Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Composite Magnetic Microspheres of Tamarind Gum and Chitosan: Preparation and Characterization

Ji Zhang[ab]; Shengtang Zhang[a]; Yunpu Wang[b]; Jiayu Zeng[a]; Xutao Zhao[b]
[a] College of Life Science, Northwest Normal University, Lanzhou, P. R. China [b] Institute of Polymers, Northwest Normal University, Lanzhou, P. R. China

To cite this Article Zhang, Ji , Zhang, Shengtang , Wang, Yunpu , Zeng, Jiayu and Zhao, Xutao(2007) 'Composite Magnetic Microspheres of Tamarind Gum and Chitosan: Preparation and Characterization', Journal of Macromolecular Science, Part A, 44: 4, 433 — 437
To link to this Article: DOI: 10.1080/10601320601188356
URL: http://dx.doi.org/10.1080/10601320601188356

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 433–437

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320601188356

Composite Magnetic Microspheres of Tamarind Gum and Chitosan: Preparation and Characterization

JI ZHANG,[1,2] SHENGTANG ZHANG,[1] YUNPU WANG,[2] JIAYU ZENG,[1] and XUTAO ZHAO[2]

[1]*College of Life Science, Northwest Normal University, Lanzhou, P. R. China*
[2]*Institute of Polymers, Northwest Normal University, Lanzhou, P. R. China*

Received August, 2006, Accepted September, 2006

In this study, composite magnetic microspheres have been synthesized based on tamarind gum and chitosan utilizing the suspension cross-linking technique for use in the application of magnetic carrier technology. The properties of the composite magnetic microsperes, such as morphological, magnetic properties, thermal stability and the functional groups of the microspheres, were characterized by different techniques (i.e., SEM, magnetometry, DSC and FT-IR). The swelling kinetics and pH responsive behaviors of the composite magnetic microspheres were also studied.

Keywords: composite magnetic microspheres; tamarind gum; chitosan; properties; kinetics

1 Introduction

In all biochemical processes, procedures such as separation, purification and unit operation (i.e., centrifugation, precipitation, mixing or the application of the high pressure) have to be performed, and these operations can result in malformation (i.e., decomposition, inactivation or deformation) of the biomolecules. Magnetic carrier technology appears to be a significant alternative for the solution of these biomolecule malformations. With this technology, magnetic carriers are used as the support materials and they can be easily separated from the reaction medium and stabilized in a fluidized bed reactor by applying a magnetic field. On the other hand, the use of magnetic particles can reduce the capital and operational costs. The most popular application of magnetic carrier technology is wastewater treatment, immobilization of enzymes or other biomolecules and the preparation of immunological assays (1–3). Magnetic carriers are most commonly manufactured from polymers, since they have a variety of surface functional groups which can be tailored to specific applications. In the literature, different types of natural and synthetic polymers (i.e., calcium alginate, polystyrene, polyacrylamide, polyvinyl alcohol, nitrocellulose and polyvinyl butyral) have been used in the preparation of magnetic carriers. Tamarind gum and chitosan can be used as base materials for magnetic carriers. They are familiar natural polymers and are very cheap biopolymers. In this study, composite magnetic microspheres were prepared and characterized for application in magnetic carrier technology (in particular, enzyme immobilization and bioaffinity chromatography). The suspension cross-linking technology was used for the production of composite magnetic microspheres and glutaraldehyde was used as a crosslinker (4). The thermal stability, magnetic properties and functional groups of the composite magnetic microspheres were evaluated. The swelling kinetics and pH responsive behaviors of the microspheres were also studied.

Address correspondence to: Ji Zhang, 967# East road of Anning, Lanzhou, Gansu, P. R. China, 730070. Fax: +86-0931-7970686; E-mail: zhangj@nwnu.edu.cn or zjltt66@163.com

2 Experimental

2.1 Materials

Chitosan, M_w 70 000, deacetylation degree 92.3% was purchased from the Yuhuan Company (Zhejiang, China). Tamarind gum was obtained from the AB Company (Tianjin, China) with the following physical data: viscosity, 5000–6000 centipoise in 5% solution. Acetic acid glacial solution was used as a solvent for the chitosan polymers and glutaraldehyde (50%) was used as the crosslinker. The suspension medium was composed of a mixture of benzene and ethyl acetate, and span-80 was added as an emulsifier. All chemicals were of analytical grade and no further purification was required.

2.2 Preparation of Magnetic Fluid

Magnetic fluid was synthesized as follows: a 35% $FeSO_4 \cdot 7H_2O$ solution (40 ml), 54% $FeCl_3 \cdot 6H_2O$ solution (50 ml) and 36% NaOH solution (50 ml) were prepared using distilled water. Then the ferrite and molysite were mixed, stirred, and heated. When the temperature reached 55°C, the alkaline solution was added to the mixture. It was continuously stirred for 30 min, 5 g of PEG-10000 was added, the temperature was raised to 80°C and the temperature was kept for 30 min. Later, dilute hydrochloric acid was used to neutralize the cooling mixture, and the magnetic fluid was prepared.

2.3 Preparation of Composite Magnetic Microspheres

In a typical procedure, a 6% tamarind gum solution (3 g) was prepared using distilled water (50 ml) containing a certain amount of magnetic fluid (2 ml). Then, chitosan (1 g) and acetic acid glacial (1 ml) were added. The mixture was then poured dropwise, into the dispersion medium, which was composed of benzene and ethyl acetate (70 ml:6 ml) and an emulsifier (Span-80, 2 ml) (5). During this process, the dispersion medium was stirred with a mechanical stirrer at 500–1000 rpm at room temperature. Twenty minutes later, glutaraldehyde (1 ml) was added to the dispersion medium and kept on stirring for about 1 h. At the end of this period, the composite magnetic microspheres were collected using a magnet and washed consecutively with petroleum ether and acetone. The microspheres were then dried in a vacuum drying oven at 40°C for two days and stored in a desiccator.

2.4 Characterization of Composite Magnetic Microspheres

2.4.1 Morphology

The morphological characterization of the composite magnetic microspheres was carried out with a scanning electron microscope (SEM, HITHCHI, S-450). A certain amount of the composite magnetic microspheres was dropped onto a sample holder and placed in a vacuum oven at room temperature to dry. The samples were coated with gold, and then SEM micrographs were obtained (5, 6).

2.4.2 Magnetic Properties

The degree of magnetism of the composite magnetic microspheres was evaluated using a vibrating-sample magnetometer (7304, VSM). A certain amount of the microspheres was balanced and placed in the magnetometer. The degree of magnetism of the microspheres was then determined by applying an increasing magnetic field over the microspheres and the results were used to calculate the magnetic quality of the microspheres. The most effective parameters determining the magnetic quality of the microspheres were the stirring rate and the magnetic materials contents of the microspheres, and these parameters varied in the range 500–1000 rpm and 1:3-1:1 ml Fe_3O_4/g chitosan, respectively (7).

2.4.3 DSC Methods

DSC was performed using a Perkin-Elmer DSC instrument with an intra-cooler. The samples were purged with the atmosphere of nitrogen. The heat flow rate was recorded from 25°C to 500°C, at a rate of 10°C/min. Indium (m.p. = 156.8°C) was used as the standard reference material to calibrate the temperature and energy scales of the DSC instrument (8–10).

2.4.4 Measurement of Swelling Kinetics of the Composite Magnetic Microspheres

Swelling kinetics of the composite magnetic microspheres was determined by swelling ratio (SR) at a given time. Dried microspheres were immersed in distilled water at each predetermined time at room temperature. Then, the sample was removed from distilled water and was frequently weighed after it was trapped with a filter paper to remove excess water on the surface. Thus, the wet weight of the microspheres was recorded during the swelling period at regular time intervals. The swelling ratio (SR), $(W_s + W_d)/W_d$, is defined as the ratio of the total weight of water in swollen microspheres to the weight of the dried microspheres, where W_s is the weight of adsorbed water and W_d is the weight of the microspheres at the dry state (11–13).

2.4.5 Measurement of pH Sensitive Behavior of the Composite Magnetic Microspheres

Measurement of pH sensitive behavior is similar to the measurement of swelling kinetics of the microspheres. It was determined by the equilibrated swelling ratio (ESR) at given pH data. ESR of microspheres was measured by immersing dry and known weight microspheres into a buffer solution with different pH data for at least 10 h at room temperature. Then, the microspheres were removed from the buffer solution and frequently weighed after being trapped with a filter paper to remove excess water on the surface. ESR is calculated from the following formula: W_e/W_d, where W_e is the weight of the solution in equilibrated swollen microspheres at each predetermined buffer solution with different pH data, the symbol of W_d is the same as defined earlier.

2.4.6 Functional Groups

FTIR spectra were recorded before and after processing of the composite magnetic microspheres form for observation of the functional groups of the microspheres. The FTIR spectra were obtained using a FTIR spectrophotometer (Alpha-centauri). In a typical procedure, around 0.25 mg of composite magnetic microspheres was thoroughly mixed with IR-grade KBr (0.1 g) and pressed (10 ton) into tablet form and the spectrum was then recorded.

3 Results and Discussion

3.1 Morphology of the Composite Magnetic Microspheres

The morphology of the composite magnetic microspheres was investigated using SEM. SEM micrographs are shown in Figures 1(a) and (b). As can be seen, the composite magnetic microspheres are well shaped spheres with a rather rough surface. Figure 1(c) shows the microstructure of the surface of the microspheres, and it can clearly be seen that Fe_3O_4 particles were achieved on the surface of the microspheres and the microspheres are porous.

3.2 Magnetic Properties

The magnetic properties of the composite magnetic microspheres were evaluated using a vibrating-sample magnetometer. The most effective parameters determining the magnetic properties were the stirring rate of the suspension medium and the Fe_3O_4/chitosan ratio.

The stirring rate of the suspension medium was varied between 500 and 1000 rpm for investigation of the effects of stirring rate on the magnetic properties of the composite magnetic microspheres. The results are shown in Figure 2. As can be seen, in all cases, a 10 KG magnetic field was found to be sufficient to excite almost all of the dipole moments of 1.0 g composite magnetic microspheres. The maximum magnetic quality (i.e., ~4.11 emu/g microspheres) was achieved at the highest stirring rate. This behavior can be explained by the change in microspheres size with a change in stirring rate. This indicates that the microspheres sizes are decreased by increasing the stirring rate, as discussed above, and magnetic excitation is easier in the case of a smaller microspheres size.

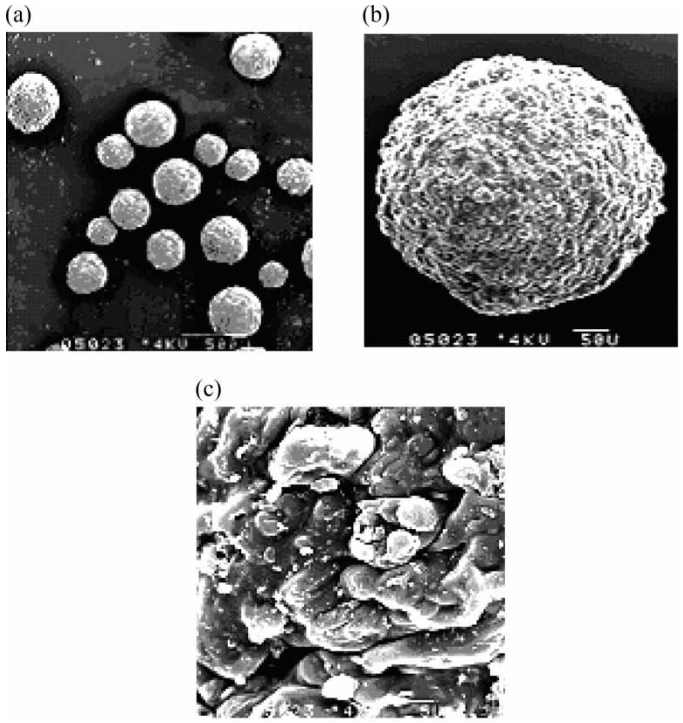

Fig. 1. Scanning electron microscopy of composite magnetic microspheres: (a) 70 times; (b) 360 times and (c) 4000 times.

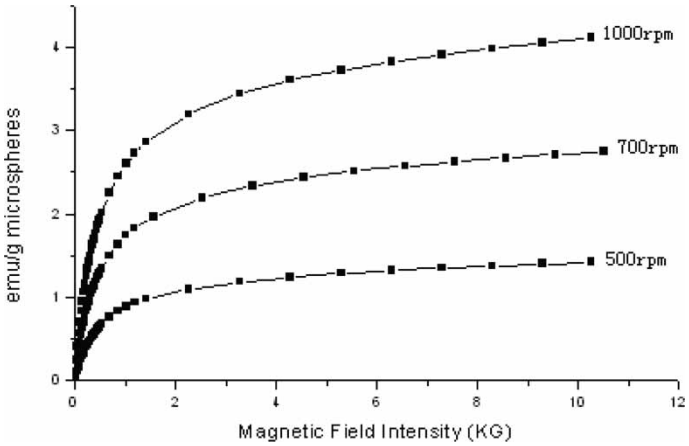

Fig. 2. Effects of stirring rate on the magnetic properties.

The Fe_3O_4/chitosan ratio was varied in the range of 1:3–1:1 (ml/g) for investigation of the effects of the Fe_3O_4/chitosan ratio on the magnetic properties. The results are shown in Figure 3. As can be seen, the magnetic quality increases significantly with Fe_3O_4 content. It is easy to explain this behavior by the relationship between emu and the Fe_3O_4 content. Furthermore, similar behavior for this parameter had been reported previously (14, 15).

3.3 DSC Analysis

Figure 4 shows the results obtained from DSC analyses of composite magnetic microspheres. Composite magnetic microspheres show a small peak at 44°C to 75°C, due to the volatilization of the solvent. Other strong transitions were found at 266, 307 and 345°C, and this may be due to the

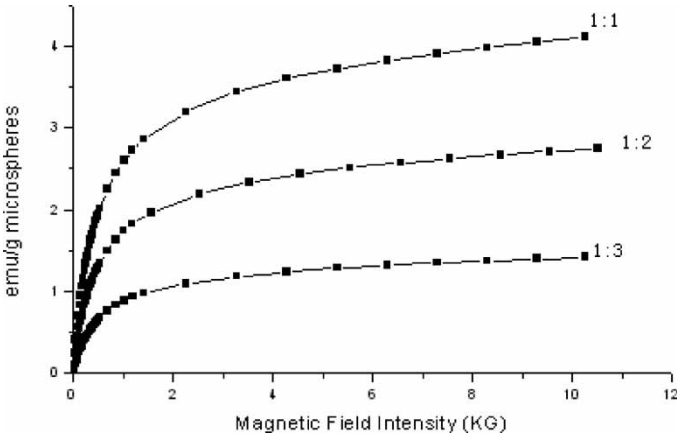

Fig. 3. Effects of Fe_30_4 content on the magnetic properties.

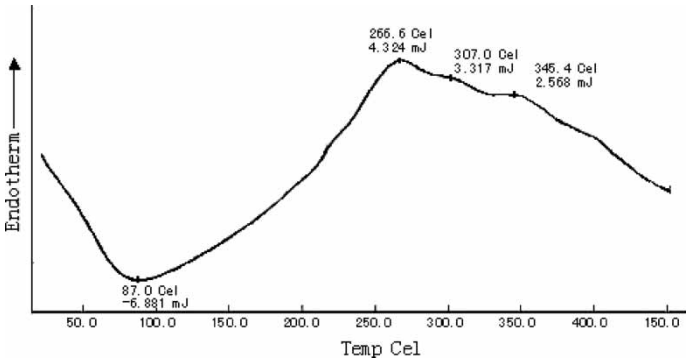

Fig. 4. DSC of composite magnetic microspheres.

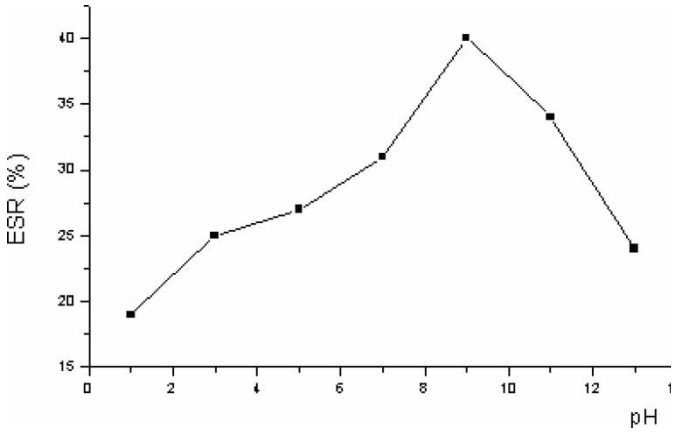

Fig. 6. pH behavior of the composite magnetic microspheres.

faster decomposition of the microspheres, and chitosan microspheres show strong transitions at 200°C (8). The reason for this phenomenon may be because of the crosslinking of tamarind gum and chitosan. Tamarind gum and chitosan are two single systems. When the crosslinker causes them to become a composite system, the free energy decreases. So the thermal stability becomes stronger than that of Tamarind gum and chitosan. The results demonstrated that the composite magnetic microspheres have a better thermal stability.

3.4 Swelling Kinetics of the Composite Magnetic Microspheres

Figure 5 shows the water swelling kinetics of the composite magnetic microspheres measured at room temperature. The samples swelled and reached equilibrium with 3 days. As is shown in Figure 5, the swelling ratio of the composite magnetic microspheres does not change noticeably during the swelling process.

3.5 pH Behavior of the Composite Magnetic Microspheres

Figure 6 shows pH effect on the swelling behavior of the composite magnetic microspheres. As shown in Figure 6, the microspheres are sensitive to pH. As the pH data increased, so did the ratio of equilibrium swelling. When pH data is higher than 9, the ESR of the composite magnetic microspheres decreased, this is attributed to the high OH- concentration screened ionic interaction, and the microspheres behaved as if they are unchanged.

3.6 Functional Groups

The functional groups of materials are very important for diverse applications, especially for biotechnological purposes. Therefore, the present functional groups should be kept even if the shape (or geometry) is changed into a new form (i.e., microspheres or membrane). FT-IR spectra of the materials and of the form processed into microspheres were recorded. The spectra are shown in Figure 7 for all forms (i.e., Tamarind gum, chitosan and composite magnetic microspheres). The OH groups present in Tamarind gum and chitosan are clearly seen at 3400 cm^{-1} and are also present in the case of the microspheres forms. In addition, the carbonyl bands at around 1700 cm^{-1} show glutaraldehyde crosslinking in the case of the microspheres forms. The other bands are similar for both materials and microspheres forms.

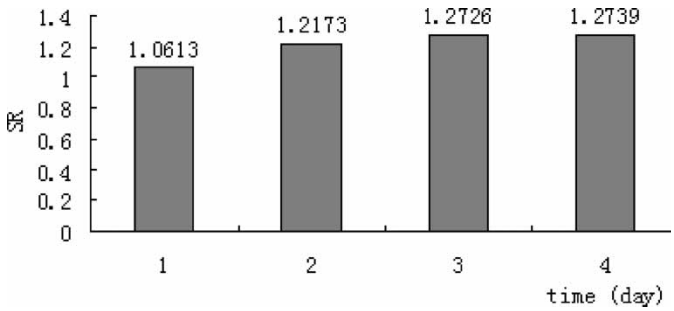

Fig. 5. The swelling kinetics of the composite magnetic microspheres.

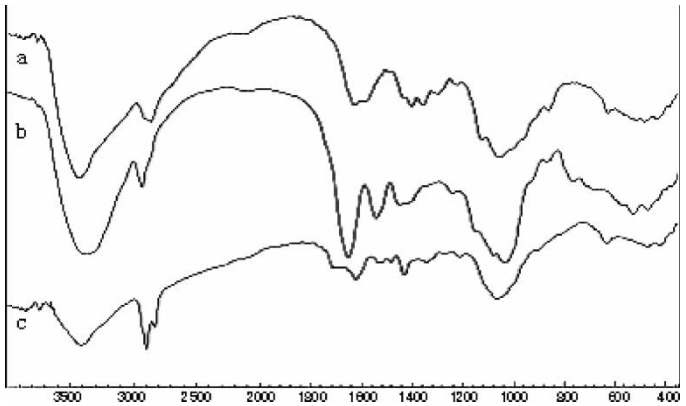

Fig. 7. FTIR spectro of (a) chitosan, (b) Tamarind gum, (c) composite magnetic microspheres.

4 Conclusion

In various kinds of biochemical and biotechnological applications (such as immobilization of biomolecules, wastewater treatment, affinity chromatography, drug delivery systems) the separation and recovery steps are difficult and expensive with respect to conventional techniques. Magnetic carrier technology is a very promising alternative to enhance the operational performance of these steps. The most important parameters in magnetic carrier technology are the economy and physicochemical characteristics of the carriers.

In this study, well shaped spherical composite magnetic microspheres were produced using a very cheap biopolymer (i.e., Tamarind gum and chitosan). The composite magnetic microspheres were evaluated based on morphology, magnetic properties, functional groups, thermal stability, swelling kinetics, shrinking kinetics and pH responsive behaviors. The results show that composite magnetic microspheres can be produced in the size range 230–460μm. The most important aspect for the magnetic carrier is a sufficient magnetic field intensity to excite all the dipole moments of each gram of magnetic carrier. This value defines the magnetic quality of the carriers and is in the range 8 to 20 KG for various applications. The magnetic field intensity for composite magnetic microspheres was found to be in the range 8 to 12 KG in this study. Therefore, composite magnetic microspheres are promising as a potentially good magnetic support to be employed in magnetic carrier technology with good economical aspects and good magnetic quality. On the other hand, the composite magnetic microspheres exhibited a swelling change in response to pH of the swelling medium, and could be useful potential modulation systems in biomedical fields.

5 Acknowledgements

This study was carried out under the auspices of the foundation of Gansu Key Laboratory of Polymer Material.

6 References

1. Lei, H., Wang, W., Chen, L.L., Li, X.C., Yi, B. and Deng, L. (2004) *Enzyme Microb. Technol.*, **35(1)**, 15–21.
2. Guo, Z., Bai, S. and Sun, Y. (2003) *Enzyme Microb. Technol.*, **32(6)**, 776–782.
3. Wang, J., Bhattachargya, D. and Bachas, L.G. (2001) *Biomacromolecules*, **2(3)**, 700–705.
4. Genta, I., Perugini, P., Conti, B. and Pavanetto, F. (1997) *Int. J. Pharm.*, **152(2)**, 237–246.
5. Berthold, A., Cremer, K. and Kreuter, J. (1996) *J. Control. Release*, **39(1)**, 17–25.
6. Madhan Kumar, A.B. and Panduranga Rao, K. (1998) *Biomaterials*, **19(7–9)**, 725–732.
7. Denkas, E.B., Kilicay, E., Birlikseven, C. and Ozturk, E. (2002) *React. Funct.*, **50(3)**, 225–232.
8. Shantha, K.L. and Harding, D.R.K. (2002) *Carbohydr. Polym.*, **48(3)**, 247–253.
9. Giunchedi, P., Genta, I., Conti, B., Muzzarelli, R.A.A. and Conte, U. (1998) *Biomaterials*, **19(1–3)**, 157–161.
10. He, P., Davis, S.S. and Illum, L. (1999) *Int. J. Pharm.*, **187(1)**, 53–65.
11. Makino, K., Hiyoshi, J. and Ohshima, H. (2000) *Colloids and Surface*, **19(2)**, 197–204.
12. Xia, X.H., Yih, J., D'Souza, N.A. and Hu, Z.B. (2003) *Polymer*, **44(11)**, 3389–3393.
13. Xue, W., Champ, S. and Huglin, M.B. (2001) *Polymer*, **42(8)**, 3665–3669.
14. Tanyolaç, D. and Ozdural, A.R. (2000) *React. Funct. Polym.*, **45(3)**, 235–242.
15. Tanyolaç, D. and Ozdural, A.R. (2000) *React. Funct. Polym.*, **43(3)**, 279–286.