

*Mykhaylo Yatsyshyn¹, Oleksandr Reshetnyak^{1, 2}, Nataliya Dumanchuk³,
Yuriy Kulyk¹, Nataliya Fartushok³ and Yuriy Stadnyk¹*

HYBRID MINERAL-POLYMERIC COMPOSITE MATERIALS ON THE BASIS OF THE POLYANILINE AND GLAUCONITE-SILICA

¹*Ivan Franko National University,
6, Kyryla & Mefodiya str., 79005 Lviv, Ukraine; M_Yatsyshyn@franko.lviv.ua*

²*Army Academy named after Hetman Petro Sahaydachnyi,
32, Gvardiys'ka str, 79012 Lviv, Ukraine*

³*Lviv Medical Institute, 76, Polishchuka str., 79015 Lviv, Ukraine*

Received: October 25, 2012 / Revised: November 30, 2012 / Accepted: February 25, 2013

© Yatsyshyn M., Reshetnyak O., Dumanchuk N., Kulyk Yu., Fartushok N., Stadnyk Yu., 2013

Abstract. Polyaniline/glaucosite-silica (PAn / Gl-Si) composite were obtained by one-step *in situ* polymerization of aniline in the presence of microdispersion of natural mineral glaucosite-silica. The physico-chemical properties (phase content, thermal stability, conductivity and magnetization) of the produced samples of composites with different ratio of components have been studied. It was shown that the polymeric component stipulates the conductivity for the synthesized composite samples, while the mineral particles stipulate their magnetic properties and higher thermal stability in comparison with individual polyaniline. Besides, it was determined that participation of the surface of glaucosite-silica microparticles in the process of aniline polymerization leads to considerable increasing of ordering of the polymer in the composite.

Keywords: polyaniline, glaucosite-silica, composites, X-ray phase analysis, thermal stability, magnetic properties.

1. Introduction

Today the materials on the basis of conducting polymers and natural minerals, namely clays [1–5] or mineral mixtures [6–9] as inorganic components, are very actively developed. The combination of the properties of different polymeric binders and inorganic fillers in the result of making of hybrid micro- and nanostructured composite materials enables to produce the hybrid composites with novel or advanced physico-chemical properties and extends the confines of their practical use [10]. Similar composites are promising particularly as elements of sensors for monitoring of

humidity or presence of noxious gases, as additives of corrosion-resistant coatings for the protection of aluminium, iron and steel hardware [10]. Insertion of iron-containing mineral glaucosite-silica (Gl-Si) as a filler in the polyaniline (PAn) matrix permits to produce conducting composite with magnetic properties. Therefore the purpose of this work was synthesis and study of physico-chemical properties of such material.

2. Experimental

Sample of glaucosite-silica was produced by enriching of natural mineral (Adamiv's'ke-2 deposit occurrence, Khmelnytskyi region, Ukraine) [7]. The chemical composition of the produced sample in oxides terms was as follows (in mass percent, ± 1.0 %): SiO₂ – 14.5; Al₂O₃ – 9.6; Fe₂O₃ – 28.8; FeO – 8.2; MgO – 6.0; Na₂O – 2.4; K₂O – 2.7; CaO – 2.8; H₂O – 12.7; silica – 12.3. The loss under combustion is 10.5 %. The fraction of Gl-Si dispersion with particles size < 20 μ m was used in this work.

Aniline (Aldrich, 99.5 %) was distilled under reduced pressure of 4 Torr and stored under argon. Water was distilled twice. Other reagents in the work (analytical grade) were used without additional purification.

Samples of PAn / Gl-Si composites with different weight ratio of components (1:0.125 (sample C-0.125); 1:0.25 (C-0.25); 1:0.5 (C-0.5); 1:1 (C-1); 1:2 (C-2); 1:4 (C-4) and 1:8 (C-8)) were synthesized in compliance with the technique described in [8]. The synthesis of the studied samples of PAn and composites was carried out in the aqueous 0.5 M H₂SO₄ medium by chemical

oxidation of aniline by sodium peroxydisulfate in the absence or presence of GI-Si microparticles.

The crystallinity of the produced samples of PAn, GI-Si and its composites were characterized with the use of the wide-angle X-ray phase diffraction (XRD) analysis (DRON-2 diffractometer, Cu K α radiation, $\lambda = 1.504 \text{ \AA}$). Derivatograph Paulic-Paulic-Erdei Q-1500 D was used under the thermogravimetric analysis (dynamic mode with the heating speed of $10 \text{ K}\cdot\text{min}^{-1}$ in air atmosphere, corundum pot, reference substance – Al_2O_3). Conductivity of the samples was measured with use of sandwich-type cell. In this case the powders of polymer or composites were pressed into pellets with the thickness of 2 mm and diameter 10 mm under pressure of $15.2 \cdot 10^6 \text{ Pa}\cdot\text{cm}^{-2}$ and $T = 293 \text{ K}$ over the time of 5 min. Specific magnetization was measured by Faraday method.

3. Results and Discussion

3.1. Crystallinity

The results of the X-ray diffraction phase analysis of the synthesized samples are present in Fig. 1. It indicates that both initial GI-Si (diffractogram 1) and synthesized PAn (form of emeraldine salt PAn/ H_2SO_4 , diffractogram 7) display crystallinity. A peak at $2q = 25.6^\circ$ can be assigned to the scattering from PAn chains at interplanar spacing [4]. A considerably greater number of peaks on the GI-Si diffractogram (Fig. 1, diffractogram 1) are connected with compound composition of this mineral. The comparison of diffractograms (Fig. 1) has shown that it is similar for the synthesized PAn/GI-Si and initial glauconite-silica. The presence of GI-Si characteristic peaks on the diffractograms of composites argues that polymer covers the particles of mineral and last enters into the composition of composite, but that PAn at the same time has no effect on crystalline performance of GI-Si. At the same time the peak of PAn does not emerge in the PAn/GI-Si composite. The observation suggests that an interaction may exist at the interface of polymer and mineral particles, which restricts aggregation of polyaniline to the form of bulk polymer. Therefore, the crystallinity degree of polyaniline decreases and the diffraction peak disappears gradually. On the other hand, essential increasing of GI-Si content in composite leads to decrease of thickness of PAn films on the surface of mineral particles and to the higher ordering of polymeric macromolecules.

3.2. Thermal stability

The difference between the curves of mass loss for the synthesized samples (Fig. 2) is connected with

contents of the composites. There are two substantial competitive processes, namely water evaporation (H-bound with nitrogen atoms in the PAn links and from the solvate shell of doping HSO_4^- -anions) and oxidative destruction of polymer (in air atmosphere). The contribution of the first process increases with increasing of mineral content in composite and vice versa, the contribution of the second process levels. The presented thermogravimetric curves indicate that increasing of PAn:GI-Si content from 4:1 to 1:4 ratio leads to the essential ($\sim 573 \text{ K}$) shift of the breaking of composite in the region of higher temperatures (Fig. 2, curves 5–8).

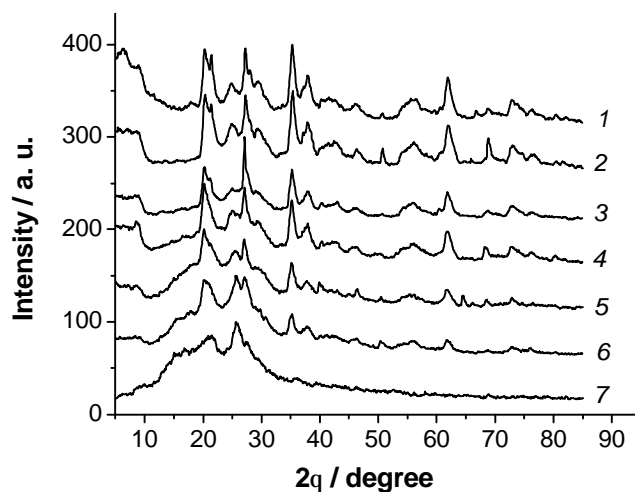


Fig. 1. X-ray diffractograms of initial GI-Si (1), C-4 (2); C-2 (3); C-1 (4); C-0.5 (5); C-0.25 (6) and PAn (7) samples

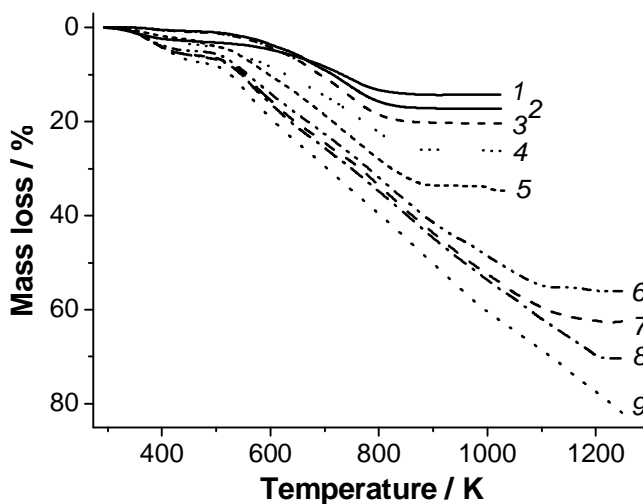


Fig. 2. TG-curves of the studied samples: initial GI-Si (1); C-0.125 (2); C-0.25 (3); C-0.5 (4); C-1 (5); C-2 (6); C-4 (7); C-8 (8) and PAn (9)

3.3. Conductivity

The results of measurements of specific conductivity (σ) of the initial GI-Si and synthesized samples of PAn and PAn/GI-Si composites are shown in Table. It confirms the tentative assumption that introduction of small quantities of GI-Si in the reaction mixture somewhat decrease the specific conductivity of such samples to the level of undoped PAn. The conductivity of the samples decrease sharply under the weight ratio of PAn:GI-Si less than 1:0.5, that is stipulated by the achievement of the threshold of percolation for nonconducting mineral particles.

Table

Conductivity of the produced samples

Samples	Conductivity $\sigma \cdot 10^3 \pm 5\%$, $\text{Sm}\cdot\text{cm}^{-1}$
PAn	68.0
C-0.125	51.5
C-0.25	22.2
C-0.5	8.0
C-1	2.0
C-2	0.2
C-4	0.01
C-8	0.015
GI-Si	0.0023

3.4. Magnetic Properties

The dependences of specific magnetization of the studied samples on the strength of imposed magnetic field are shown in Fig. 3. The insertion of the micro-

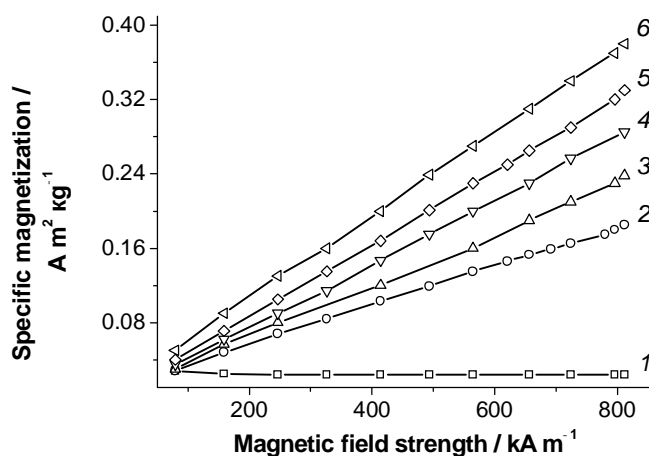


Fig. 3. The dependence of specific magnetization of produced samples on the strength of imposed magnetic field: PAn (1); C-1 (2); C-2 (3); C-4 (4); C-8 (5) and initial GI-Si (6)

particles of iron-containing mineral as a filler in the PAn matrix led to occurrence of magnetic properties of polymeric samples. The specific magnetization of the samples practically linearly increases with the increase of both strength of imposed magnetic field and weight fraction of GI-Si particles in the composite. Sufficiently great values of magnetization is reached under the PAn:GI-Si content more than 1:1.

4. Conclusions

The polymer-mineral composites produced by one-step *in situ* polymerization of aniline in the presence of microdispersed system of glauconite-silica show the properties which are typical of both initial components of the material. The presence of polymer (PAn) in the synthesized samples stipulates their conductivity, while the particles of mineral component stipulate the magnetic properties of composites in comparison with individual polyaniline. The combination of such characteristics makes PAn/GI-Si composites attractive for their potential commercial applications as fillers for electromagnetic shielding materials, conductive coatings and magnetics materials.

The studied properties of the produced samples are directly dependent on the GI-Si content in the composite. Besides, it was determined that participation of the surface of glauconite-silica microparticles in the process of PAn polymerization leads to considerable increasing of ordering of the polymer in the composite and also to the increasing of the thermal stability of composite in comparison with individual polyaniline.

References

- [1] Vitoratos E., Sakkopoulos S., Dalas E. *et al.*: *Curr. Appl. Phys.*, 2007, **7**, 578.
- [2] Sudha J. and Reena V.: *Macromol. Symp.*, 2007, **254**, 274.
- [3] Binitha N. and Sugunan S.: *J. Appl. Polym. Sci.*, 2008, **107**, 3367.
- [4] Li X., Li X., Dai N. and Wang G.: *Appl. Surf. Sci.*, 2009, **255**, 8276.
- [5] Hsieh T.-H., Ho K.-S., Bi X. *et al.*: *Eur. Polym. J.*, 2009, **45**, 613.
- [6] Duran N., Karakisla M., Aksu L. and Sacak M.: *Mater. Chem. Phys.*, 2009, **118**, 93.
- [7] Yatsyshyn M., Grynda Yu., Kunko A. *et al.*: *Pat. Ukr.* 62888, Publ. Sept. 26, 2011.
- [8] Yatsyshyn M., Grynda Yu., Kun'ko A. and Dumanchuk N.: *Visnyk Lviv Univ., Ser. Chem.*, 2011, **52**, 268.
- [9] Koval'chuk E., Yatsyshyn M. and Dumanchuk N.: *Praci Nauk. Tov. Shevchenka, Khemia, Biokhemia*. 2008, **21**, 108.
- [10] Wan M.: *Conducting Polymers with Micro or Nanometer Structure*. Springer, Berlin-Heidelberg-New York 2010.

ГІБРИДНІ МІНЕРАЛ-ПОЛІМЕРНІ КОМПОЗИТНІ МАТЕРІАЛИ НА ОСНОВІ ПОЛІАНІЛІНУ ТА КРЕМНЕЗЕМ-ГЛАУКОНІТУ

Анотація. Мінерал-полімерні композити поліанілін-кремнезем-глауконіт одержано *in situ* одностадійною полімеризацією аніліну в присутності мікродисперсних частинок природного мінералу кремнезем-глауконіт. Досліджено фізико-хімічні властивості (фазовий склад, термічну стійкість, електропровідність та намагнічуваність) отриманих зразків композиту різного складу. Вста-

новлено, що полімерний компонент композиту визначає електричну провідність зразків синтезованого композиту, тоді як мінеральні частинки зумовлюють його магнітні властивості та вищу термічну стабільність порівняно з поліаніліном. Окрім того виявлено, що участь поверхні мікрочастинок глауконіт-кремнезему у процесі полімеризації аніліну призводить до суттєво зростання структурованості полімеру в композиті.

Ключові слова: поліанілін, кремнезем-глауконіт, композити, X-променевий фазовий аналіз, термічна стабільність, магнітні властивості.