Digest Journal of Nanomaterials and Biostructures Vol. 10, No. 4, October - December 2015, p. 1475 - 1483

SYNTHESIS AND PERFORMANCE OF POLYMER BASED MAGNETIC COMPOSITE SENSING ELEMENT

H. EL SWIE[a], V. RADOJEVIĆ[a], L. BRAJOVIĆ[b], J. STAJIĆ-TROŠIĆ[c], V. ĆOSOVIĆ[c], A. GRUJIĆ[c*], R. ALEKSIĆ[a]
[a]*Faculty of Technology and Metallurgy, University of Belgrade, Serbia*
[b]*Faculty of Civil Engineering, University of Belgrade, Serbia*
[c]*Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia*

The commercial multi-mode optical fiber was coated with magnetic composite material prepared using Nd-Fe-B permanent magnet powder dispersed in poly (ethylene-co-vinyl acetate)-EVA. Characterization of microstructure, thermal stability and mechanical properties of the composite coatings with different Nd-Fe-B powder content were performed using Scanning Electron Microscope (SEM), Differential Scanning Calorimetry (DSC), and standard tensile tester, respectively. Experimental results show that composites with higher content of Nd-Fe-B powder have improved thermal and mechanical properties. Propagation characteristics of the constructed optical fiber magnetic sensing element (OFMSE) in the external magnetic field were investigated in relation to quality and composition of the applied composite coatings. The attenuation of optical signal with applied external magnetic field intensity was monitored and the results suggest that the sample with 50 wt-% of Nd-Fe-B provides the greatest sensitivity of the sensor element.

(Received February 20, 2015; Accepted December 28, 2015)

Keywords: Magnetic composite coating; Nd-Fe-B; Magnetic field sensing element; Optical fiber

1. Introduction

In recent years, there has been a surge of research interest in the field of smart multifunctional materials.[1,2] Generally, the types of materials that are very useful in technology applications are those that change one of their properties: shape, electrical, magnetic, and optical, in response to an external stimulus like temperature, stress, applied fields etc. If the resulting change in properties of the multifunctional material follows a simple mathematical function of the change in stimulus than it can be used to measure and control the stimulus itself. In practice, such materials can be used for sensing and actuation simultaneously.[3]

In case of intensity-based fiber optic sensors there are many transduction mechanisms that can cause the change in light intensity when light passes through an optical fiber. These mechanisms may include: micro bending loss, breakage, fiber-to-fiber coupling, modified cladding, reflectance, absorption, attenuation, molecular scattering, molecular effects or evanescent fields.[4]

Modification of optical fibers by application of different coatings can alter their propagation characteristics and general behaviour of the material in different environments. Magnetostrictive or metal jacket deposited on the fiber could induce change of the optical phase when immersed in a magnetic field due to strain or Lorentzian force, respectively [5,6], e.g. iron film deposited on a side-polished fiber Bragg grating would shift the reflective wavelength of the fiber grating as a result of the strain induced by applied magnetic field.[7,8].

[*]Corresponding author: gruja@tmf.bg.ac.rs

The optical fiber magnetic sensing element (OFMSE) based on the optical fiber coated with polymer– magnetic powder composite coating has been already introduced in magnetic field sensing. [9-12] Essentially, a fiber end was coated with a magnetic composite material and butt coupled to another optical fiber with its original cladding. When the fibers are collinear the light passes throw both and the signal is stable. Under the influence of the applied external magnetic field the fiber with magnetic composite coating is displaced and the optical coupling between the fibers changes with this transverse displacement. The sensitivity of OFMSE is not depending on the wavelength of the light because the intensity of signal is modulated just due to changing of the direction of propagation.

Composite magnetic coating is very important part of the OFMSE. A polymer matrix protects the optical fiber and preserves its mechanical properties, while the magnetic particles in composite have functional role - sensing of external magnetic field.[13] Polymer matrix provides a good magnetic isolation for the hard magnetic particles and restricts its oxidation.[14-17] The magnetic component of the composite coating can be selected from a variety of permanent magnetic powders (hard ferrite, Sm-Co, Nd-Fe-B).[18] For the presented investigations Nd-Fe-B permanent magnet powder was dispersed in poly (ethylene-co-vinyl acetate)-EVA.

When considering Nd-Fe-B/polymer magnetic composite materials as an optical fiber coating, the balance between magnetic properties and corresponding mechanical and thermal behaviour becomes an important issue.[19,20] Since structure, thermal, magnetic and mechanical properties of the composite coating strongly affect sensitivity of the OFMSE to external magnetic field characterization and testing of the starting components and composites with different composition was performed in this work as well as investigation of sensitivity of the OFMSE to external magnetic field.

2. Experimental

As a magnetic component of the composite coating, powder of rapid quenched and optimally annealed Nd rich Nd_{14}-Fe_{79}-B_7 alloy was used. Since mean particle size of the starting Nd-Fe-B powder was between 100 and 150 μm, in order to use it as a magnetic component in the composite coating, the Nd-Fe-B powder was milled under protecting inert fluid toluene for 2.5 hours and subsequently dried at room temperature in argon atmosphere. Characterization i.e. morphological tests of the magnetic powder was carried out before and after milling using scanning electron microscopy (SEM) (JEOL JSM-5800). Image analysis was done with corresponding software.[11] Magnetic properties of the Nd-Fe-B alloy were measured at ambient temperature using Quantum Design MPMS 5XL Superconducting Quantum Interference Device (SQUID) magnetometer with magnetic field strength in range −4 to 4 MAm^{-1}.

As a polymer matrix of composite EVA - poly (ethylene-co-vinyl acetate) produced by DuPont under commercial name ELVAX 265 was used in a form of a toluene solution with 33.33 wt-% of polymer. By using EVA, it was possible to produce coating without the application of UV or thermal curing process, thus reducing the number of process parameters. After dissolving EVA in toluene, magnetic powder was dispersed in the solution using ultrasonic mixing at 60 °C. Three different composite compositions with: 20, 30 and 50 wt-% of magnetic powder were processed.

Fourier transform infrared (FTIR) - spectrum of the Nd-Fe-B powder, pure EVA and composites was obtained using FTIR transmission-KBr disk spectroscopy (Hartmann & Braun, MB-series). The scanning range of FTIR was between 4000 and 400cm^{-1} with a resolution of 4 cm^{-1}.

Thermal properties of the starting magnetic powder, pure EVA and synthesized composites were investigated employing the DSC technique using TA Instruments SDT Q-600 thermal analyzer. All experiments were performed under dynamic nitrogen atmosphere of a flow rate of 100 ml/min, in a temperature interval ambient temperature to 1000°C at a heating rate of 20 °C/min.

The tensile testing of Nd-Fe-B-EVA magnetic composites was performed. The samples were processed by Laboratory mixing moulder, Dynisco, USA and subsequent tensile tests were carried out using Universal hydraulic tensile-compressive testing machine, Instron 1332 with applied load of 100 kN according to ASTM standard D 3039-00.[22]

For the purpose of testing of functionality of the composite magnetic coatings under external magnetic field the optical fiber magnetic sensing element (OFMSE) containing studied composite coatings was produced. Construction of the OFMSE and the testing procedure that was used is identical to one used in previous experimental work.[9-12] As the OFMSE belongs to a class of Intensity Based Fiber Optic Sensors, a normalized modulation index (*m*) can be defined as:[23]

$$m = \frac{\Delta A}{P} \tag{1}$$

Where, ΔA (dB) is change of optical signal attenuation, and P (T) is external magnetic field strength.

3. Results and discussion

Magnetic properties of the used Nd-Fe-B magnetic powder are illustrated by corresponding hysteresis loop presented in Fig. 1, obtained by measurements on SQUID magnetometer.

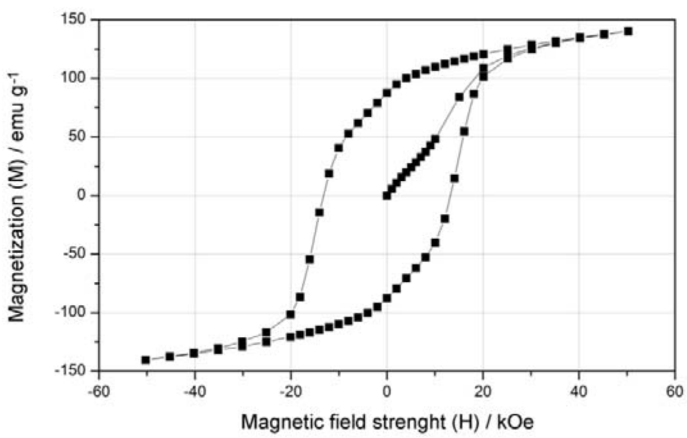

Fig. 1. SQUID hysteresis loop of used Nd-Fe-B powder

The shape of the obtained hysteresis loop corresponds to an almost monophase structure of the alloy in the optimized state with dominant content of main Nd_2-Fe_{14}-B hard magnetic phase (up to 95 wt-%) determined by structural and phase analysis given in[24-27] and demonstrates its hard magnetic quality.

3.1 SEM investigations

SEM images of a polymer magnetic composite material are presented in Fig. 2. Image analysis revealed that the mean size of magnetic particles is about 5 μm. It is obvious that the agglomeration of particles is present and that the surface is very rough. This can be attributed to the applied coating process and attraction between magnetic particles.

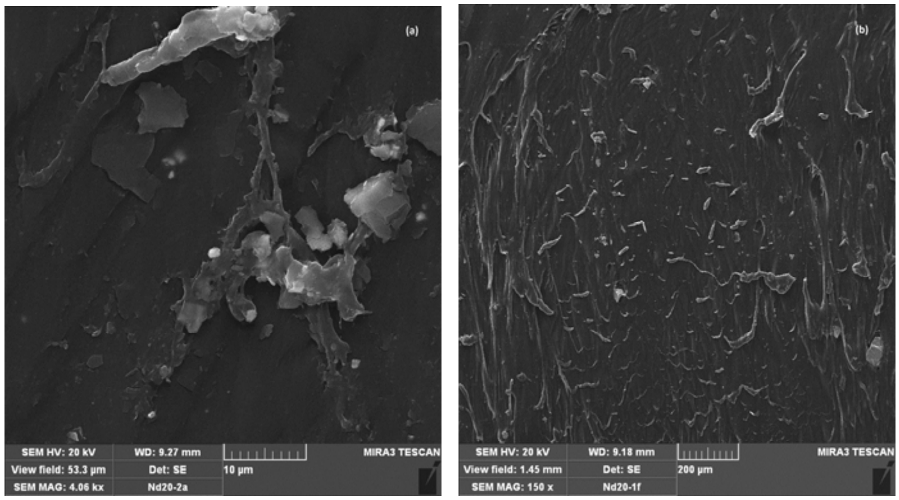

Fig. 2. SEM micrographs of magnetic polymer composite with 20 wt-% of magnetic powder.

3.2 Fourier transformed infra-red spectroscopy

In order to determine whether there are any chemical reactions between magnetic powder and polymer matrix in composite, FTIR analysis was carried out for pure powder, polymer and produced composites. In the FTIR spectrum of EVA (Fig. 3) the characteristic band of C-O stretching of ester is observed in 1245 cm^{-1}. The band at around 1460 cm^{-1} is due to the CH_2 scissoring and bands at around 1744 cm^{-1} stand for C=O stretching of ester. The characteristic bands at 2848 cm^{-1} and 2928 cm^{-1} correspond to C-H symmetric stretching and asymmetric stretching of CH_2 or CH_3, respectively. In the Nd-Fe-B FTIR spectrum bands for vibrating of Fe (570 cm^{-1}) and B (1060 cm^{-1}) bonds are observed as well as O-H deformation of moisture water at 1619 cm^{-1}and O-H stretching of water at 3437 cm^{-1}.

Since these characteristic peaks can be observed in FTIR spectrum of the composite EVA-50 wt-% Nd-Fe-B (Fig. 3) and no additional peaks are present, it can be assumed that are no chemical reactions between powder and EVA polymer.

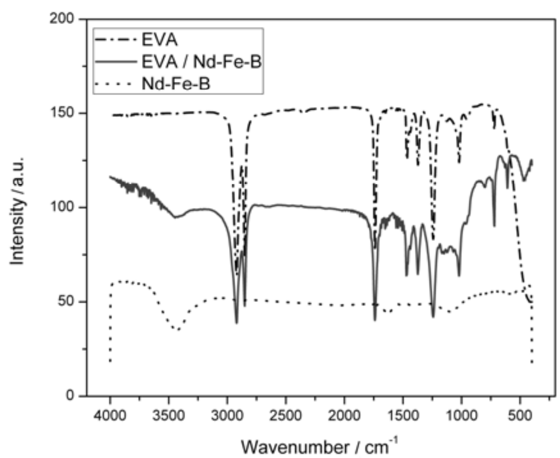

Fig. 3. FTIR spectra of EVA, Nd-Fe-B powder and composite

3.3 Thermal analysis

Thermal analysis was carried out in order to investigate whether presence of the used magnetic powder will modify thermal behaviour of polymer and composite in general, which could influence subsequent coating process and functional properties of OFMSE. Thermal behaviour of the Nd-Fe-B powder, EVA polymer and composite was investigated by DSC (Fig. 4). Obtained DSC curve of the Nd-Fe-B powder shows the Curie point (T_c) of the main hard Nd_2-Fe_{14}-B magnetic phase of the used magnetic powder at 316°C.[28,29] After this transformation, two reactions are detected: at 596°C (T_{1cr}) and 669°C (T_{2cr}) which can be attributed to the crystallization of the remnant amorphous phase within the Nd-Fe-B alloy.[29]

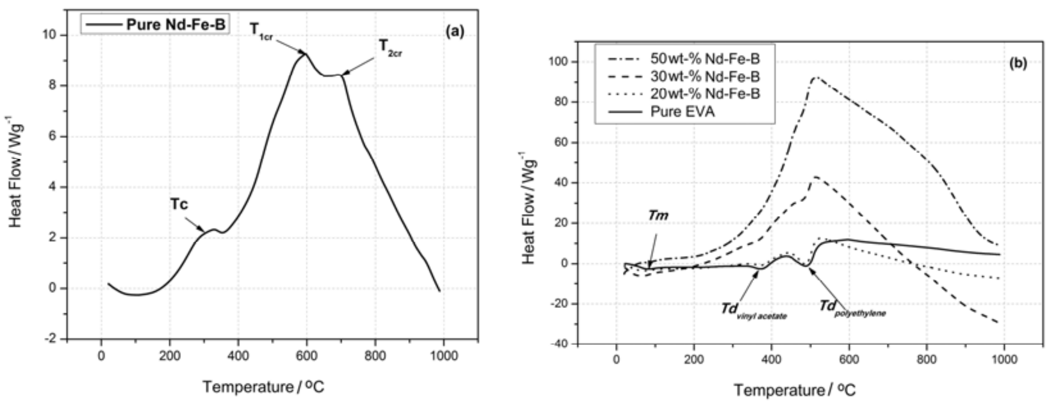

Fig. 4. DSC of a) pure EVA, and b) Nd-Fe-B/EVA composites

EVA DSC curve shows a melting temperature (T_m) near 81°C. It can be seen that melting temperatures of the composites are lower than those of the pure EVA. The melting behaviour where the T_m depression occurs by the addition of Nd-Fe-B nanoparticles is already reported elsewhere.[30-33] On heating the virgin EVA decomposes within the temperature range of 270 – 520°C in N_2 atmosphere: The first stage (340 – 420°C) is attributed to the evolution of acetic acid due to the decomposition of vinyl acetate groups. The second step (450 – 520°C) corresponds to degradation of the polyethylene chains, which has been ascribed to the breakdown of the cross linked polyethylene structure into volatile products. This has been attributed to the formation of a graphite-like structure [34]. DSC curves for the composites are following the same transitions as for pure EVA.

3.4 Mechanical properties – tensile testing

Mechanical tests were carried out on the separate bulk samples of pure EVA and composites i.e. not as a coating on the optical fiber. The obtained experimental results of mechanical testing, presented in Fig. 5 and Table 1, illustrate change of elasticity of composites with different powder content.

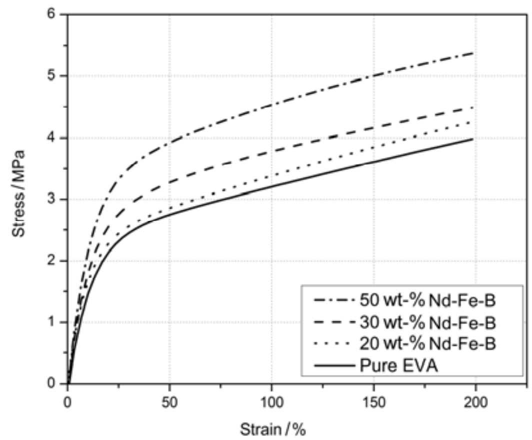

Fig. 5. Tensile strength curves for composite coating materials with different Nd-Fe-B content and pure EVA polymer.

Table 1. The values of E and σ taken from stress – strain diagram

Nd-Fe-B / wt-%	*E* / MPa	*σ* / MPa (at ε = 200%)
0	14.31	1.01
20	20.05	4.23
30	20.31	4.52
50	78.11	5.45

The composites were found to have higher values of modulus of elasticity than pure EVA polymer and from the presented results of the tensile tests it is obvious that the tensile strength and modulus of elasticity (E) of composites increases with an increase of the magnetic powder content. EVA shows the pure viscous-elastic response to the load, time dependent, while higher content of powder in composite coating led to higher values of modulus of elasticity and to higher share of pure elastic composite response to the load. Hence, the higher the content of the magnetic powder, the faster the signal response of the OFMSE. However, there is limit regarding the increase of the magnetic powder content in order to preserve flexibility of the coating.

3.5 Sensitivity to external magnetic field

The influence of the magnetic powder content in polymer composite coating on the propagation characteristics of OFMSE is studied. Analyzing the intensity of signals when the external magnetic field is applied, from maximal to minimal values (with increasing and decreasing values of magnetic field strength), diagram optical signal intensity versus changes of magnetic induction is obtained and presented in Fig. 6.

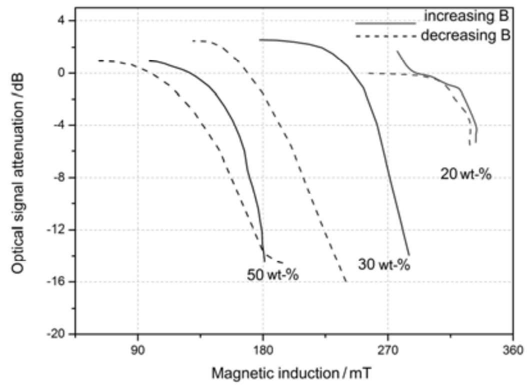

Fig. 6. Optical signal intensity versus magnetic induction changes for three investigated samples

All three studied compositions of the coatings show good response to external magnetic field i.e. significant signal modulation. The presented relations of optical signal versus magnetic field strength i.e. magnetic induction are not linear. The range of maximal sensitivity exists for all tested samples e.g. for the sample with 50 wt-% in range from 134 up to 180 mT, for the sample with 30 wt-% from 242 up to 291 mT and for the sample with 20 wt-% from 313 up to 320 mT.

Fig. 6 shows that optical signal intensity does not have the same values when magnetic field strength is increasing and/or decreasing. This is due to a fact that material has its own hysteresis and no collinear characteristic of the OFMSE.

The values of modulation index *m*, calculated from the overall optical signal attenuation changes and overall applied magnetic field strength by equation (1) are presented in Table 2. Due to hysteresis characteristics of OFMSE (Fig. 6) *m* is calculated for both, increasing and decreasing magnetic induction.

Table 2. The values of modulation index m

Magnetic field direction	ΔA / dB	B_m / mT	m / dB mT^{-1}
	20 wt-% of Nd-Fe-B		
Increase	5,5	335	-0,016
Decrease	-4,6	328	-0,014
	30wt-% of Nd-Fe-B		
Increase	-17,1	286	-0,059
Decrease	-18,5	240	-0,077
	50 wt-% of Nd-Fe-B		
Increase	-15,3	182	-0.084
Decrease	14,8	182	-0,081

The calculated values of modulation index could find significance as a parameter for the switching application in the operating range of the OFMSE. It is obvious that the sensitivity of the OFMSE and *m* increase with an increase of the content of magnetic powder in composite coating. Therefore, by selecting the appropriate concentration of magnetic powder the range of maximal sensitivity of sensor element can be modulated. The obtained values suggest that the sample with 50 wt-% of Nd-Fe-B provides the greatest sensitivity of the sensor element.

However, since the OFMSE is intensity modulated sensing element, there are series of limitations imposed by variable losses in the system to be measured, that are not related to the effect of external magnetic field. Due to connectors and splices, micro and macro bending losses, mechanical creep and misalignment of light source and detector, only the relative change in the optical signal intensity could be considered. Accordingly, further scrutiny and improvement in design and processing of the OFMSE are needed, particularly depending on the desired application of the element whether as a magnetic field linear sensor or a magnetic field switch. Very important fact is that the transmission properties of the optical fiber were not affected by the applied magnetic composite coating.

4. Conclusions

In this work the possibility of use the magnetic composite coating on optical fiber in magnet sensing element was investigated. In order to use the starting magnetic Nd-Fe-B alloy as a magnetic component in the composite coating it was initially milled into fine powder with particles diameter about 5 μm. The results of SQUID magnetic measurements indicate good hard magnetic properties of the selected Nd-Fe-B powder, which makes it a suitable material for making OFMSE. Mixture of magnetic powder and EVA polymers proved to be suitable for coating the fibers due to good adhesion, homogeneity and the magnetic properties. FTIR and DSC analysis of bulk composites were carried out to monitor the process of forming the coating. The results of FTIR measurements show that there are no chemical reaction and appearing the new bonds during forming the coating. DSC test depict that the thermal properties of polymers change slightly with the addition of powder. These results indicate that the magnetic composite coatings can be processed in an identical manner as the polymer coating when dragging the optical fiber.

Although morphological analysis of the obtained polymer magnetic coatings shows agglomeration of the magnetic particles their quality was acceptable. Construction difficulties in sensory fibers alignment have not substantially affected the sensitivity of OFMSE.

The best signal response was achieved with the composite coating with 50 wt-% of magnetic powder. Having in mind the obtained results, it can be said that this is promising functional composite material for magnetic field sensing since the composite coating can be made by adapting the existing process of manufacturing of optical fibers in stage in which polymer coating is applied to the drawn fiber. Instead of a solely polymer coating, a composite coating with particles of magnetic powder can be used.

These results demonstrate the potential of a polymer magnetic coating for sensing of the magnetic field. However, the proposed fiber sensing element needs further improvement for possible sensing applications.

Acknowledgments

This work has been supported by the Ministry of Education, Science and Technological Development, Serbia [Projects TR34011, III45019 and ON172037].

References

[1] A. M. Behl, M. Y. Razzaq, A. Lendlein, Adv Mater **22**, 3388 (2010).
[2] B. J. M. Cuevas, J. Alonso, L. German, M. Iturrondobeitia, J. M. Laza, J. L. Vilas, L. M. León, Smart Mater Struct **18**, 075003 (1) (2009).
[3] C. J. W. Sohn, S. B. Choi, C. H. Leel, Smart Mater Struct **18**, 074004 (1) (2009).
[4] B. Gholamzadeh, H. Nabovati, WASET **42**, 297 (2008).
[5] A. Yariv, H. V. Winsor, Opt Lett **5**, 87 (1980).
[6] H. Okamura, J Lightwave Technol **8**, 1558 (1990).
[7] C. L. Tien, C. C. Hwang, H. W. Chen, W. F. Liu, S. W. Lin, IEEE T. Magn **42**, 3285 (2006).
[8] C. L. Tien, H. W. Chen, C. C. Hwang, W. F. Liu, Meas Sci Technol **20**, 075202 (16) (2009).
[9] V. Radojevic, D. Nedeljkovic, N. Talijan, D. Trifunovic, R. Aleksic, J Magn Magn Mater **272–276**, e1755 (2004).

[10] D. Nedeljkovic, V. Radojevic, V. Cosovic, T. Serbez, N. Talijan, R. Aleksic, Sensor Mater **18**, 63 (2006).
[11] V. Radojevic, D. Nedeljkovic, A. Grujic, N. Talijan, V. Cosovic, R. Aleksic, J Optoelectron Adv Mater **9**, 2873 (2007).
[12] A. Milutinovic-Nikolic, N. Talijan, K. Jeremic, R. Aleksic, Mater Lett **56**, 148 (2002).
[13] K. Barczak, T. Pustelny, Z. Zycki, T. Blazejczyk, Acta Phys Pol A **116**, 250 (2009).
[14] W. Liu, Y. Yang, Y. Meng, J. Wu, Mater Trans **44**, 1159 (2003).
[15] L.A. Dobrzański, M. Drak, J Mater Process Technol **175**, 149 (2006).
[16] M. Kokabi, F. Arabgol, M. Manteghian, Iran Polym J **14**, 71 (2005).
[17] M. Drak, B. Ziębowicz, L. A. Dobrzański, JAMME **31**, 91 (2008).
[18] V. Radojevic, T. Serbez, R. Aleksic, D. Nedeljkovic, Lj. Brajovic, J Min Metall Sect B **41B**, 103 (2005).
[19] M. G. Garrell, B. M. Ma, A. J. Shih, E. Lara-Curuzio, R. O. Scattergood, Mater Sci Eng A **359**, 375 (2003).
[20] A. Grujic, N. Talijan, D. Stojanovic, J. Stajic-Trosic, Z. Burzic, Lj. Balanovic, R. Aleksic, J Min Metall, Sect B **46B**, 25 (2010).
[21] A. Grujic, N. Lazic, N. Talijan, V. Spasojevic, J. Stajic-Trosic, V. Cosovic, R. Aleksic, Acta Phys Pol A **117**, 859 (2010).
[22] ASTM standard D 3039/D 3039M–00: (2000). Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials, American Society for Testing and Materials.
[23] F. Yu, S. Yin, Marcel-Dekker Inc. New York: Basel, (2002), p.147-150.
[24] V. Cosovic, N. Talijan, A. Grujic, J. Stajic-Trosic, T. Zák, Z. Lee, V. Radmilovic, Sci Sinter **41**, 209 (2009).
[25] N. Talijan, V. Cosovic, T. Žák, A. Grujic, J. Stajic-Trosic, J Min Metall Sect B **45B**, 111 (2009).
[26] N. Talijan, V. Cosovic**,** J. Stajic-Trosic, T. Žák, J Magn Magn Mater **272**, e1911 (2004).
[27] A. Grujic, N. Talijan, A. Maricic, J. Stajic-Trosic, V. Cosovic, V. Radojevic, Sci Sinter **37**, 139 (2005).
[28] P. Campbel, Cambridge University Press, New York, (1994), p.45.
[29] L. Schultz, K. Schnitzke, J. Wecker, J Magn Magn Mater **80**, 115 (1989).
[30] J. W. Gilman, C. L. Jackson, A. B. Morgan, E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, S. H. Phillips, Chem Mater **12**, 1866 (2000).
[31] C. J. Perez, V. A. Alvarez, J Appl Polym Sci **114**, 3248 (2009).
[32] V. Krikorian, D. J. Pochan, Macromolecules **37,** 6480 (2004).
[33] P.Svoboda, Ch. Zeng, H. Wang, L. James Lee, D. L. Tomasko, J Appl Polym Sci **85**, 1562 (2002).
[34] J. Wang, X-ray Photoelectron Spectroscopy (Electron Spectroscopy for Chemical Analysis) Studies in Flame Retardancy of Polymers, in Nelson GL (ed) Fire and Polymers II, ACS Symposium Series, (1995), pp.51-55.