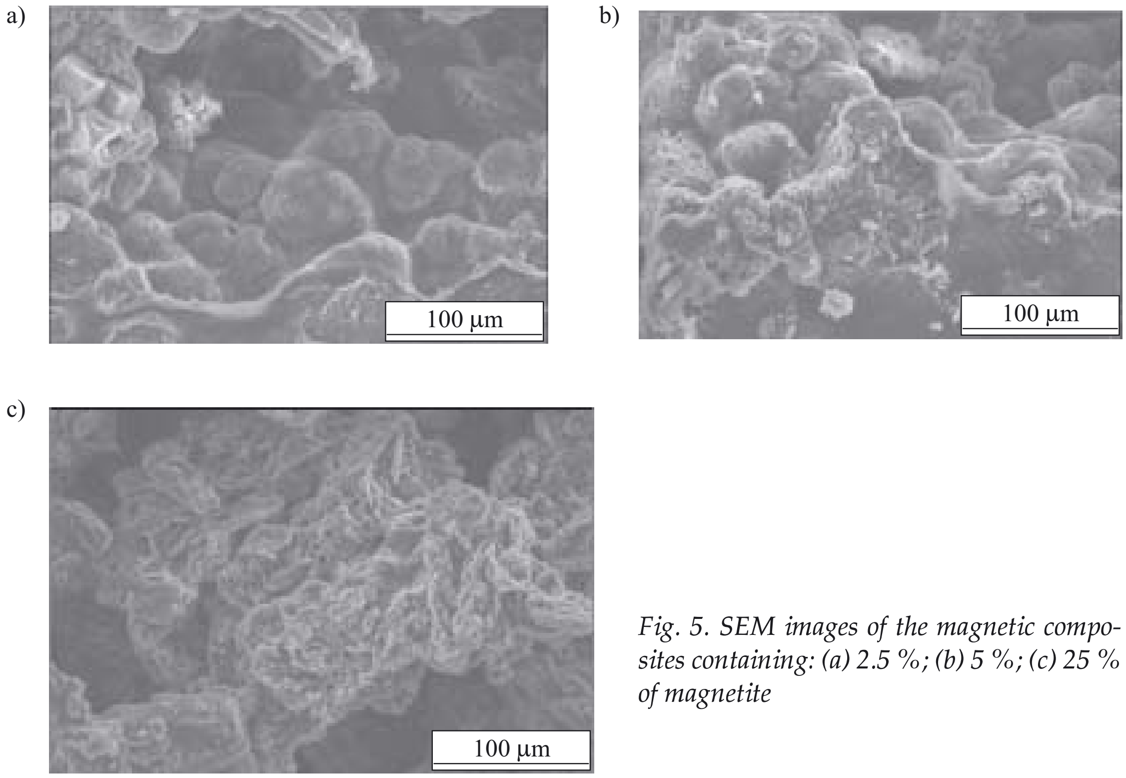


Fig. 5. SEM images of the magnetic composites containing: (a) 2.5 %; (b) 5 %; (c) 25 % of magnetite

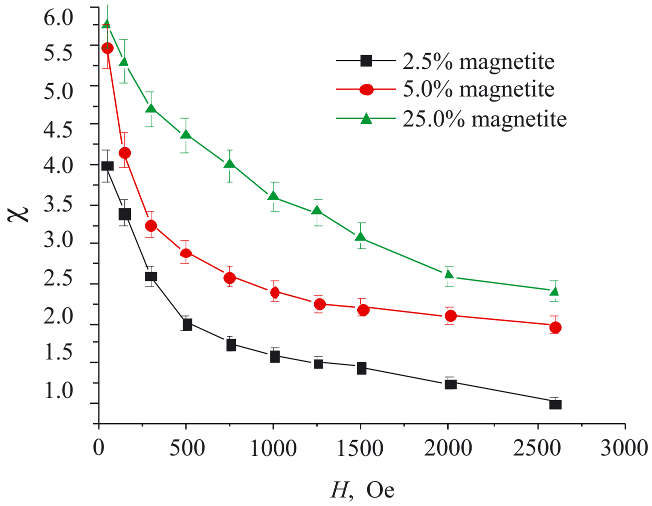


Fig. 6. Evolution of the magnetic susceptibility (χ) of magnetic composites with different content of magnetite versus magnetite field intensity (H)

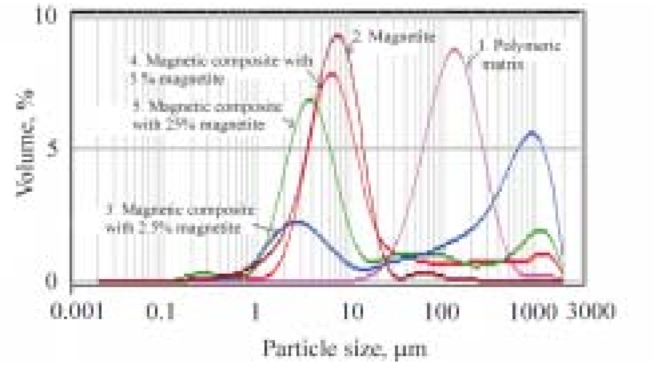


Fig. 7. Particle size distribution of the polymeric matrix (1), magnetite (2), and magnetic composites with different contents of magnetite (3, 4, 5) curves

There are registered 3 processes of thermal decomposition — each of them having specific rate corresponding to the particular component of the magnetic composite. In the interval from 100 °C to 400 °C the magnetic composites present higher thermal stability than the polymeric matrices. The weight loss values of the prepared magnetic composites (determined from thermogravimetric analyses) are presented in Table 3. Thus, 10 % weight loss of the polymeric template (control sample) goes up to 120 °C, in contrast to the composites. For them much higher temperatures were registered depending on the magnetite content as for example up to 140 °C (in case of 25 % magnetite content), 235 °C (2.5 % magnetite content) and 240 °C (5 % magnetite content). At the same time the higher magnetite content induces diminished thermal stability, phenomenon attributed to the ferric oxides that act as catalysts [31]. Up to temp. 750 °C, the second interval of temperature, higher rate of thermal decomposition is registered, again attributed to the magnetite presence. The values of weight loss at the end of the thermal decomposition processes (750 °C) do not surpass 39—48 % of the samples weights owing to Na and Fe presence.

SEM images were used to evaluate the morphological aspects of the magnetic composites prepared. Figure 5 illustrates a self-assembling of the magnetic particles. The polymeric surface with homogeneous structure — the macromolecular chains including functional groups able for coupling the magnetic material — was primarily smooth, although some roughness could be identified in certain areas. The magnetite performs a relatively spherical geometry of particles deposited onto the surface of the matrix and encapsulated onto the entire surface of the polymeric template, being also evident with the increase in magnetite content. Small quantities of magnetite (2.5 %) are not able to perform a continuous phase on the polymeric surface what reflects also in the worse magnetic properties of the composite (see Fig. 6). Growth of the magnetite content in the magnetic composite (5 % or 25 %) do not induce congestion; the magnetic product remains uniform and well dispersed onto the polymeric matrix which determines also the improvement in magnetic properties of the composite. The homogeneity of the magnetic particles dispersion on the polymeric surface in case of samples with 25 % magnetite content is also caused to some degree by uniformity of the synthesized magnetic particles what was underlined and evidenced by the size distribution of the magnetic composite particles (see Fig. 7).

The magnetic susceptibility determined for the prepared magnetic composites is presented in Fig. 6. Growth of the magnetic susceptibility corresponds to the higher magnetite content. Also, the magnetic susceptibility values demonstrate the possibilities to use the composites for example for biochemical separation.

The analysis of particle size distribution (Fig. 7) shows the polymeric matrices capacity for coupling the magnetite; practically, a reduction of the particle size takes place after preparation of the magnetic composites. The synthesized particles varied in size from the micron and submicron range with a relatively broad size distribution. This was not unexpected since it was well known that small changes in the synthesis procedure could result in significant changes in the resulting microspheres. It is important that the size distribution of the magnetic microspheres was less broad than for the non-magnetic batch. This behavior is attributed to the wrapping and compatibility of polymeric template and magnetite. This is due to sodium poly(aspartate) capacity as dispersant, as an absorbent resin, chelating and complexing agent, as well as to the functional groups of the carboxymethyl starch able to couple the magnetite [32—34].

CONCLUSIONS

The study confirms the possibility to use the polymeric composite template based on carboxymethyl starch and sodium polyaspartate as a matrix for magnetic composites with different magnetite content, respectively 2.5 %, 5 % or 25 %. Thermal analysis proves the stability of the composites increase with the magnetite content. SEM images confirm good dispersion of magnetic compound on the matrix surface — for a magnetite content till about 25 % — as well as the self-asemby of magnetite and the polymeric template. At the same time, the size distribution of the magnetic composites shows the compatibility as well as the affinity between the polymeric matrix and the magnetite. Thus, after the coupling process between polymeric template and magnetite, reduced dimensions of the magnetic particls are registered in comparison with their precursors.

The importance of the prepared magnetic composites derives also from the magnetic susceptibility values of the synthesized magnetic particles as well as the biodegradability and biocompatibility of the polymeric matrix and the presence of the multiple functional groups able to couple either magnetite or further bioactive substances.

ACKNOWLEDGMENTS

The authors thank Dr. V. Badescu for magnetic measurements (National Institute of Research & Development for Technical Physics, Iasi, Romania).

The work was supported by the CEEx Grant 8151051/ 12.09.2007.

REFERENCES

1. Horak D., Semenyuk N., Lednicky F.: *J. Polym. Sci. Part A: Polym. Chem.* 2003, **41**, 1848.
2. Spanova A., Horak D., Soudkova E., Rittich B.: *J. Chromatogr. B* 2004, **800**, 27.
3. Bizdoaca E. L., Spasova M., Farle M., Hilgendorff M., Caruso F.: *J. Magn. Magn. Mater.* 2002, **240**, 44.
4. Sauzedde F., Elaissari A., Pichot C.: *Colloid Polym. Sci.* 1999, **277**, 1041.
5. Xulu M., Filipcsei G., Zrinyi M.: *Macromolecules* 2000, **33**, 1716.
6. Jones F., Colfen H., Antonietti M.: *Colloid Polym. Sci.* 2000, **278**, 491.
7. Ji Z., Shengtang Z., Yunpu W., Jiayu Z.: *J. Magn. Magn. Mater.* 2007, **309**, 197.
8. Wenru Z., Jinlou G., Lingxia Z., Hangrong C., Jianlin S.: *J. Am. Chem. Soc.*, 2005, **127**, 8916.
9. Glogowski E., Tangirala R., Russell Th. P., Emrick T.: *J. Polym. Sci.: Part A: Polym. Chem.* 2006, **44**, 5076.
10. Turečková J., Prokopová I., Niklová P., Šimek J., Šmejkalová P., Keclík F.: *Polimery* 2008, **53**, 634.
11. Sobczak M., Olędzka E., Kołodziejski W. L., Kuźmicz R.: *Polimery* 2007, **52**, 411.
12. Wilpiszewska K., Spychaj T.: *Polimery* 2008, **53**, 268.
13. Raveendran P., Fu J., Wallen S. L: *J. Am. Chem. Soc.* 2003, 125, 13 940.
14. Stojanović Z., Jeremić K., Jovanović S.: *Starch/Stärke* 2000, **52**, 413.
15. Mitchell G., Wijinberg A. C.: *Starch/Stärke* 1995, **47**, 46.
16. *Pat. USA* 5 859 149 (1999).
17. Tomida M., Nakato T., Matsunami S., Kakuchi T.: *Polymer* 1996, **37**, 4435.
18. Tomida M., Nakato T., Matsunami S., Kakuchi T.: *Polymer* 1997, **38**, 2791.

19. Tomida M., Nakato T., Matsunami S., Kakuchi T.: *Polymer* 1997, **38**, 4733.
20. Wang Y., Zhang J., Hou Y., Ruan G., Pan M., Liu T.: *J. Therm. Anal. Calorim.* 2003, **73**, 923.
21. Wang Y., Hou Y., Ruan G., Pan M., Liu T.: *J. Macromol. Sci., Part A* 2003, **40**, 293.
22. Nakashima T., Yamada Y., Yoshizawa H.: *Colloid Polym. Sci.* 2007, **285**, 1487.
23. Schwamborn M.: *Polym. Degrad. Stab.* 1998, **59**, 39.
24. Tylek E., Polaczek J., Pielichowski J.: *Polimery* 2005, **50**, 341.
25. Nita L. E., Chiriac A. P., Neamtu I., Vasile C.: *J. Appl. Polym. Sci.* 2006, **100**, 4133.
26. Badilescu S., Toader M., Giurginca M., Talpus V.: "IR Spectroscopy of Polymers and Auxiliary", Technical Publishing House, Bucharest (Romania), 1982.
27. Park S. I., Lim J. H., Kim J. H., Yun H. I., Kim C. O.: *J. Magn. Magn. Mater.* 2006, **304**, 406.
28. Alexiou C., Arnold W., Hulin P., Klein R. J., Renz H., Parak F. G., Bergemann C., Lübbe A. S.: *J. Magn. Magn. Mater.* 2001, **225**, 187.
29. Bergemann C., Müller-Schulte D., Oster J., Brassardà L., Lübbe A. S.: *J. Magn. Magn. Mater.* 1999, **194**, 45.
30. Hong R.Y., Pan T. T., Han Y. P., Li H. Z., Ding J., Han S.: *J. Magn. Magn. Mater.* 2007, **310**, 37.
31. *Pat. USA* 4 854 981 (1989).
32. Xianqiao L., Kaminski M. D., Riffle J. S., Haitao C., Torno M., Finck M. R., Taylor La T., Rosengart A. J.: *J. Magn. Magn. Mater.* 2007, **311**, 84.
33. Liu X., Kaminski M. D., Guan Y., Chen H., Liu H., Rosengart A. J.: *J. Magn. Magn. Mater.* 2006, **306**, 248.
34. Thombre S. M., Sarwade B. D.: *J. Macromol. Sci., Part A* 2005, **42**, 1299.

Received 29 XI 2008.