OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 8, August 2008, p. 474 - 477

Microwave absorbing nonwoven textile from electrospun magnetically responsive nanofibres

P. BABINEC[*], O. JIRSÁK[a]
Department of Nuclear Physics and Biophysics, Comenius University, Mlynská dolina F1, 842 48 Bratislava, Slovak Republic
[a]*Department of Nonwoven Textiles, Faculty of Textile Engineering, Technical University of Liberec, Hálkova 6, 461 17 Liberec, Czech Republic*

Magnetically responsive nonwoven textile formed by electrospinning polyvinyl acohol polymer containing embedded functionalized superparamagnetic nanoparticles has been prepared and investigated as a microwave heating material in MHz frequency range as well as possible ultra-lightweight microwave absorbing material in GHz frequency range which may have far reaching appplications.

(Received June 24, 2008; accepted June 30, 2008)

Keywords: Nonwoven textiles, Magnetic nanofibres, Microwave absorption, Electromagnetic heating

1. Introduction

Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibers. Various polymers have been successfully electrospun into ultrafine fibres in recent years. Nonwoven fabrics composed of electrospun nanofibers have a large specific surface area, a high porosity, and a small pore size in comparison with commercial textiles making them excellent candidates for use in protective clothing, catalysis, electronics, filtration, biomedical materials and membrane applications [1-5]. Bringing materials into the nanometre range has been observed to not only improve material properties, but also to create new advanced characteristic not observed for bulk materials.

As has been found formulation and application of polymer particles and hybrid particles composed of polymeric and magnetic material are of great interest for applications in biotechnology. Recently we have investigated a new kind of magnetically responsive materials were prepared, namely the magnetosensitive gels [6,7]. These materials are usually polymer networks sustaining solution containing magnetic particles. Their possible applications include controlled material release, separation systems and artificial muscles. Due to their superparamagnetic properties they are potential candidates as agents for electromagnetic hyperthermia [8,9]. These subdomain superparamagnetic particles produce substantially more heat per unit mass than the 1000 times larger multidomain ferrite particles of similar composition, when exposed to radiofrequency field [10-14]. The mechanism of heating is based on Brownian relaxation (rotation of the particle as a whole according to external magnetic field) and Neél effect (reorientation of the magnetization vector inside the magnetic core against an energy barrier).

Our first aim in this paper is to evaluate the microwave heating properties of electrospunned nanofibers from polyvinyl alcohol polymer with embedded magnetic nanoparticles in MHz frequency range.

The use of electronic devices for communication, computation, and automatization rapidly increases and the electromagnetic radiation interference is one of unfortunate products. The nanostructured materials are promising for microwave radiation absorbing and shielding in GHz frequency range due to their unique chemical and physical properties. Ferrite is one of the principal constituents of the microwave absorbing materials [15]. The volume to weight ratio of shielding material is very important therefore our second aim is to investigate the possible applications of nonwoven nanofabric sheet with embedded magnetic nanoparticles (synthesized from ferrite) for these purposes to achieve thinness, lightness, width, and strength.

2. Experimental procedure

2.1. Preparation of magnetic nanofibers using Nanospider™ technology.

The Nanospider™ (Elmarco s.r.o., Liberec, Czech Republic) device (Fig. 1) for the large-scale production of nanofibres from polymer solution using electrostatic spinning in an electric field was used. We have created potential difference of 40 kV between a charged electrode and a counter electrode. Between electrodes we have placed container filled with 12 % solution of polyvinyl alcohol polymer containing 4 mg/ml of fluidMAG-PVA stabilized magnetic nanoparticles with diameter of 200 nm (Chemicell GmbH, Berlin, Germany), 0.4 % of phosphoric acid, and 0.8 % glyoxal as a crosslinking agents. The surface of rotating cylinder draws the polymer solution out of the cylinder and owing to the electrodes Taylor cones are formed producing nanofibres with diameter of 100-300 nanometres with embedded magnetic nanoparticles.

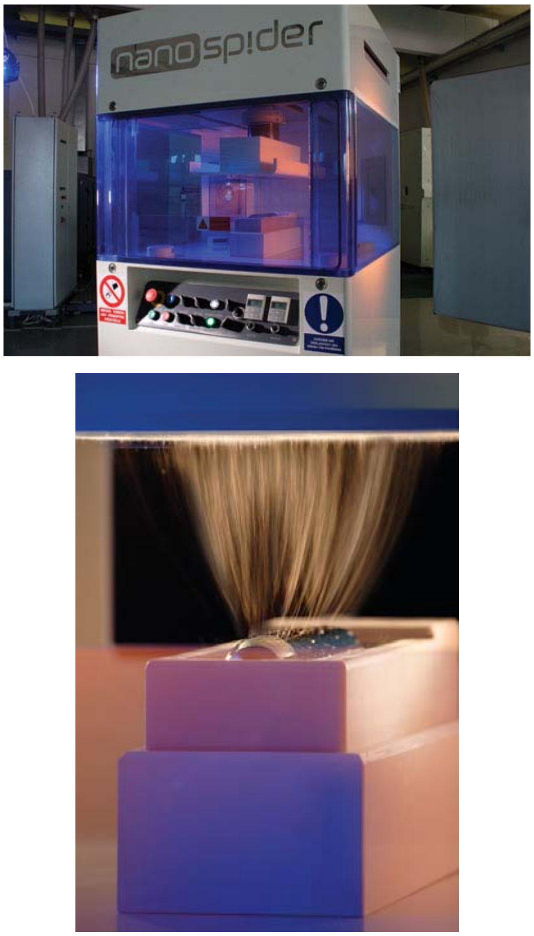


Fig. 1. Magnetically responsive nanofibres were prepared using recently developed Nanospider™ technology. Above, the whole equipment is shown and underneath is the detail on the jet of electrospunned nanofibres.

2.2. Measurement of magnetic properties

Magnetization measurement was done using a SQUID magnetometer MPMS-XL7 (Quantum Design, San Diego, CA, USA).

2.3. Experimental setup for microwave heating of nanofibre fabric

For this study we have modified experimental setup (Fig. 2) used previously in the study of influence of electromagnetic field on the liposomes [9]. The magnetic field with the amplitude 9.6 kA/m and frequency 3.5 MHz was achieved inside the water-cooled cooper induction coil with radius r=12 cm (n=10 turns with turn to turn distance z=0.7 cm).

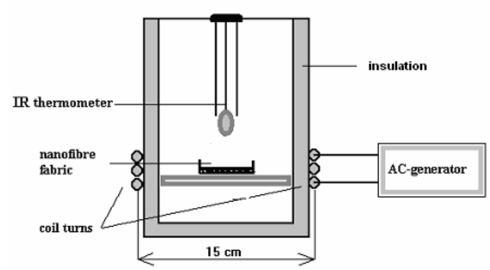


Fig. 2. Experimental setup for the heating of magnetic nanofibre fabric in microwave field with frequency 3.5 MHz.

2.5. Magnetic nanoparticle iron staining in nanofibre fabric sheet using Perl's Prussian blue reaction

Perl's Prussian blue reaction involves the treatment of sections with acid solutions of ferrocyanides. Any ferric ion (Fe^{+3}) present in the specimen (iron in magnetic nanoparticles) combines with the ferrocyanide and results in the formation of a bright blue pigment called Prussian blue, or ferric ferrocyanide. This is one of the most sensitive histochemical tests able to demonstrate e.g. even single granules of iron in blood cells. 20% aqueous solution of hydrochloric acid has been mixed just prior staining with 10% aqueous solution of potassium ferrocyanide and small drop of this mixture has been applied to fabric.

2.6. Measurement of microwave absorption using coaxial method

The shielding effectiveness was measured using coaxial cable method using network analyzer HP8510C (Agilent Technologies, Santa Clara, CA, USA). The samples were in an annular form with outer diameter 97 mm and inner diameter 32 mm. Reflection losses were calculated by the following equations [16]:

$$\frac{Z_s}{Z_o} = \sqrt{\frac{\mu^*}{\varepsilon^*}} \tanh\left[j\frac{2\pi}{c}\sqrt{\mu^*\varepsilon^*} fd \right]$$

$$R = -20\log \left| \frac{\frac{Z_s}{Z_o} - 1}{\frac{Z_s}{Z_o} + 1} \right|$$

where Z_o is impedance in air, Z_s is impedance in the material, μ^* is complex permeability, ε^* is complex permittivity, c is light velocity, f is frequency, d is thickness of the absorber and R is the reflection loss in decibel.

3. Results and discussion

Magnetism is the most important property of magnetically responsive nanofibres. Therefore, M-H curves (change of magnetization versus the magnetic field) of the nanofabric was measured (Fig. 3) using SQUID magnetometry at room temperature. Magnetization diagram was obtained for a sheet of 5x5 mm. The curve exhibit properties of superparamagnetism, characterized by the absence of hysteresis, due to the thermal activation of spin rotation. Saturation magnetization of the nanofabric is ~ 15 emu/g reflecting its excellent magnetic properties, visible also using simple experiment using small permanent magnet attached to the solution of magnetic nanoparticles used for the preparation of nanofibres as well as to the nanofabric sheet (Fig. 4), showing that nanofibres are easily magnetized by external magnetic field.

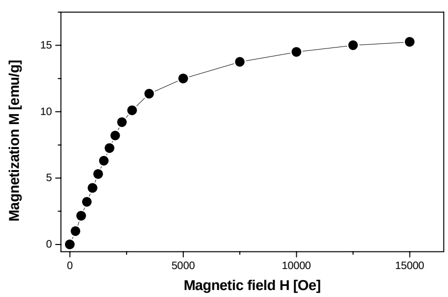


Fig. 3 Magnetization curve of magnetic nanofibre fabric at 300 K.

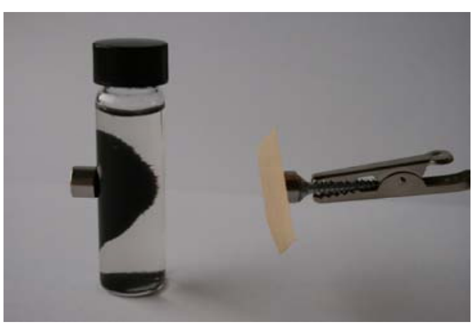
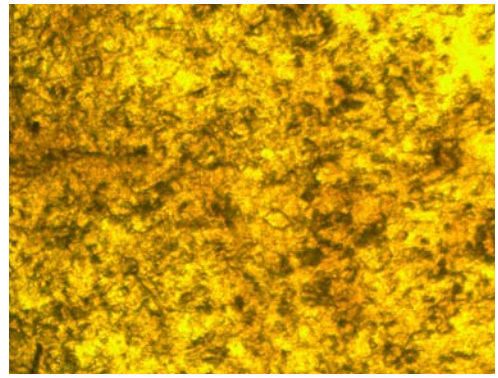
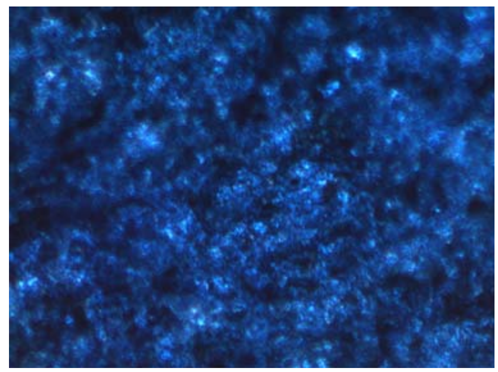


Fig.4.Magnetic responsiveness of magnetic nanoparticles used for electrospun of nanofibres as well as final fabric can be easily illustrated using small NdFeB magnets.

Such an excellent magnetic properties were achieved using very homogeneous and dense distribution of magnetic nanoparticles in a unique nanostructure of polymer fibres (Fig. 5).



(a)



(b)

Fig. 5. Demonstration of dense and homogeneous distribution of magnetic nanoparticles in microscopic specimen of nonwoven textile fabric using Perl's Prussian blue reaction: (a) fabric without Prussian blue; (b) fabric immediately after Perl's staining.

The effect of microwave irradiation on the heating of 3x3 cm nanofabric sheet is shown in Fig. 6. We have achieved temperature increase from 22 ^oC to 43 ^oC in 10 min, which is sufficiently efficient for various applications.

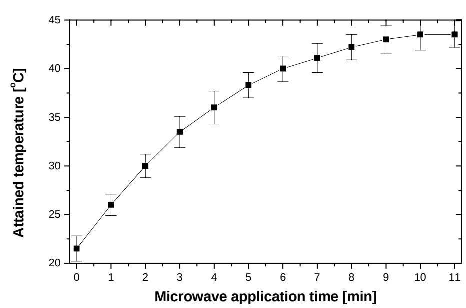


Fig. 6. Time course of magnetic nanofibre fabric heating in microwave field with frequency 3.5 MHz.

Fig. 7 shows microwave reflection loss calculated from the measured complex permeability and permittivity. Reflection is especially pronounced in the range 3-8 GHz, being almost -25 dB near 5 GHz. Ruan et al. [17] reported that a better microwave absorption can be achieved for nanometre sized ferrite particles than for micrometer sized spinel ferrite materials which is accord with our study.

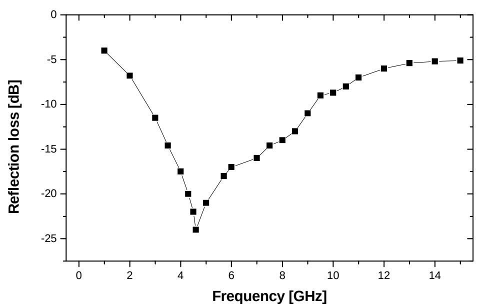


Fig. 7. Frequency dependence of microwave reflection loss in magnetic nanofibre fabric.

In this study we were inspired partly by the recent study of microwave absorption [18] of a wood coated with 87 µm ferrite particles as well as their older study [19] of microwave heating of such impregnated wood composite.

It is well known that the quantum size effect in nanostructures split the electronic energy level. The gap between adjacent energy states increases inversely with the volume of the particle. If the particle size of absorber is small enough and the discrete energy level spacing is in the energy range of microwave, the electron can absorb the energy as it leaps from one level to another, which may lead to the increment of attenuation. When the particle size is in nanoscale we have single magnetic domain and the coercive force of the material increases largely. This may lead to large hysteresis attenuation and the absorbing properties can be improved greatly.

3. Conclusions

The observed data reveals that ultra-lightweight magnetically responsive nonwoven textile successfully fabricated with a simple and effective technology has unique properties what concern its interaction with microwave radiation, and may find a far-reaching application in a diverse fields as a heating material using microwaves in MHz frequency range or as a shielding material in GHz range.

Acknowledgment

This work was supported by VEGA grants 1/0082/08.

References

[1] O. Jirsak, L. Wadsworth, Nonwoven Textiles, Carolina Academic Press, Prague, 1998.
[2] O. Jirsak, R. Bharanitharan, J. Ruzickova, E. Kostakova, J. Hruza, Asian Textile J. **13**, 53 (2004).
[3] O. Jirsak, K. Kalinova, D. Stranska, VDI Berichte **1940**, 41 (2006).
[4] J. Mosinger, O. Jirsák, P. Kubát, K. Lang, B. Mosinger Jr., J. Mater. Chem. **17**, 164 (2007).
[5] M. Wang, H. Singh, T.A. Hatton, G.C. Rutledge, Polymer **45**, 5505 (2004).
[6] M. Babincova, D. Leszczynska, P. Sourivong, P. Cicmanec, P. Babinec, J. Magn. Magn. Mater. **225**, 109 (2001).
[7] M. Babincova. J. Novotny, J. Rosenecker, P. Babinec, J. Optoel. Adv. Mater. Rapid Commun. **1**, 644 (2007).
[8] A. Jordan, P. Wust, H. Fahling, W. John, A. Hinz, R. Felix, Int. J. Hyperthermia **9**, 51 (1993).
[9] M. Babincová, P. Cicmanec, V. Altanerová, C. Altaner, P. Babinec, Bioelectrochemistry, **55**, 17 (2002).
[10] M. Babincová, Bioelectrochem. Bioenerg. **32**, 187 (1993).
[11] I. Nedkov, J. Optoel. Adv. Mater. **9**, 24 (2007).
[12] O. Rotariu, L.E. Udrea, N.J. Strachan, S.D. Heys, A.C. Schofield, F.J. Gilbert, V. Badescu, J. Optoel. Adv. Mater. **8**, 1758 (2006).
[13] M. Babincová, V. Altanerová, C. Altaner, P. Cicmanec, P. Babinec, Medical Physics **31**, 2219 (2004).
[14] M. Babincová, V. Altanerová, C. Altaner, C. Bergemann, P. Babinec, IEEE Trans. NanoBiosci. **7**, 15 (2007)
[15] T. Nakamura, J. Appl. Phys. **88**, 348 (2000).
[16] Y. Hwang, Mater. Lett. **60**, 3277 (2006).
[17] S. Ruan, B. Xu, H. Suo, F. Wu, S. Xiang, M. Zhao, J. Magn. Magn. Mater. **212,** 175 (2000).
[18] H. Oka, Y. Kataoka, H. Osada, Y. Aruga, F. Izumida, J. Magn. Magn. Mater. **310,** e1028 (2007).
[19] H. Oka, H. Fujita, J. Appl. Phys. **85,** 5732 (1999).

*Corresponding author: babinec@fmph.uniba.sk