Organic–inorganic hybrids obtained by in situ polymerization of aniline in silica/phosphonate matrix

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Abstract A method for preparing organic–inorganic hybrids containing organophosphorus compounds, silica, and polyaniline (PANI) was developed using sol–gel technique. This method allows the in situ synthesis of organic–inorganic hybrids by reacting tetraethoxysilane (TEOS), aniline, initiator, organophosphorus compound in formic acid. The formic acid has multiple functions: as solvent and acidic media for polymerization of aniline and reagent for sol–gel process. The use of an organophosphorus compound as coupling agent and the introduction of a conductive polymer in silica matrix was investigated.

Introduction

Conducting polymers have attracted attention due to their electric and optical characteristics with potential application in batteries [1], electrochromic devices [2], sensors [3], protection against corrosion [4]. Polyaniline (PANI) is a special case due to its environmental stability in the conducting form, ability to interact with many other components through hydrogen bonding and π–π stacking, convenient and low cost of synthesis, and high conductivity. But the main disadvantage remains its poor processibility.

A promising way to improve the processibility of conductive polymer refers to the blends, composites, and hybrids [5–8].

The properties of these composite materials are based on the synergism between the properties of the individual components. The combination of organic and inorganic components in a single material makes new materials with attractive properties. This is a result of their structural and chemical composition and can be tailored in order to obtain required properties. It is recognized that an organic–inorganic hybrid material presents attractive properties (mechanical, electric, optical, textural, catalytic, etc.) [9–13].

The sol–gel process, presents some advantages like: the possibility of the introduction of organic molecules into an inorganic network and improving the matrix characteristics by adjusting the reaction parameters [14]. This technique allows the preparation of organic–inorganic hybrids with improved physical and chemical properties by fine dispersion at the molecular level [15]. The hybrids synthesized by sol–gel technique present attractive properties and have potential for application as biomaterials, membranes, non-linear optics, coatings, catalysis, optics or electro-optics, and solid electrolytes [16, 17]. PANI/silica matrices have been obtained by sol–gel technique [6–8]. Doped silica sol–gel was obtained by polymerizing aniline during the processing [18]. It is difficult to polymerize aniline, once the dried gel was obtained. Wei et al. [19] obtained PANI–silica composite by sol–gel method with physically superior properties compared to PANI alone. Another route to obtain PANI/silica matrices implies the dissolution PANI in an organic solvent and subsequently depositing a sol–gel composite of this polymer [20].

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In this work we tried to improve the processibility of PANI and to obtain a well-dispersed conductive PANI in an unusual matrix—phosphonate/silica "network". This matrix has not been reported in the literature thus far.

Organophosphorus acids (phosphoric, phosphonic, and phosphinic) and their derivatives (salts, esters) are highly promising coupling molecules that allow the anchoring of organic groups to inorganic solids [21].

These compounds appear to be complementary of organosilanes. So, it is possible to obtain phosphorus silica network. Surface modification of various inorganic supports by these coupling molecules has already led to several applications in the fields of composite materials [22], separation [23], and catalysis [24], for the elaboration of photovoltaic [25] and optical devices [26] or in the biomedical area [27].

The combination of these materials generates a new class of high performance or highly functional organic–inorganic hybrid. Also sol–gel method using formic acid was chosen. Formic acid plays two roles: solvent for PANI and catalyst-reagent for silica–phosphonate network [18].

Results and discussion

The hybrids were prepared by simultaneous hydrolysis–polycondensation of TEOS with DEBP and oxidative polymerization of aniline. The reagent ratios and PANI content are presented in Table 1.

The formic acid plays two roles: solvent for PANI and catalyst for polysilicates–polyphosphonate network. During the acidolysis, silanol groups are formed and ethanol is released as an intermediate [28, 29]. The DEBP precursor hydrolyzes as well in formic acid, ethanol is eliminated and phosphonic acid is formed as an intermediate.

The formation of hybrids implies condensation and polycondensation reactions between silanol–silanol, silanol–ester, and P–OH groups. Self-condensation between P–OH groups does not occur under the sol–gel conditions. The PANI formed by oxidative polymerization is entrapped into the organic–inorganic matrix (Scheme 1).

It is reported that the time of gelation can be reduced by up to two orders of magnitude, depending on reaction conditions employed, when the silicon alkoxide mixture
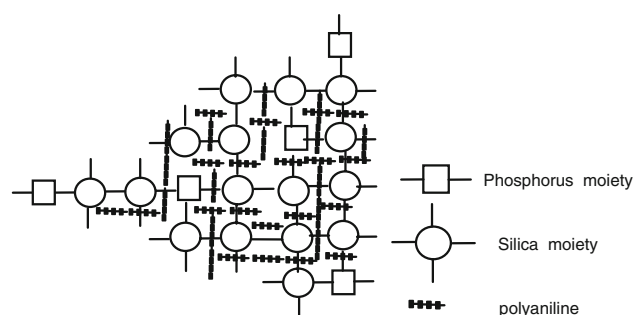
Scheme 1 PANI entrapped into organic–inorganic matrix

reacts with formic acid instead of water [28, 29]. The hydrolysis of alkoxysilane in formic acid is fast and the gelation time depends on the amount of alkoxysilane in the precursor mixture [28, 29].

At the same concentration of TEOS in precursor mixture, the presence of DEBP increases the gelation time. The gelation time increases from 5 to 30 min at room temperature, comparatively with the case of A2 without DEBP at which gelation time is very short.

The gelation time is affected by the DEBP content. The gelation time increase linearly with the DEBP content (Fig. 1).

The increase of gelation time is a consequence of the two factors: one the lower hydrolysis rate of phosphorus ester group and second the lower rate condensation process between P–OH groups and Si–OH groups comparatively with the self-condensation rate between Si–OH groups.
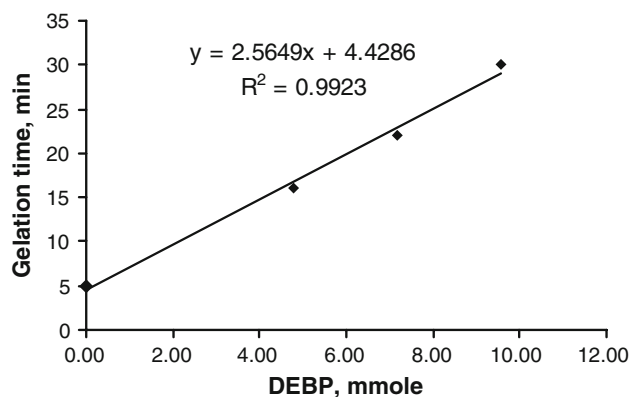

Fig. 1 Gelation time versus DEBP content in mixture

Table 1 Reagent used in synthesis of hybrids

Sample	Formic acid (mL)	TEOS (mL)	Aniline (mL)	DEBP (mL)	Ammonium peroxidisulfate (g)	% PANI in sample
A1	15	1.07	0.435	1	1.09	12.25
A2	15	1.07	0.435	–	1.09	17.58
A3	20	2.14	0.435	2	1.09	7.60
A4	50	1.07	0.435	1.5	1.09	4.18

The presence of the characteristic peaks of the emeraldine salt form of PANI in the FTIR spectrum of hybrids demonstrates the formation of PANI. The intensities of some of the peaks, e.g., 1560, 1480, 1290, 1130, and 807 cm^{-1}, are affected by the presence of silica and phosphorus network and can be explained on the basis of constrained PANI growth and restricted modes of vibration.

The main characteristic bands of doped PANI are assigned as follows: the band at 3300 cm^{-1} is attributed to N–H stretching mode, the C=N and C=C stretching mode for the quinoid (Q) and benzenoid (B) rings at 1562 and 1480 cm^{-1}, the C–N stretching mode for benzenoid ring bands at about 1296 and 1241 cm^{-1} and the peak at 1118 cm^{-1} is assigned to the in-plane bending vibration of C–H (mode of N=Q=N, Q=N^{+}H–B, and B–N^{+}H–B), which is formed during protonation [30–32].

The silica–phosphorus network leads to the shift of PANI bands to the lower wave numbers with a decreased intensity in the hybrid samples comparing to the corresponding peaks of pure PANI (at 1584, 1474, 1295, and 1131 cm^{-1}, respectively, indicating the formation of hydrogen bonds between silica phosphorus network and the imine groups in the polyaniline molecular chains.

These differences in the FTIR spectra can be related to constrained growth and restricted modes of vibrations in PANI in the presence of silica phosphorus network, similar phenomena was observed in the case of TiO$_2$ [33].

In the range from 400 to 1200 cm^{-1}, pure silica shows several characteristic peaks. They are assigned to the Si–O–Si and Si–O– stretching vibrations. With the addition of DEBP, the absorption peak at 1080 cm^{-1} is broadened and shifted to lower wave numbers due to the presence of Si–O–P–O bond [34] at 1020 cm^{-1}. The 1114 cm^{-1} is assigned to the overlap peaks of the Si–O–Si symmetric stretching mode and the CH stretching mode in plane bend. The band at 815 cm^{-1} is assigned to the overlap peaks of Si–O and CH out of plane bend. The band associated to –Si–O [30] is located at 474 cm^{-1}. The 900–1300 cm^{-1} region corresponds to the vibrations of the phosphonate.

In the case of pure PANI, the bands at 574 and 610 cm^{-1} show the same relative intensities [35]. The band at 574 cm^{-1} was assigned to the formation of phenazine structures produced in hybrids by crosslinking among PANI chains (Scheme 2).

The band at 610 cm^{-1} was assigned to the benzene ring deformation [36, 37]. In the hybrids A1, A3, A4, the band at 610 cm^{-1} is stronger than the band at 574 cm^{-1}. The decrease of the relative intensity of the band at 574 cm^{-1} in hybrids spectra would indicate that a high amount of silica and phosphorus within conducting polymer chains avoids the inter-chain interaction of PANI chains during preparation.
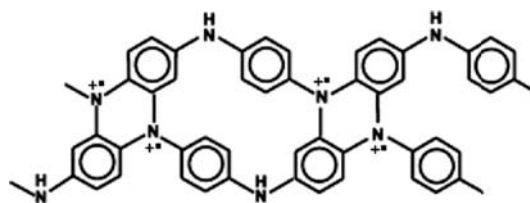
Scheme 2 Phenazine structure

In the case of A2 the intensity of the band at 610 cm^{-1} indicates a more homogeneous dispersion of conducting material comparatively with the A1. The presence of organic phosphorus compound allows the crosslinking among PANI chains in hybrid and the formation of phenazine structures.

The phosphorus content of hybrids A1, A3, A4 was determined by Schöningen method. The results are presented in Table 2 and are in good agreement with the quantity of DEBP used in synthesis.

The thermal behavior of obtained organic–inorganic hybrids was evaluated from TG data recorded in air atmosphere and under nitrogen. In air, there are four major stages of weight loss for all samples (Table 3).

The first weight loss below 120 °C is a result of the release of moisture. The other three decomposition stages in the temperature range 120–1000 °C are associated with the release of PANI dopant (120–160 °C), decomposition of PANI chain above 380 °C and the release of the structural water resulted from the bonded hydroxyl groups. For the hybrids with moiety (A1, A3, and A4) in temperature domain 200–500 °C, in air DEBP decompose with the formation of phosphorus pentoxide (P$_2$O$_5$). The weight residue in thermograms (remaining for all samples recorded in air at 1000 °C) was regarded as the real silica content.

In nitrogen, the samples present three major weight loss presented in Table 3. The first weight loss is associated with the release of moisture (90–120 °C). The temperature range 200–1000 °C presents an apparently complicated weight loss. In this temperature range the entire weight loss is mainly attributed to the release of the structural water resulted from the bonded hydroxyl groups and to the other process like: release of PANI dopant (120–160 °C),

Table 2 Phosphorus content of hybrids determined by Schöningen method

	mg P/g hybrids	
	Experimental	Calculated
A1	40.02	40.60
A2	–	–
A3	59.36	60.90
A4	79.23	81.20

Table 3 The TG data for hybrid sample

Sample/atmosphere	Temperature range (°C)	Weight loss (%)
A1/air	90–120	0.49
	200–350	35.30
	350–500	13.38
	500–1000	14.07
Residue	750 °C	17.22
A1/nitrogen	90–120	0.47
	200–350	57.33
	350–1000	17.64
Residue	1000 °C	23.11
A2/air	90–120	0.75
	200–350	42.43
	350–500	15.54
	500–1000	15.95
Residue	750 °C	17.02
A2/nitrogen	90–120	0.76
	200–350	45.21
	350–1000	21.91
Residue	1000 °C	30.16
A3/air	90–120	0.59
	200–350	47.72
	350–500	20.02
	500–1000	17.71
Residue	750 °C	17.32
A3/nitrogen	90–120	0.42
	200–350	63.60
	350–1000	18.70
Residue	1000 °C	27.11
A4/air	90–120	0.46
	200–350	35.30
	350–500	13.38
	500–1000	14.07
Residue	750 °C	17.61
A4/nitrogen	90–120	0.43
	200–350	64.85
	350–1000	19.06
Residue	1000 °C	28.16

decomposition of PANI chain (above 350 °C), and degradation of P–C bonds.

The phosphorus content can be evaluated for hybrids containing organophosphorus compounds, silica, and PANI from TG data recorded in air, if equivalent hybrids without DEBP are prepared. In our experiments the hybrids A1 and A2 are equivalent except the fact that in A2 only DEBP is missing. It is known that in oxygen atmosphere, hybrids containing organophosphorus compounds release P_2O_5 (from DEBP). The weight loss in the temperature range 200–500 °C can be used for the evaluation of phosphorus content (Fig. 2).

In the temperature range 200–500 °C sample A2 presents a higher weight loss comparatively with sample A1.

The difference in the weight loss is attributed to the increased content of Si–OH groups in the A2 sample, due to the higher content of TEOS. Sample A2 contains more TEOS comparatively with A1. Knowing the initial mixture weight of each hybrid samples (m_i), the weight loss due only to the TEOS content can be evaluated.

The TEOS content in sample A1 can be calculated with the formula (1):

$$m_{TEOSA1} = \frac{m_{sA1} \cdot m_{iTEOS}}{m_{iA1}} \tag{1}$$

Similarly, the TEOS content in sample A2 can be considered (2):

$$m_{TEOSA2} = \frac{m_{sA2} \cdot m_{iTEOS}}{m_{iA2}} \tag{2}$$

The TEOS difference between hybrid samples can be calculated (3):

$$\Delta m_{TEOS} = \frac{m_{iTEOS}(m_{sA2} * m_{iA1} - m_{sA1} * m_{iA2})}{m_{iA1} * m_{iA2}} \tag{3}$$

where $m_{iA1,A2}$ represents the initial weight of mixture A1, respectively A2; m_{iTEOS} represents the TEOS content in initial mixture, mg; $m_{sA1,A2}$ represents the sample weight in TG, mg; m_{TEOSA1}, m_{TEOSA2} represents the TEOS content in TG hybrids sample A1, respectively A2, mg.

The weight loss of sample A1 due only to the TEOS content can be calculated from TG weight loss of sample A2 with the formula (4):

$$\Delta m_{A1calc} = \frac{\Delta m_{sA2} \cdot m_{TEOSA1}}{m_{TEOSA2}} \tag{4}$$

where Δm_{A1calc} represents the weight loss due only to the TEOS content, mg; Δm_{sA2} represents the experimental weight loss of hybrid sample A2 in the range 200–500 °C.

The experimental weight loss of sample A1, obtained from TG data is higher than the calculated one. The difference represents the weight loss due to the oxidation of DEBP at P_2O_5 (Δm_{DEBP}).

$$\Delta m_{DEBP} = \Delta m_{exp} - \Delta m_{calc} \tag{5}$$

Based on this difference the phosphorus content in the sample can be calculated in mg per gram hybrids with the formula:

$$P = \frac{\Delta m_{DEBP} \cdot 2A_p}{M_{P_2O_5} \cdot m_{sA1}} \tag{6}$$

where A_P represents the relative atomic mass of phosphorus; $M_{P_2O_5}$ represents molar mass of P_2O_5.

The same calculation can be done for the sample A3 and A4. The calculated values are presented in Table 4.
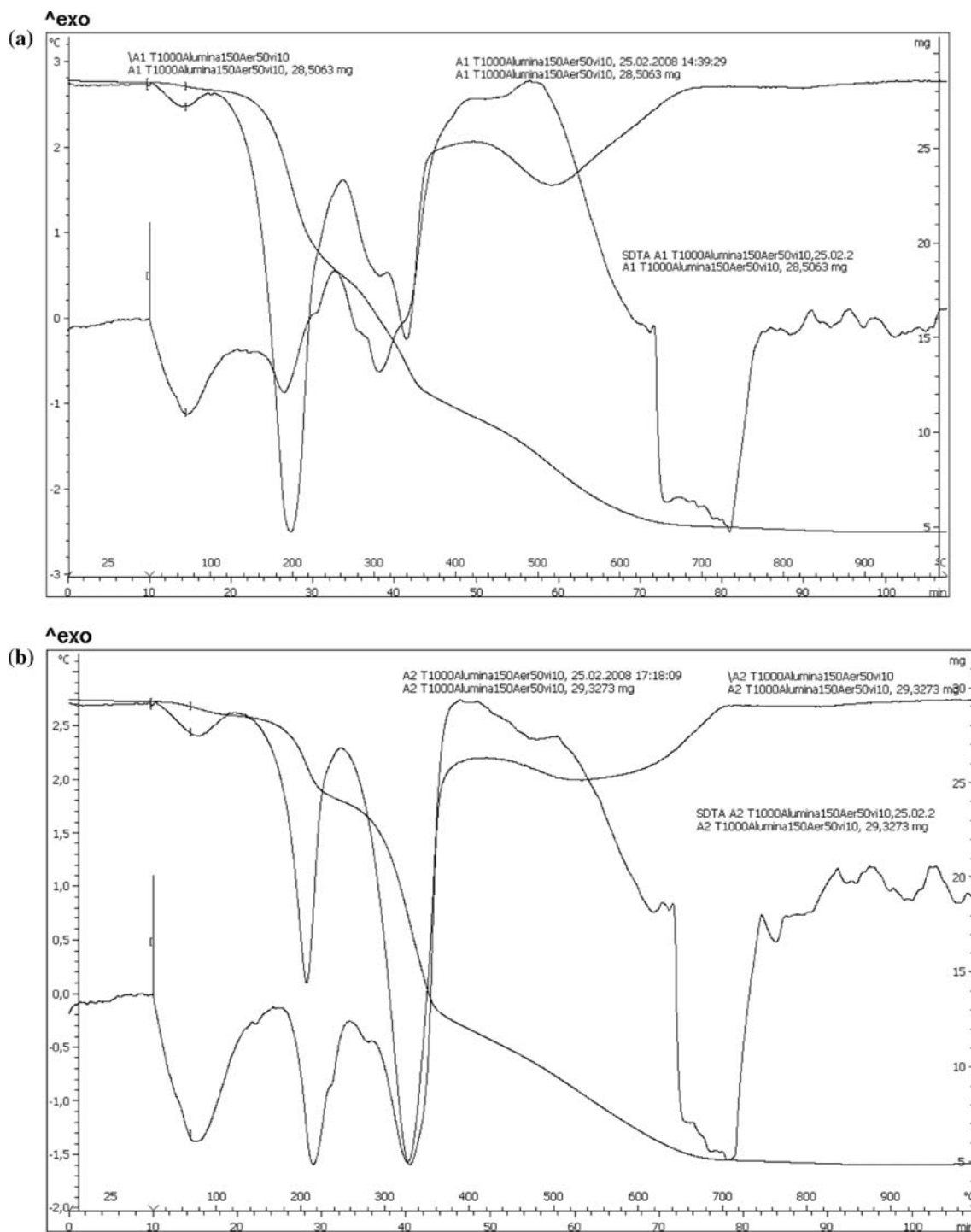
Fig. 2 TG sample in air. **a** Hybrid A1 and **b** hybrid A2

The obtained values are in accordance with the results obtained by Schoningen method and are in agree with the calculated values. The condensation between P–OH groups and Si–OH groups can be evaluated from TG data too. By comparing the TG data recorded in nitrogen in the temperature range 200–750 °C (Fig. 3), the weight loss difference between hybrid sample with and without phosphorus moiety are mainly attributed to the condensation between P–OH groups and Si–OH groups.

Each phosphorus moiety is bifunctional (has two OH groups) and each silicon moiety is tetrafunctional (contain four OH groups). As a result in sample A2 the weight loss due to the water release is higher than in the sample with phosphorus moiety.

Table 4 Phosphorus content of hybrid samples calculated from TG data in air

Sample	m_i (g)	m_s (mg)	m_{iTEOS} (g)	Δm_{exp}[a] (mg) (200–500 °C)	Δm_{DEBP} (mg)	mg P/g hybrids
A1/air	3.6244	28.5063	0.9938	14.3714	2.6190	40.12
A2/air	2.5344	30.0980	0.9938	16.9902	–	–
A3/air	7.3244	34.0254	1.9987	13.7982	3.1918	60.04
A4/air	4.1244	32.8835	0.9938	11.6818	5.3082	81.32

[a] The experimental weight loss of hybrid sample in the range 200–500 °C from TG data calculated for a hybrid sample equal to 28.5063 mg

The difference between sample A2 and A1 is 1.7684 mg. So, this difference in mass loss is a result of higher number of hydroxyl group content in sample A2.

It is possible to calculate the weight loss of a silica–phosphorus hybrid sample due only to the Si–OH groups. The $Si(OH)_4$ content in sample A1 can be calculated with the formula (7):

$$m_{Si(OH)_4A1} = \frac{m_{sA1} \cdot m_{iSi(OH)_4}}{m_{iA1}} \qquad (7)$$

Similarly, the $Si(OH)_4$ content in sample A2 can be calculated (8).

$$m_{Si(OH)_4A2} = \frac{m_{sA2} \cdot m_{iSi(OH)_4}}{m_{iA2}} \qquad (8)$$

Sample A2 contain more Si–OH group comparatively with A1 and so the weight loss are higher due to the increased water release in condensation process.

Knowing the initial mixture weight of each hybrid samples (m_i) the $Si(OH)_4$ difference between hybrid samples can be calculated (9).

$$\Delta m_{Si(OH)_4} = \frac{m_{iSi(OH)_4}(m_{sA2} * m_{iA1} - m_{sA1} * m_{iA2})}{m_{iA1} * m_{iA2}} \qquad (9)$$

where $m_{iA1,A2}$ represents the initial weight of mixture A1, respectively A2; m_{iTEOS} represents the $Si(OH)_4$ content in initial mixture, mg; $m_{sA1,A2}$ represents the sample weight in TG, mg; $m_{Si(OH)_4A1}$, $m_{Si(OH)_4A2}$ represents the $Si(OH)_4$ content in TG hybrids sample A1, respectively A2, mg.

The weight loss of sample A1 due only to the $Si(OH)_4$ content can be calculated from TG weight loss of sample A2 with the formula (10):

$$\Delta m_{A1calc} = \frac{\Delta m_{sA2} \cdot m_{Si(OH)_4A1}}{m_{Si(OH)_4A2}} \qquad (10)$$

where Δm_{A1calc} represents the weight loss due only to the $Si(OH)_4$ content, mg; Δm_{sA2} represents the experimental weight loss of hybrid sample A2 in nitrogen in the range 200–750 °C.

The experimental weight loss of sample A1 is higher than the calculated one and the difference represents the water weight loss due the condensation of P–OH groups (Δm_{H_2O}) (11). The results are summarized in Table 5.

$$\Delta m_{H_2O} = \Delta m_{exp} - \Delta m_{calc} \qquad (11)$$

The release of one molecule of water occurs by the reaction of two P–OH groups. The calculated mmol of water are in good agreement with the initial mixture content of DEBP of each hybrid sample. The composition of hybrid sample is summarized in Table 6. The exact silica content was determined from the weight of the residue at 750 °C [38] and these values were in excellent agreement with those calculated from stoichiometry of the starting materials.

The PANI content (Table 6) was calculated assuming that the polymer is homogenous dispersed in phosphorus silica network.

The SEM images indicate the formation of mesoporous PANI–phosphorus–silica hybrids (Fig. 4).

The obtained hybrids are fine dark green powders at macroscopic level. The homogeneity of color at macroscopic level points out homogeneous hybrid with good interaction between PANI and organic–inorganic network with no tendency of phase separation. A few optical images at 40× magnification are presented (Fig. 5).

The homogeneity of the samples results from the optical and SEM images. In presented figures the magnification is 40× (optical microscope) and 12000× (SEM). At this magnification we observed a well distribution of PANI in the organic–inorganic matrix.

The morphology of the PANI hybrids is represented by fused granules in all the samples (Fig. 4). Fused granules having the size of 300–850 nm are obtained in the case of PANI–phosphonate–silica network matrix. The size of hybrid granules increases with the increase of the content in silica and phosphonate (higher content of phosphonate–silica network matrix, e.g., sample A3) as a result of the increase of gelation time.

The PANI appears to be well-dispersed in the phosphonate–silica network. The decrease in pore volume of hybrids with the increase of PANI content indicates that the polymers are well-packed inside the network.

Experimental

Reagent aniline (Chemopar Bucharest), TEOS, formic acid (Sigma–Aldrich), ammonium peroxidisulfate (Merck), and
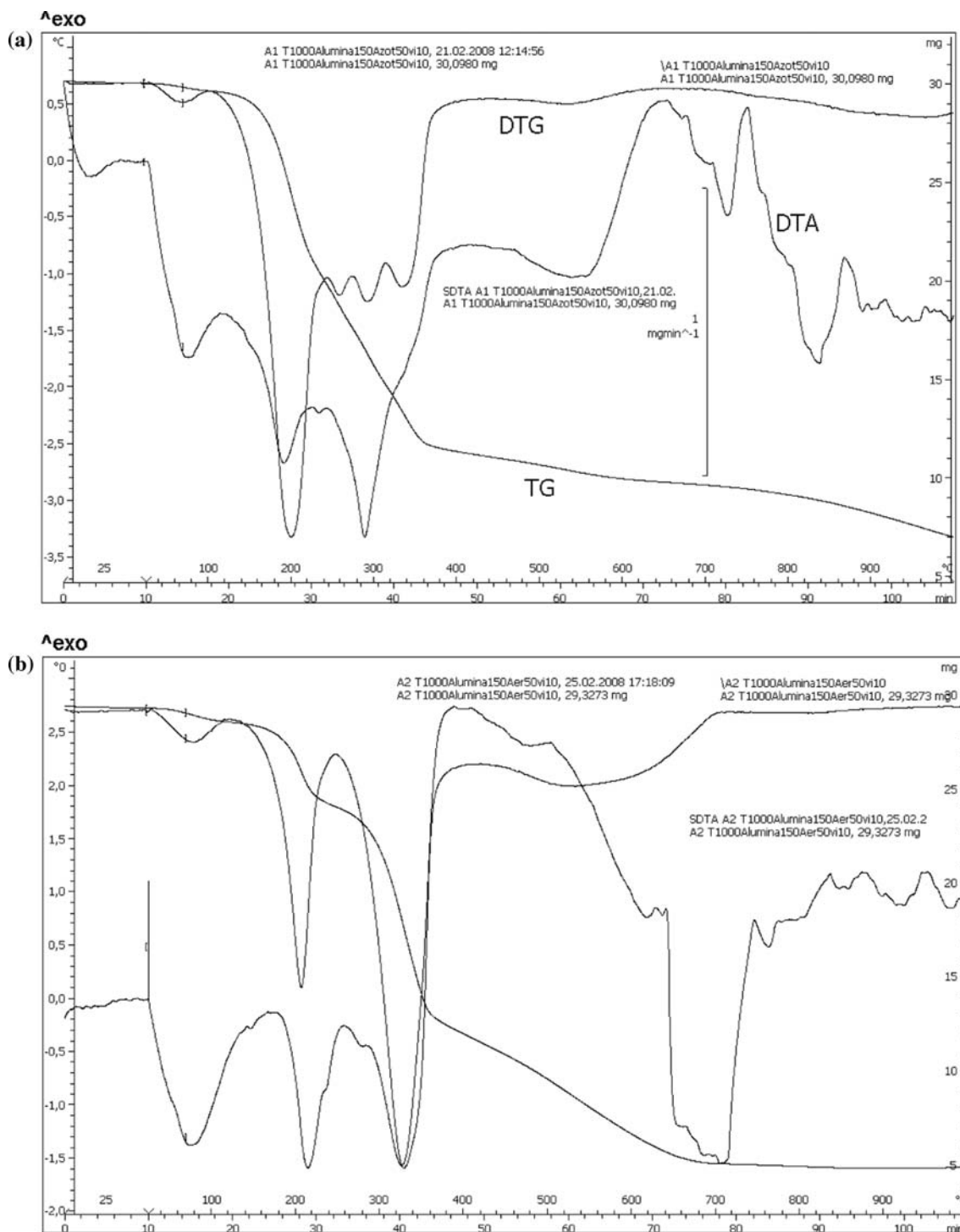
Fig. 3 TG sample in nitrogen. **a** Hybrid A1 and **b** hybrid A2

diethylbenzyl phosphonate (DEBP-Merck) were used as received except aniline which was double distilled prior use. The hybrid composites were obtained in one pot synthesis. First, oxidant ammonium peroxodisulfate was added in formic acid and vigorously stirred until the oxidant was dissolved. Then, the aniline was added and the

mixture was vigorously stirred at ambient temperature until the slightly blue color appeared and then TEOS and DEBP were added. The reagent ratios are presented in Table 1.

The mixture was stirred for 5–30 min (depending on the quantity of DEBP added) at room temperature and after that allowed to complete the reaction for 1 day at 75–85 °C.

Table 5 Water release due to the P–OH groups (mg per gram hybrid) calculated from TG data in nitrogen

	m_i (g)	m_s (mg)	$m_{iSi(OH)_4}$ (g)	Δm_{exp}[a] (mg) (200–750 °C)	Δm_{H_2O} (mg)	mmol H_2O
A1/nitrogen	3.6244	30.0980	0.4584	14.9464	3.2463	0.18
A2/nitrogen	2.5344	30.0419	0.4584	16.7148	–	–
A3/nitrogen	7.3244	34.0254	0.9219	18.5094	6.8435	0.36
A4/nitrogen	4.1244	32.8835	0.4584	16.5689	4.8621	0.27

[a] The experimental weight loss of hybrid sample in the range 200–750 °C from TG data calculated for a hybrid sample equal to 30.0980 mg

Table 6 The composition of hybrid sample

Sample	mg PANI/g hybrids	mg P/g hybrids			Silica content (%)	
		Schöningen method	Experimental[a]	Calculated	Experimental[b]	Calculated
A1	12.25	40.02	40.12	40.60	17.22	17.5
A2	17.60	–	–		17.02	17.5
A3		59.36	60.04	60.90	17.32	17.5
A4		79.23	81.32	81.20	17.61	17.5

[a] From TG weight loss in 200–500 °C, air

[b] From TG residue at 750 °C, air

Fig. 4 SEM images for **a** hybrid A1 (12.25% PANI), **b** hybrid A2 (17.58% PANI), and **c** hybrid A3 (7.60% PANI)
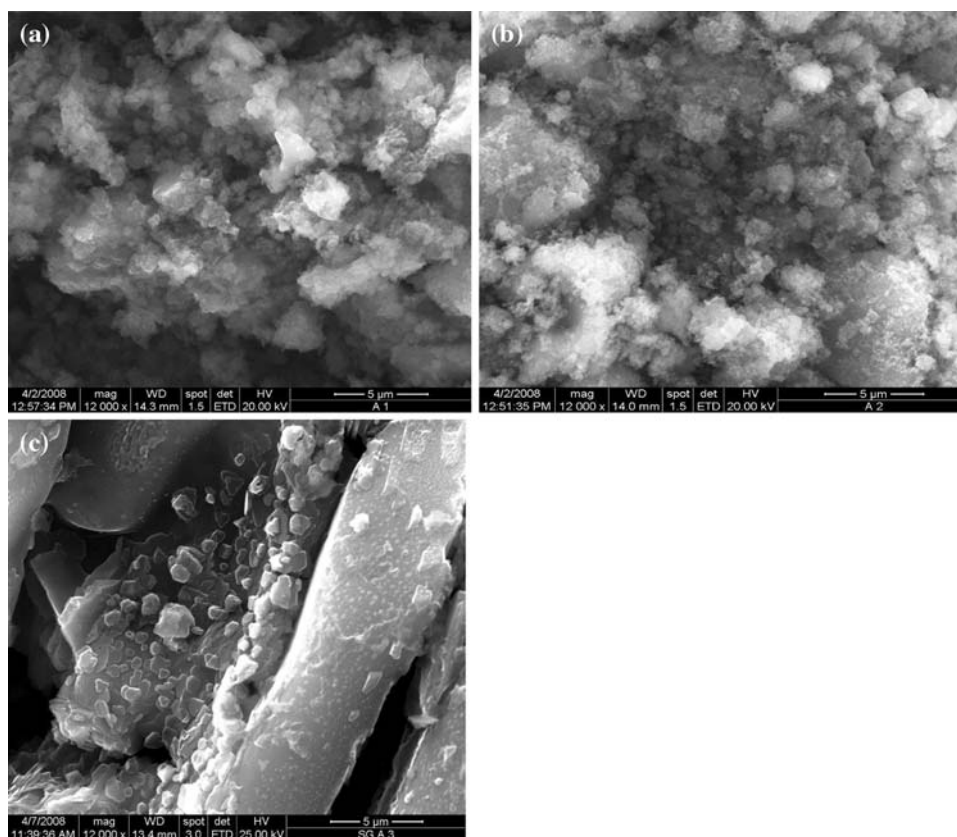

After the addition of DEBP the viscosity of mixture increased. The gelation time is determined from viscosimetric measurements. The gelation time (t_{gel}) was arbitrarily taken as the time at which the viscosity of solution increased rapidly.

The obtained hybrids were investigated using FTIR, SEM, and TG measurements.

The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000–400 cm^{-1}, 256 scans, and resolution 2 cm^{-1}) using KBr pellets.

Fig. 5 Optical images of synthesised samples
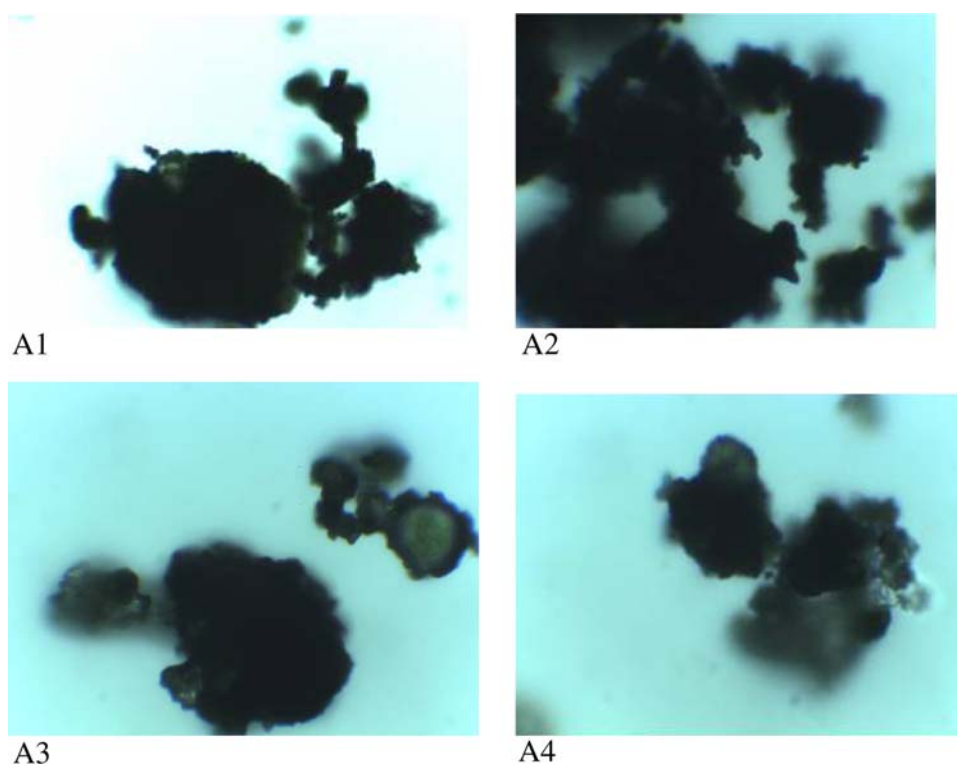
The SEM images were obtained using Inspect S microscope.

Thermogravimetric analyses were performed on a TGA/ SDTA 851-LF 1100-Mettler. The working conditions were: samples amount 29–31 mg for the hybrid samples; aluminum crucible, heating rate 10 K/min; atmosphere nitrogen and air.

The phosphorus content in hybrids was determined according to the Schöningen method [39]. A sample of hybrids precisely weighed was burnt out in an oxygen atmosphere and the P_2O_5 formed was absorbed in water. The solution obtained was titrated with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black T as indicator.

Conclusions

This method allowed obtaining in one pot synthesis new organic–inorganic hybrids containing organophosphorus compounds, silica, and polyaniline. This method allowed us to obtain organophosphorus network by a simple sol–gel technique, due to the higher hydrolysis of organic phosphorus esters. With the increase of PANI content the mesopore volume of hybrids decrease as a result of the homogenous dispersion of PANI inside the network. Thermogravimetry prove to be a simple and satisfactory method to determine the phosphorus content of hybrids and to evaluate the condensation between P–OH groups and Si–OH groups in hybrids.

References

1. Matsunaga T, Daifuku H, Nakajima T, Kawagoe T (1990) Polym Adv Technol 1:33
2. Duek EAR, De Paoli M-A, Mastragostino M (1992) Adv Mater 4:287
3. Boyle A, Genies EM, Lapkowski M (1989) Synth Met 28:769
4. Sathiyanarayanan S, Muthukrishnan S, Venkatachari G, Trivedi DC (2005) Prog Org Coat 53:297
5. Paoli De (1997) In: Nalwa HS (ed) Handbook of conductive molecules and polymers: vol 2: conductive polymers. Synthesis and electrical properties. Wiley, London
6. Boonstra AH, Bernardes JNM (1988) J Non-Cryst Solids 105:207
7. Castro EG, Zarbin AJG, Galembeck A (2005) J Non-Cryst Solids 351:3704
8. de Azevedo WM, Brondani DJ (2001) J Non-Cryst Solids 296:224
9. Judeinstein P, Sanchez C (1996) J Mater Chem 6:511
10. Loy DA, Shea KJ (1995) Chem Rev 95:1431
11. Sanchez C, Ribot F, Lebeau B (1999) J Mater Chem 9:35
12. Judeinstein P, Livage J, Zarudiansky JA, Rose R (1988) Solid State Ionics 28–30:1722
13. Brinker CJ, Scherrer GW (1990) Sol–gel science, the physics and chemistry of sol–gel processing. Academic Press, San Diego, CA
14. Izumi K, Tanaka H, Murakami M, Degushi T, Morita A, Toghe N, Minami T (1990) J Non-Cryst Solids 121:344
15. Novak BM (1993) Adv Mater 5:422
16. de Azevedo WM, de Souza JM, de Melo JV (1999) Synth Met 100:241

17. Sivaraman P, Rath SK, Hande VR, Thakur AP, Patri M, Samu AB (2006) Synth Met 156:1057
18. Ita M, Uchida Y, Matsui K (2003) J Sol-Gel Sci Technol 26:479
19. Wei Y, Yeh JM, Jin D, Jia X, Wang J, Jang G-W, Chen C, Gumbs RW (1995) Chem Mater 7:969
20. Mattes BR, Knobbe ET, Fuqua PD, Nishida F, Chang E-W, Pierce BM, Dunn B, Kaner RB (1991) Synth Met 43:3183
21. Mutin PH, Guerrero G, Vioux A (2003) C R Chimie 6:1153
22. Nakatsuka T, Yamashita S (1983) J Appl Polym Sci 28:3549
23. Randon J, Blanc P, Paterson R (1995) J Membr Sci 98:119
24. Villemin D, Jaffres P-AN, echab B, Courivaud F (1997) Tetrahedron Lett 38:6581
25. Bonhote P, Moser J, Humphry-Baker R, Vlachopoulos N, Zakeeruddin SM, Walder L, Gratzel M (1999) J Am Chem Soc 121:1324
26. Will G, Nagaraja Rao JSS, Fitzmaurice D (1999) J Mater Chem 9:2297
27. Michel R, Lussi JW, Csucs G, Reviakine I, Danuser G, Ketterer B, Hubbell JA, Textor M, Spencer ND (2002) Langmuir 18:3281
28. Panitz JC, Wokaun A (1997) J Sol-Gel Sci Technol 9:251
29. Sharp GK (1994) J Sol-Gel Sci Technol 2:35
30. Peng L, Weimin L, Qunji X (2004) Mater Chem Phys 87:109
31. Li XW, Wang GC, Lu DM (2004) Appl Surf Sci 229:395
32. Dimitriev OP (2004) Macromolecules 37:3388
33. Somani PR, Marimuthu R, Mulik UP, Sainkar SR, Amalnerkar DP (1999) Synth Met 106:45
34. Matsuda A, Kanzaki T, Yoshinori K, Tatsumisago M, Minami T (2001) Solid State Ionics 139:113
35. Pereira da Silva JE, de Faria DLA, de Torresi SIC, Temperini MLA (2000) Macromolecules 33:3077
36. Louarn G, Lapkowski M, Quillard S, Pron A, Buisson JP, Lefrant S (1996) J Phys Chem 100:6998
37. Cochet M, Louarn G, Quillard S, Boyer MI, Buisson JP, Lefrant S (2000) J Raman Spectrosc 31:1029
38. Li S, Shah A, Hsieh AJ, Haghighat R, Praveen SS, Mukherjee I, Wei E, Zhang Z, Wei Y (2007) Polymer 48:3982
39. Albert F, Barbulescu N, Holzky C, Greffs C (1970) Analiza chimica organica (Organic chemical analysis), Ed. Tehnica, Bucuresti