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PROPERTIES OF THE HYBRID GLAUCONITE/POLYANILINE COMPOSITES SYNTHESIZED IN THE AQUEOUS CITRATE ACID SOLUTIONS

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Abstract. For the first time the series of the composites of aniline and natural mineral glauconite with different ratio of components has been synthesized by oxidation of aniline by ammonium peroxydisulfate in 0.5 M citrate acid aqueous solutions in the presence of dispersion of mineral filler. X-ray phase analysis confirms the amorphous-crystalline structure of produced composites. Results of FTIR spectral analysis show that the samples contain PAn in the form of emeraldine salt and also indicate the presence of weak interfacial interaction between particles of glauconite and polyaniline macrochains in the result of the formation of hydrogen bonds. The results of thermogravimetric analysis of synthesized samples with different composition showed that thermal stability of composites samples increases under the higher glauconite content. It is determined that the thermodestruction of composites is a multistage process. The electric conductivity of composites produced samples with high content of polyaniline is on the level of pure polyaniline. The specific magnetization of synthesized composites in applied magnetic field increases to the value which is characteristic of the pure mineral under the increasing of glauconite content in the composite.

Keywords: polyaniline, glauconite, composites, X-ray phase analysis, thermal stability, electric conductivity, specific magnetization.

1. Introduction

The study of conducting polymers (CP) – a new class of organic polymers, which are also named synthetic metals, began 40 years ago [1, 2]. Polyacetylene, polyparaphenylene, polyaniline (PAn), polypyrrole, polythiophene and others refer to the class of CP. PAn is the most studied conducting polymer [1, 3–5]. The three main forms of PAn can be produced depending on synthesis conditions, namely emeraldine base $[(–B–N=Q=N–)_n(–B–NH–)_{2n}]$ with blue colour, colourless leucoemeraldine base $[(–B–NH–)_n]$ and violet pernigraniline base $[(–B–N=Q=N–)_n]$. Base forms of PAn protonate in the solutions of inorganic or organic acids (H*A*) and pass into the salt forms, particularly into the green emeraldine salts $[(–B–NH^+=Q=NH^+–)_n(–B–NH–)_{2n}](A^-)_{2n}$ or blue pernigraniline salt $[(–B–NH^+=Q=NH^+–)(A^-)_{2n}$ $[(–B–NH^+=Q=NH^+–)](A^-)_{2n}$ [4] (where *B*, *Q* and A^- symbolize a benzenoid ring, quinonoid ring and dopant anion, respectively). The leucoemeraldine (LEm), emeraldine (Em) and pernigraniline (PNAn) base forms of PAn are insulators, while emeraldine (EmS) and pernigraniline (PNAnS) salts are electroconductive forms of PAn [6], which contain different proportions of diamagnetic $[(–B–NH^+=Q=NH^+–)_n(–B–NH–)_{2n}]$ and paramagnetic [(–B–NH+·–B–NH–) n](A–) units.

Every year the subject matter of researches of CP in general and PAn in particular is expanding considerably [6]. In particular, the interest to PAn increases significantly in recent years due to the possibility of synthesis of nanostructurized PAn [6-8]. The main goal of the researches is the search for new methods of synthesis and application of PAn and composites on its basis. It was proposed recently the synthesis of the so-called hybrid composites, which are based on PAn and natural clays or minerals, for example montmorillonite, zeolite, kaolin, perovskite, silica, glauconite-silica, glauconite, *etc*. The combination of the properties of PAn and natural minerals enables to produce micro- and nanocomposite materials with perfected physicochemical properties [9-13] and the phenomenon of synergism can also takes place [14]. Crystallinity, high thermal stability, magnetism and high values of conductivity, especially for the nanostructurized samples are typical of hybrid composites [15]. Such composites use as sensitive layers of chemo- and biosensors, components of anticorrosive and other protective coatings [5, 16]. From this point of view, the synthesis of composite materials on the basis of PAn filled by micro- or nanoparticles of low-price natural minerals is a very perspective direction of CP development. On the other hand, nano- and microdispersed particles of natural minerals or oxides are the templates for the synthesis of nanostructurized PAn that is also very important during production of PAn-mineral composites. Therefore, the developing of conductive inorganic /polymer composites arouses great interest of scientists today [17].

The most popular methods of such composite materials synthesis are the aniline (An) chemical oxidation by various oxidants in the presence of dispersion of natural minerals [18, 19]. Usually such *in situ* synthesis is one-stage process which is carried out mainly in aqueous solutions of inorganic or, infrequently, organic acids [4, 9-12, 18] and leads to the formation of doped polyaniline layers on the surface of dispersed mineral. Synthesis of composites by *in situ* method has a practical importance. Such approach gives an opportunity to combine easily the properties of natural minerals and PAn in the produced new composites materials.

The effectiveness of PAn layer deposition on the surface of inorganic/mineral filler depends on the conditions of the An oxidation (ratio of monomer/oxidant, synthesis temperature, nature of acid–dopant) and, mainly, nature of mineral component, method of its surface preparatory treatment or its dispersion degree. Among the natural minerals, which are used for the synthesis of natural mineral/CP composites, the glauconite (Gl) is studied insufficiently completely [13, 20]. This mineral contains aluminum, titanium, silicon, and, that is most importantly, iron. Therefore the actuality of the problem on synthesis and properties study of the glauconite/polyaniline composites (Gl/PAn) is evident; exactly it is the creation of conductive hybrid composites which are capable of magnetization in an external magnetic field [21, 22]. On the other hand, the citric acid (CA) is perspective and very interesting doping agent. The use of this tribasic acid that also contains HO-group as a dopant, must promote both better binding of polymer macromolecules with Gl particles and intermolecular binding of PAn chains between themselves. Therefore, the aim of our work was Gl/PAn composite synthesis in the presence of CA as a dopant and studies of the influence of Gl content upon the structure, thermal stability, conductivity and specific magnetization of produced samples, which were characterized by X-ray powder diffraction (XRD) analysis, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry (TG) and differential thermogravimetry (DTG) methods, its conductivity and specific magnetization were also evaluated.

2. Experimental

Aniline (ALDRICH, 99.5 %) before its use for chemical syntheses of PAn and Gl/PAn composites was distilled under reduced pressure of 5.2 kPa and stored under argon. Citrate acid (2-hydroxy-1,2,3-propanetricarboxylic acid) and ammonium peroxydisulfate (APS) were chemically grade and were used without additional purification. All solutions were prepared using distilled water.

Sample of glauconite was produced by enriching of natural mineral (from Adamivs’ke-2 deposit occurrence, Khmelnytskyi region, Ukraine) by the method described in work [23]. The chemical composition of the used glauconite sample (determined by energy-dispersive X-ray spectroscopy method) was (mas %): SiO_2 – 56.6; Al_2O_3 – 11.4; FeO and Fe_2O_3 – 14.2; MgO – 3.8; TiO_2 – 0.8; K_2O – 5.0; CaO – 1.8; Na_2O – 0.4 and H_2O ~6 (by the results of thermal analysis). The Gl sample density was 2.1750 ± 0.0050 g/cm^3. The fraction of Gl dispersion with particles size < 2 µm was used in this work.

Samples of PAn and Gl/PAn composites with different weight ratio of components (0.125:1 (sample C-0.125); 0.25:1 (C-0.25); 0.5:1 (C-0.5); 0.75:1 (C-0.75); 1:1 (C-1); 2:1 (C-2); 4:1 (C-4) and 8:1 (C-8)) were synthesized in the aqueous 0.5 M CA medium by the chemical oxidation of An by APS in the absence or presence of Gl microparticles (Table 1). The details of syntheses are described in [13].

X-ray powder diffraction (XRPD) data were collected in the transmission mode on STOE STADI P diffractometer (radiation Cu Kα $\lambda = 0.15404$ nm) [24] with the following setup: Cu $K\alpha_1$-radiation, curved Ge (111) monochromator on primary beam, $2q/w$-scan, angular range for data collection 4.000–70.225 °$2q$ with increment 0.015, linear position sensitive detector with step of recording 0.480 °2θ and time per step 60–120 s, $U = 40$ kV, $I = 35$ mA.

FT-IR spectra of the synthesized samples, pressed into a pellet, were recorded on NICOLET IS 10 spectrophotometer over 4000–650 cm^{-1} range. Spectra were recorded in the reflection mode, which was transformed lately in the transmittance mode.

TG and DTG analysis was carried out using derivatograph Q-1500 D (MOM Paulik-Paulik-Erdei, Hungary) at a heating rate of 10 K/min in air atmosphere with α-Al_2O_3 as the standard. The weight of the sample was 100 mg. The open-type platinum crucibles were used in this work.

Table 1

Composition of initial polymerization mixture during synthesis of PAn and Gl/PAn composites (mixing of the reaction mixture over 1 h; mass of APS - 2.7 g; T = 293±1 K)

Sample	Mass of Gl, g	Mass of An, g	Gl/An mass ratio	*w*(An), mas %
PAn	–	1.0	–	100.0
C-0.125	0.125	1.0	1 : 8	88.9
C-0.25	0.25	1.0	1 : 4	80.0
C-0.5	0.50	1.0	1 : 2	66.7
C-0.75	0.75	1.0	1 : 1.33	56.5
C-1	1	1.0	1 : 1	50.0
C-2	2	1.0	2 : 1	33.3
C-4	4	1.0	4 : 1	20.0
C-8	8	1.0	8 : 1	11.1

Conductivity of samples was measured in the sandwich-type cell. In this case the polymer or composites powders were pressed under pressure 147 kPa·cm^{-2} and T = 293 K over the time of 5 min into pellets with the thickness of 2 mm and diameter of 10 mm.

Specific magnetization of samples was measured by Faraday method.

3. Results and Discussion

3.1. Structure

The structure of Gl (Fig. 1, diffractogram 10) is polycrystalline. The most intense peaks are at $2q$ = 8.3°, 19.6°, 24.3°, 26.7°, 29.0°, 34.7°, 55.5 and 61.3°. As it is shown in Fig. 1 (diffractograms 2–9), all synthesized composites contain some crystalline phase, exactly Gl particles. It confirms the presence of characteristic peaks of mineral in the diffractograms of Gl/PAn composites.

There is amorphous halo in $2q$ = 10–35° interval on the diffractogram of PAn (Fig. 1, diffractogram 1). Three characteristic peaks, at $2q$ = 15.1°, 20.7 and 26.2° respectively, which correspond to amorphous-crystalline form of PAn, are observeed on background of this halo in the case of Gl/PAn composites [9, 12, 13, 25], namely two broad peaks at 20.7° and 26.2° can be ascribed to periodicity parallel and periodicity perpendicular to the polymer chains, respectively [26]. Higher intensity peaks at $2q$ = 15.1 and 26.2° show that PAn is mainly in the crystalline form of emeraldine salt of citric acid, and the presence of less intensive peak at 20.7° indicates that a part of PAn is also in the form of leucoemeraldine base [26].

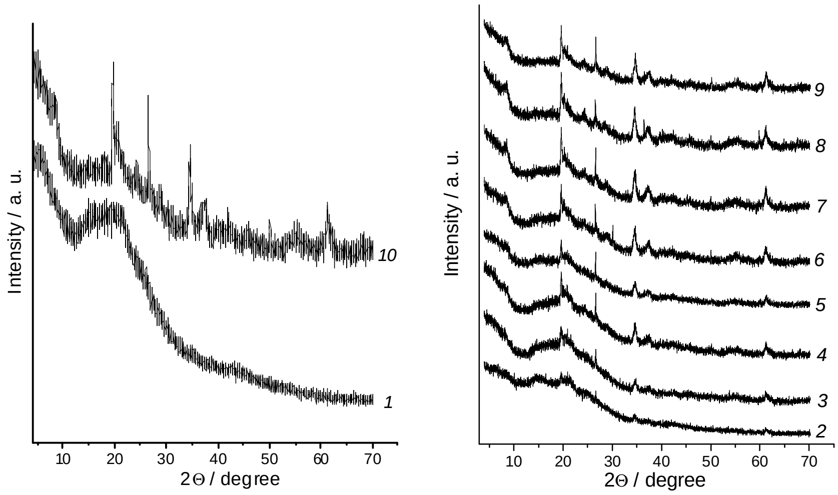


Fig. 1. X-ray diffractograms of PAn (1); C-0.125 (2); C-0.25 (3); C-0.5 (4); C-0.75 (5); C-1(6); C-2 (7); C-4 (8); C-8 (9) and Gl (10) samples

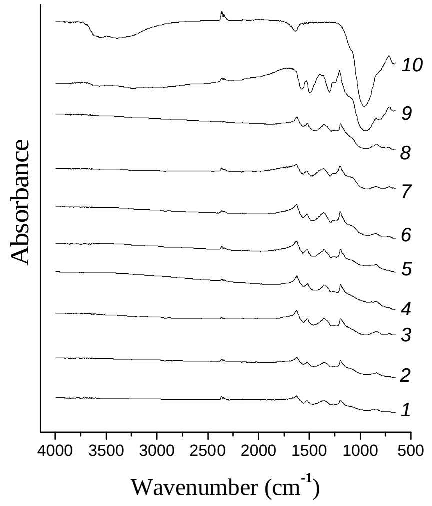


Fig. 2. FTIR spectra of PAn (1); C-0.125 (2); C-0.25 (3); C-0.5 (4); C-0.75 (5); C-1(6); C-2 (7); C-4 (8); C-8 (9) and Gl (10) samples

Synthesized samples of Gl/PAn composites consist of the Gl particles which are coated by PAn layer. Thickness of PAn layer on the mineral particles surface depends on the Gl : PAn ratio in the initial polymerization mixture and, as a result, in the produced composite sample. Thickness of the PAn layer on mineral particles decreases under the increasing of the Gl content in the mixture. As a result, the diffractograms of Gl and C-8 composite are practically identical (Fig. 1, diffractograms 10 and 9 respectively), because the thickness of PAn layer for this composite sample is very small and practically does not affect the character the composite diffractogram.

The ordering of PAn macromolecules deposited on the surface of Gl particles and, respectively, crystallinity of PAn increase under the higher content of mineral component in composites [27-29]. Particularly, it confirms increasing of the intensity of PAn characteristic peaks, namely at $2q = 15.1°$, 20.7°, and 26.2° (see Fig. 1, diffractograms 2–9). The structure of composites C-0.50, C-0.75, C-1 and C-2 is the most well-ordered. High ordering of PAn layers on the Gl particles surface can be explained by participation of Gl particles as a template in the synthesis of PAn micro- or nanostructures on their surfaces.

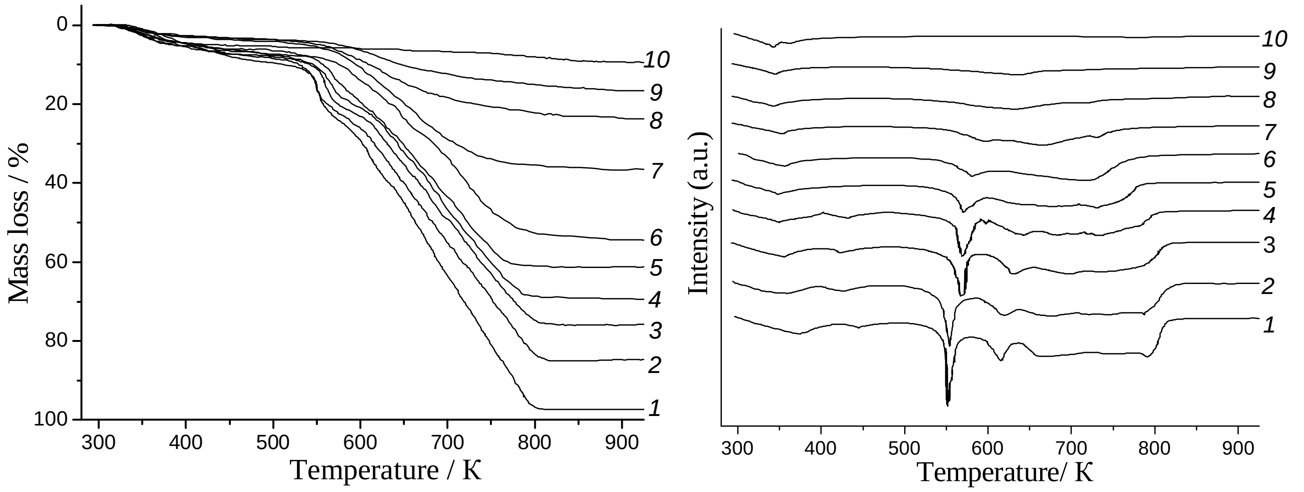
The form and a set of characteristic bands in the FTIR spectrum in the 4000–650 cm^{-1} wavenumber interval of produced aniline polymerizate (Fig. 2, spectrum 1) corresponds to PAn [12, 28]. The characteristic bands which correspond to Pan are observed in the FTIR spectra of synthesized samples of Gl/PAn composites in 1600–650 cm^{-1} region (spectra 2–9). In particular, the two peaks observed at ~1577 and ~1485cm^{-1} in the FTIR spectrum of PAn and Gl/PAn composite (Fig. 2, spectra 1–9) correspond to C–N stretching mode for quinoid and benzenoid rings, respectively [12, 25]. Also the bands at 1305 ± 7 and 1237 ± 7 cm^{-1} which correspond to the C–N stretching vibration of secondary aromatic amine in PAn chains and to the $–C–N^{+}–$ stretching vibration due to polaron structure, respectively, are clearly apparent [12, 25]. Band at 1305 ± 7 cm^{-1} corresponds to the emeraldine salt of PAn and indicates the high doping degree of the polymer [12, 25]. Bands at 1140 ± 7 and 752 ± 7 cm^{-1} correspond to the in-plane and out-of-plane, respectively, C–H bending vibrations on benzene rings and confirm the para-coupling of aniline molecules in the synthesized samples of both PAn and Gl/PAn composites (Fig. 2, spectra 1–9) [30-32]. The characteristic absorption bands of PAn in 3400–2800 cm^{-1} wavenumber interval (so-called "H-peaks", see Fig. 2, spectra 1–9) attribute to the formation of $–N^{+}–H \ldots N–$ hydrogen bonds between neighbour regularly situated chains of PAn [33, 34].

Form of FTIR spectra of Gl (Fig. 2, spectrum 10) corresponds to the spectra of the similar materials [25, 35, 36]. Their main feature is the presence of two broad bands in 3720–2900 interval with peaks at 3584 and 3397 cm^{-1} and high-intensive broad characteristic band at ~960 cm^{-1}. The broad absorption peak at 3435 cm^{-1} and peak at 1641 cm^{-1} can be attributed respectively to the H–O–H symmetric and asymmetric stretching vibrations of water which is absorbed on the polymer chains and is coordinated with Gl particles surface through the cations of metals [25, 37]. The broad intensive band in 1220–715 cm^{-1} interval is superposition of bands which are connected with Si–O vibrations [26], Si–O–Si stretching vibrations and *Me*–*Me*–OH deformation vibrations, namely Al−Al−OH, Al−Fe−OH, Al−Mg−OH *etc.* [12, 25, 35].

It should be noted, that C=N, C=C, and C–N valence band for the samples of Gl/PAn composites at ~1577, ~1485 and ~1305 cm^{-1}, respectively, is shifted to the region of higher values of wavenumbers in comparison with spectrum of individual PAn (Fig. 2) [12, 25]. It indicates the weak interaction between components of composites, exactly in the result of electrostatic interaction or H-bonding between the electronegative surface of Gl particles and protonated $^{+}N−H$ groups of PAn macromolecules [33]. Besides, the polybasicity of dopant (CA) also leads to the H-bonding between adjacent polyaniline macrochains. Such effect is in good agreement with previously published results [38].

3.2. Thermal Stability

The results of thermal analysis of the produced samples of PAn and Gl/PAn composites, exactly TG and DTG curves, are presented in Fig. 3. Mass loss of samples during its heating is caused by the release of different components which enter the composition of composites. In particular, there are four main stages of decomposition for the samples of PAn and Gl/PAn composites (see Fig. 3, *curve* 1): 1) in 323–383 K interval – the loss of physically bounded water; 2) in 383–473 K interval – the negligible weight loss connected with destruction of dopant (CA); 3) in 473–593 K interval – the loss of dopant (CA) and remnants of water, exactly the water from the hydration shell of dopant anions and H-bonding water with PAn macromolecules; 4) in 593–813 K interval – thermo-oxidative destruction of PAn, when oxidation of both PAn and solid products of its decomposition takes place [27]. Three stages of mass loss are observed for individual Gl sample, namely in 323–383, 383–473 and 773–973 K temperature intervals, respectively (Fig. 3, *curve* 10).



a) b)

Fig. 3. TG- (a) and DTG-curves (b) of the samples: PAn (1); C-0.125 (2); C-0.25 (3); C-0.5 (4); C-0.75 (5); C-1(6); C-2 (7); C-4 (8); C-8 (9); Gl (10)

Table 2

Calculated compositions of the produced samples of PAn and Gl/PAn composites calculated on the basis of the result of its thermogravimetrical studies

Sample	Mass after synthesis, g	Yield ±3.0, %	Total mass loss after heating to 973 K, %	Gl/PAn mass ratio	*w*(PAn), mas %
PAn	0.751	75.1	97.3	–	100.0
C-0.125	0.896	79.6	84.7	1 : 5.98	85.7
C-0.25	1.012	81.0	75.7	1 : 3.10	75.6
C-0.5	1.245	83.0	69.4	1 : 2.14	68.1
C-0.75	1.575	90.0	61.3	1 : 1.33	59.0
C-1	1.847	92.3	54.4	1 : 1.05	51.3
C-2	2.753	91.8	36.6	2.24 : 1	30.9
C-4	4.825	96.5	23.7	5.10 : 1	16.4
C-8	8.611	95.7	16.5	11.3 : 1	8.1
Gl	1.0	–	9.5	–	0

Table 3

Characteristics of the produced samples

Sample	ρ, Ohm·cm	$s\cdot10^{5}$, Sm·cm^{-1}
Gl	30707000.0	0.0032
C-8	47900.0	2.089
C-4	7930.0	12.62
C-2	5892.0	16.97
C-1	3441.0	29.06
C-0.75	2457.0	40.71
C-0.5	1361.0	73.5
C-0.25	934.6	107.0
C-0.125	878.6	113.8
PAn	818.3	122.0

The total mass loss for the Gl sample was total 9.5 % at 973 K. The maximal mass losses were typical for samples PAn and C-0.125, C-0.25, C-0.5 samples of Gl/PAn with the highest content of PAn, while the minimal mass losses were observed for C-4 and C-8 sample (see Fig. 3, *curves* 1–9), because mass losses are connected mainly with thermooxidative destruction of PAn. The values of the final masses of samples after the thermogravimetrical analysis (after heating to the final temperature 973 K, see Fig. 3a) give an opportunity to estimate the composition of synthesized samples. The results from Table 2 indicate the ratios of components in the composite samples are sufficiently approximate to the Gl : An ratios in the initial polymerization mixtures. Some enrichment of samples by mineral component is connected with the fact that oligomeric PAn is left in the mother liquor after filtration of the polymerization mixture.

The characteristic of thermal stability of samples is DTG-curves, which illustrate the changes of mass loss rate during heating of samples (see Fig. 3b) [21, 22, 39-43]. Thermal stability characterizes the displacement of the inflection points of TG-curves at the temperatures of destruction (Fig. 3a) and shift of DTG peaks, which corresponds to the stage of PAn destruction (Fig. 3b). Results of thermogravimetrical studies indicate that increasing of the Gl content in the composite leads to the reduction of the stages quantity of thermal destruction and to the shift of the mass losses maxima, which corresponds to the second and third stages of Gl/PAn samples destruction, in the region of higher temperature values in comparison to DTG curve for individual PAn. These results confirm the content of Gl in the composites and its influence on the increasing of the thermal stability of the polymeric component in the Gl/PAn composites.

3.2. Conductivity and Magnetic Properties

The results of the studies of the specific electrical conductivity *s* of the samples of PAn and Gl/PAn are shown in Table 3. As it was expected, the highest and lowest values of conductivity posses the samples of pure PAn and Gl, respectively. The conductivity for the Gl/PAn samples synthesized in the presence of 0.5 M CA are close to the values of conductivity for the PAn/glauconite-silica composite synthesized in 0.5 M H_2SO_4 aqueous medium [38] or for the PAn/kaolinite composites synthesized in the different acids solutions [36]. In our case, the difference between electrical conductivities of synthesized Gl/PAn conposites predetermines the content of nonconducting Gl, as its increasing leads to the decreasing of this physico-chemical characteristic (Table 3).

The dependence of specific magnetization of produced samples on the strength of imposed magnetic field is presented in Fig. 4. Sample of PAn is nonmagnetic (Fig. 4, *relationship* 1), while the sample of Gl is characterized by relatively high magnetization (Fig. 4, *relationship* 10). Specific magnetization of the samples of Gl/PAn composites synthesized in the presence of 0.5 M CA is close to the values of specific magnetization of the samples of of PAn/glauconite-silica composites synthesized in 0.5 M H_2SO_4 aqueous medium [38].

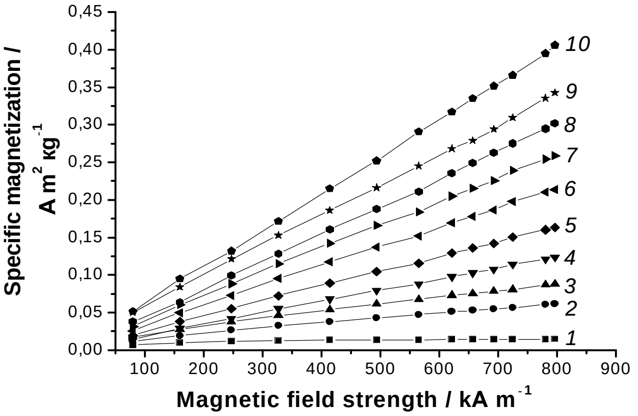


Fig. 4. The dependence of specific magnetization of produced samples on the strength of imposed magnetic field: PAn (1); C-0.125 (2); C-0.25 (3); C-0.5 (4); C-0.75 (5); C-1 (6); C-2 (7); C-4 (8); C-8 (9); Gl (10)

The introduction of Gl dispersed filler in a polymeric matrix leads to the acquisition of magnetic properties of the composites samples in comparison to individual PAn and the value of magnetization in the external magnetic field increases under the higher Gl content in the composite (Fig. 4, *relationships* 2–9).

4. Conclusions

Thus the use of citric acid during the synthesis of glauconite/polyaniline composites promotes the formation of resistant polyaniline layers on the surface of the mineral component particles. Such effect is ensured increasingly by polybasicity of citric acid due to the presence of HO-group in its structure. These factors foster the formation of H-bonds both between adjacent polyaniline macrochains and between the polyaniline layer and the surface of the glauconite particles. Besides, citric acid is an effective dopant and assures the electrical conductivity of synthesized composites on the individual polyaniline level under the low (≤ 20 mas %) content of glauconite. At the same time the use of glauconite as a filler leads to the acquisition of magnetic properties by polymeric composites that extends the application limits of PAn and composites on its base.

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ВЛАСТИВОСТІ ГІБРИДНИХ КОМПОЗИТІВ ГЛАУКОНІТ/ПОЛІАНІЛІН, СИНТЕЗОВАНИХ У ВОДНИХ РОЗЧИНАХ ЦИТРАТНОЇ КИСЛОТИ

Анотація. *Окисненням аніліну пероксодисульфатом амонію в 0,5 М водних розчинах цитратної кислоти за наявності природного мінералу глауконіту синтезовано ряд композитів із різним співвідношенням глауконіт/поліанілін. За допомогою рентгенофазового аналізу показано, що структура отриманих композитів є аморфно-кристалічною. Результати ІЧ-ФП спектрального аналізу зразків показали, що зразки містять ПАн у вигляді емеральдинової солі, а також вказують на наявність слабкої міжфазової взаємодії між частинками глауконіту і макроланцюгів поліаніліну внаслідок утворення водневих зв'язків. Порівняння результатів дериватографічних досліджень синтезованих зразків з різним складом показало, що зі збільшенням вмісту глауконіту підвищується термічна стійкість зразків композитів. Виявлено, що процес термодеструкції композитів є багатостадійним. Питома електропровідність отриманих композитів при високих вмістах поліаніліну знаходиться на рівні таких показників, як для чистого поліаніліну. Питома намагніченість отриманих композитів в прикладеному магнітному полі при збільшенні вмісту глауконіту в композитах зростає до значень близьких для чистого мінералу.*

Ключові слова: *поліанілін, глауконіт, композити, структура, термічна стабільність, електропровідність, питома намагніченість.*