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STUDY OF THERMAL STABILITY OF SOME POLYANILINE–DVB GELS

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In contrast with other conductive polymers with metallic behavior, polyaniline (Pani) is readily prepared in aqueous acid solution, and stable in air and water. The study of thermal stability of Pani is very important for film preparation and processability. The effect of Styrene-2% Divinylbenzene gels (DVB) and synthesis conditions on the conductivity and thermal stability of the PAni-DVB have been investigated. It was established a correlations between synthesis conditions and thermal stability of PANI-DVB gels.

Keywords: polyaniline; polyaniline composite; thermal stability

INTRODUCTION

Conducting polymers are still the most promising category of polymer due to the various domains of possible applications. Among the conductive polymers, polyaniline is fascinating due to good conductivity, special doping mechanism, excellent chemical stability [1,2]. It's poor solubility in many solvents remains the main disadvantage. One of the advantage of making the composite and blends of conducting polymer is to improve the low procesability, to obtain high performance of the former which combines the desirable mechanical properties of insulating host matrix together with the electrical and optical properties of polyaniline quest. Conducting polyaniline composite and blends can be prepared by melt processing, by casting the solution which contains the component of blends or by chemical or electrochemical polymerization of aniline in presence of an insulating polymer [3–15].

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For these special polymers, the temperature affects the conductivity and determines the domains of applications. Beside the temperature, the synthesis parameters and nature of dopant affect the structure and properties of obtained material. The thermal analysis allowed to establish the performance of the polymer for different applications.

The thermal behavior of polyaniline-DVB gels obtained by chemical polymerization of aniline in the presence of DVB gels using ammonium peroxodisulphat as oxidant agent, in different acid media, was investigated and correlated with the parameters of synthesis.

EXPERIMENTAL

Polyaniline-DVB Synthesis

Aniline freshly distilled and kept at −4°C, polystiren-2(-7)% divinyl benzene gels (DVB) – a strong base anion exchanger type I trimetil-ammonium Dowex 1 Fluka AG, phenylphosphinic acid (Aldrich) (APP), hydrocloric acid and ammonium peroxodisulphat (Merck) were used. Polyaniline-DVB doped APP (Pani-DVB-APP) was obtained by oxidation of aniline with ammonium peroxodisulphate, in the presence of DVB gels, in dilute APP aqueous solutions. The syntheses procedure is the same for all samples: first the aniline salt is formed by the dropwise addition of aniline to APP aqueous solutions, under continuous stirring and precooling, then the DVB gels were added under continuous stirring and precooling and finally an aqueous solution of ammonium peroxodisulphate was added drop wise under stirring for about 30 min. Synthesis were performed at aniline/oxidant molar ratio: 1, 1.33, 2, 4, aniline/acid: 1/1; 1/2 and aniline /DVB weight ratio 0.1 and 0.2. The reaction was carried out at 0°C and 25°C. At about 10 hours after the adding of oxidant, the stirring is stopped and the reaction mixture was filtered and washed several times with a 1 M APP. In order to remove the resulting polyaniline homopolymer, the resulting precipitate was extracted for four hours with N-methyl pyrrolidone (NMP) in Soxhlet equipment. The resulting Pani-DVB was dry in vacuum for several hours. In order to compare the thermal stability and conductivity of resulting Pani-DVB, the Pani was prepared in the same condition without DVB gels, both in hydrocloric acid and APP.

Characterization

The resulting polymer samples were characterized by IR spectroscopy, electrical conductivity measurements and thermal analysis. The inherent viscosity of Pani doped with hydrochloric and phenyphosphinic acid was determined using solution 0, 1% polymer in 97% sulphuric acid, with Ubbelohde viscosimeter.

The thermal analysis of samples was performed with TG 209 and DSC 204 (Netzsch) in nitrogen atmosphere with a heat rate of 25 K/min in range 20°C to 990°C, and allowed to obtain the thermal stability.

The conductivity is measured by two-point method, at ambient temperature. The results represents the average of 4 measurements.

RESULTS AND DISCUSSION

The IR spectra recorded with Specord 75 in KBr pellets indicate the presence of the characteristic peaks of Pani in all samples [1,6]. The IR spectrum of polyaniline base show characteristic peak absorption due to: vibration of Ar-N bond (1297 cm^{-1} şi 1380 cm^{-1}) vibration of N-H bond (3300 cm^{-1}); vibration of C = N bond (1587 cm^{-1}); vibration of $NH_2{}^+$ group (2250–2700 cm^{-1}, 2000 cm^{-1}, 1575–1600 cm^{-1}) vibration of $-NH^+$ group (2250–2700 cm^{-1}).

Due to the proton doping process, the corresponding peak appears for protonated aminic group ($-NH_2-^+$). The intensity of this peaks increased with the concentration of acid.

The electrical conductivity of Pani doped with HCl (Pani-HCl). Pani doped with APP (Pani-APP) and Pani–DVB doped with APP (Pani-DVB-APP) as function of synthesis condition were illustrated in Figures 1 and 2.

It is known that the molar mass of Pani has almost no effect on the electrical conductivity [1,10]. Such behavior has been theoretically predicted

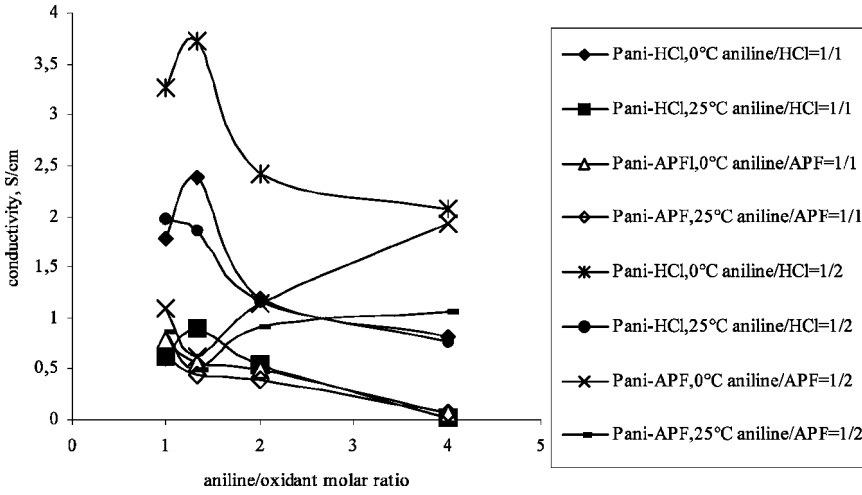

FIGURE 1 Variation of electrical conductivity as a function of monomer/oxidant ratio for Pani-HA.

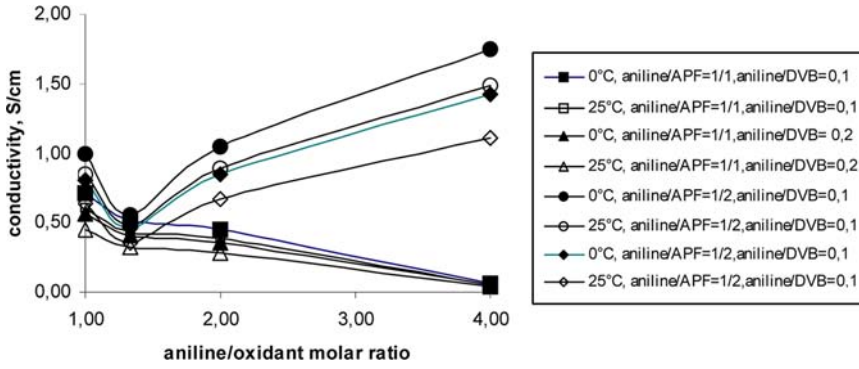

FIGURE 2 Variation of electrical conductivity of Pani-DVB doped with APP as a function of monomer/oxidant ratio.

for the cases when the charges hopping from one polymer chain to another are much faster in comparison with the life time of the charge on the chain, i.e. when interchain transport occurs more readily than the intrachain one. However, the conductivity show a small variation with the acid concentration in reaction media aniline/oxidant molar ratio, nature of acid, and with the reaction temperature, the conductivity shows a small tendency to increases with increase of the acid concentration and decrease with the reaction temperature [11]. The conductivity increase with the concentration of protons in the aqueous acid media due to the formation of the doped polymer, which is less soluble than the undoped form and due to the existence of a remanent quantity of acid retained by the polymer chain [1,10,12]. Increasing the amount of oxidant in the reaction medium, the concentration of formed radical cations forms will be higher and the resulting polymer chain will be shorter; the inherent viscosity and conductivity will be a little lower [12] (Fig. 3).

Conductivity of polyanilines obtained in APP was lower (compared with the polyaniline prepared in hydrochloric acid), due to the formation of low molar mass and nature of dopant.

Conductivity decreases with the increase of temperature reaction because the reaction will be thermodynamically favored if Gibbs free energy (ΔG) are more negative.

The conductivity of obtained Pani-DVB depends on synthesis parameters, especially on the variation of oxidant concentration, and was lower than for Pani synthesis in APP (Fig. 2).

The thermal stability of polymers was studied by TGA; the TGA curves for some samples were presented in Figure 4 and TGA data for all samples were presented in Table 1.

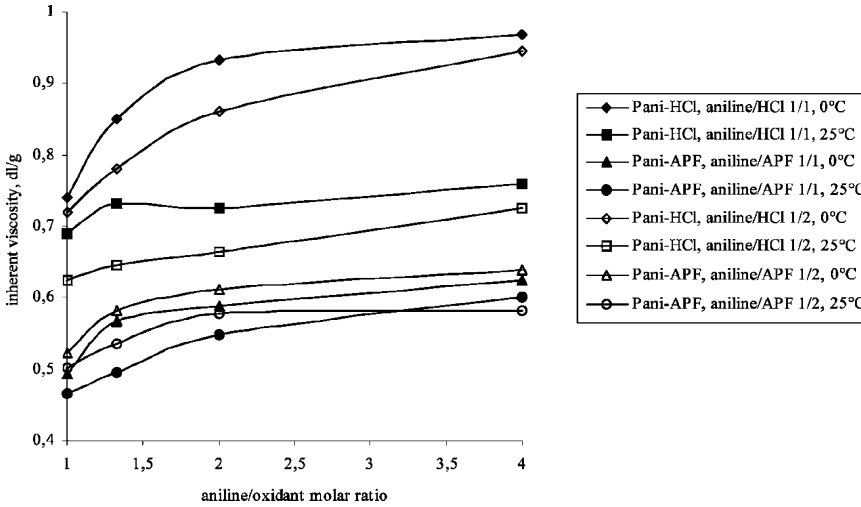

FIGURE 3 Variation of inherent viscosity of Pani doped with HCl and APP as a function of monomer/oxidant ratio.

In general the thermal behavior of Pani samples show a characteristic "three step" weight loss, as can be seen from DSC curve illustrated in Figure 5.

During heating till 150°C the weight losses are due to residual water presented in all Pani samples, and situated between 5.98% for Pani-HCl

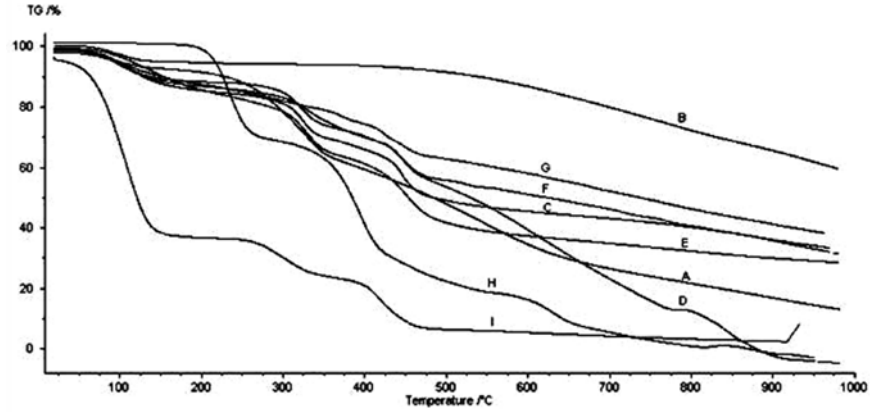

FIGURE 4 Thermogravimetric curve for A: Pani–HCl sample 2; B: Pani–HCl sample 1; C: Pani-APP sample 10, D: Pani- DVB-APP sample 25; E: Pani-APP sample 14, F: Pani- DVB- APP sample 26; G: Pani-DVB-APP sample 31; H:APP; G: DVB.(no sample from table 1).

TABLE 1 Termogravimetric Data for Polyaniline Samples

	Synthesis conditions				Temperature, 0°C			Temperature, 25°C		
Sample	HA	A/O	A/HA	A/DVB	$\triangle m_{(150oC)}$*%	$T_{\Delta m=50\%}$,**°C	$T_{d,}$***°C	$\Delta m_{(150°C)}$*%	$T^{**}_{\Delta m=50\%}$°C	T_d***°C
1		1			5.91	497.2	331.8	6.83	421.3	287.1
2		1.33			5.11	988.1	342.2	6.95	687.6	291.7
3		2	1/1		5.91	877.3	349.7	6.81	506.1	290.8
4	HCI	4		—	5.98	687.5	351.1	6.22	489.8	297.3
5		1			5.16	485.6	259.1	11.57	418.6	243.2
6		1.33			5.21	596.1	278.3	9.12	581.2	241.5
7		2	1/2		5.45	502.8	277.4	8.76	511.5	240.6
8		4			5.73	507.5	298.3	8.81	476.1	236.9
9		1			8.91	487.3	327.4, 404.8	10.11	471.4	317.3, 401.9
10		1.33			11.05	489.2	327.4, 445.8	9.78	470.3	320.6, 405.7
11		2	1/1		6.25	491.6	331.5, 409.0	11.14	474.6	327.1, 417.6
12	APP	4		—	7.12	487.7	342.1, 413.5	10.24	478.5	330.4, 421.1
13		1			9.45	461.8	302.2, 454.3	10.58	472.4	297.2, 419.8
14		1.33			8.15	477.3	329.9, 454.6	9.92	473.1	301.5, 415.6
15		2	1/2		8.12	479.4	322.5, 410.8	9.19	474.0	318.2, 421.3
16		4			8.26	477.5	325.4, 413.9	9.78	479.1	311.7, 431.0

17		1			10.58	454.1	330.2, 445.5	11.98	441.4	320.1, 430.2
18		1.33			12.13	532.3	333.6, 454.6	12.68	519.6	330.5, 432.7
19		2			9.78	487.2	348.4, 468.0	11.02	474.5	329.8, 452.0
20	APP	4	1/1	0.1	8.15	489.6	337.2, 456.8	10.86	476.9	330.1, 458.6
21		1			9.56	462.0	320.1, 421.6	11.28	449.3	309.4, 402.6
22		1.33			15.11	569.5	341.2, 456.7	18.21	556.8	332.3, 447.6
23		2	1/2		12.31	512.3	345.0, 432.7	17.26	499.6	331.9, 425.1
24		4			13.02	509.2	339.4, 447.4	16.89	496.5	318.5, 436.2
25		1			10.58	498.3	330.2, 445.5	10.08	425,7	294.9, 425.1
26		1.33			9.47	478.5	325.1, 448.0	12.13	503,9	291.3, 438.1
27		2	1/1		10.03	481.6	314.8, 423.9	12.45	458,8	301.2 412.5
28	APP	4		0.2	11.12	493.8	309.8, 431.2	11.78	461,2	294.1, 416.8
29		1			9.89	479.7	315.0, 432.7	10.91	433,6	301.0, 423.1
30		1.33			10.11	463.0	310.6, 435.9	10.23	541,1	296.4, 425.6
31		2	1/2		11.03	454.3	316.4, 440.1	11.15	483,9	301.5, 412.9
32		4			10.23	467.6	328.3, 426.8	16.84	480,8	298.2, 425.1

* $\Delta m_{(150\%C)}$ represents the weight loss corresponding to the temperature of 150°C,%

** $T_{\Delta m=50\%}$, -Temperature corresponding to the weight loss equal to 50%,°C

*** Temperature corresponding to the maximum decomposition rate (inflexion point),°C

A-aniline, O-oxidant, HA-acid

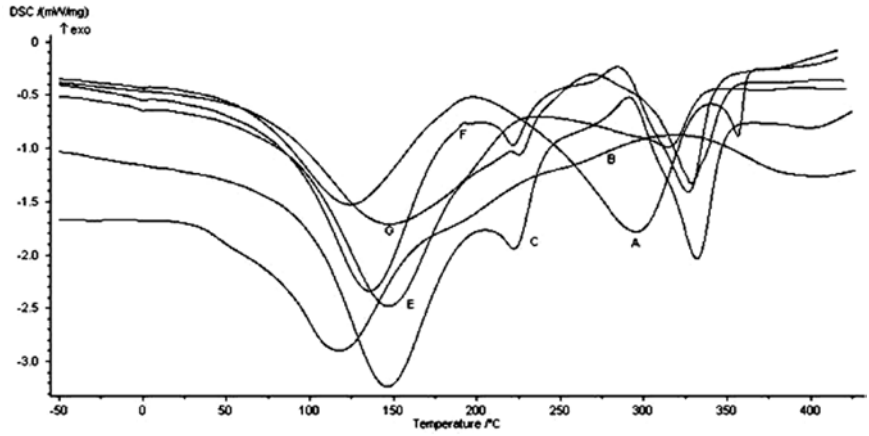

FIGURE 5 DSC curves for for A: Pani–HCl sample 2; B: Pani–HCl sample 1; C: Pani-APP sample 10; E: Pani-APP sample 14, F: Pani- DVB- APP sample 26; G: Pani-DVB-APP sample 31; H:APP; G: DVB. (no sample from table 1)

(Fig. 4 curve A, B), 9.45% for Pani-APP (Fig. 4 curve C, E) and maximum15.11% for Pani-DVB doped APP (Fig. 4 curve D, F, G).

This residual water cannot be attributed to be humidity because all the samples were dried before TGA measurements. Water molecules are able to occupy sites instead of dopant in polyaniline, process also observed by some authors [4,7,11,13–15]. The high value for remanent water presented in all samples Pani-DVB may by attributed partially to the lose of water from DVB gels. The DVB gels (Fig. 4 curve I) presented the major weight loss 55,06% in domain of temperature from 50°C and 150°C associated with the loss of water and Cl^- existing in the structure with a maximum decomposition rate at 109,7°C. From 100°C to 150°C the Pani samples loss weight due to the of dopant HCl in Pani-HCl samples [11–15], and for Pani-DVB due to the decomposition of DVB gels. The polymer samples shows weight loss between 150°C and 990°C which are related to the degradation of dopant, polymer main chain and depends on nature and quantity of dopant, aniline/acid, aniline/oxidant molar ratio and presence of DVB gels.

The weight loss in the temperature domain 150°C to 400°C was situated between 1,09 and 33,24% for Pani samples obtained in HCl and doped Cl^- and are related to dopant loss and degradation of polyaniline chain. With the increase of oxidant, acid concentration and temperature the weight loss increase, due to the increase of dopant content and formation of short polymer chain. The Pani samples obtained in APP and doped with APP present a weight loss in the domain situated between 18,21 and

26,79% and are related to the dopant and Pani degradation. In this domain the Pani-APP sample presented two-inflexion point corresponding to the decomposition of dopant. The APP (Fig. 3 curve H) remains stable till 200°C, after that the APP started to decompose gradually till 410°C with two maximum decomposition rate at 239,0°C and 401,5°C and with the weight loss in this domain 60,86%. The weight loss in this domain (150°C to 400°C) increase with the oxidant and acid concentration and temperature of synthesis. The maximum weight loss (26,79%) was observed for Pani-APP obtained at aniline/oxidant molar ratio = 1, aniline/APP = 1/2 and 25°C and the minimum loss (18,21%) was observed for Pani-APP obtained at aniline/oxidant molar ratio = 1.33, aniline/APP = 1/1 and 0°C. The Pani-DVB doped APP samples present weight loss between 18,11% and 22,17%, a little lower than Pani-APP and two important inflexions corresponding to maximum decomposition rate at around 300°C and 400–450°C. In domain of temperature 150°C–270°C the DVB gels remains stable and then started to decompose slowly till 500°C, with two maximum decomposition rates at 279,5°C and 413,8°C. For the DVB gels the weight loss in the domain of temperature 150°C–500°C was 17.15%.

The weight loss 50% ($\Delta m = 50\%$) (Table 1) for the Pani –HCl samples obtained at aniline/acid ratio 1/1, aniline/oxidant molar ratio1.33 and 2, performs at higher temperatures ($T_{\Delta m=50\%}$) 988,1°C, respectively 877,1°C. This is in accordance with the inherent viscosity value which indicate a higher molar mass. It was observed an increase of temperature were the decomposition process took place with the increase of aniline/oxidant molar ratio, due to the increase of molar mass, as can be seen from inherent viscosity (Fig. 3). At higher concentration of oxidant with the increase of synthesis temperature, the control of aniline/oxidant molar ratio upon thermal stability decrease. For the sample synthesized at a higher temperature, 25°C, the weight loss 50% ($\Delta m = 50\%$) appears at a lower temperature comparative with the sample synthesized at 0°C; the differences were situated around at 200°C–300°C. The temperature assigned to maximum decomposition rate in this case, is situated around 230°C–300°C, and decrease comparative with the sample obtained at 0°C, due to the decrease of molar mass.

In general, both, the decomposition temperature and weight loss were affected by the molar mass and decrease with the decrease of molar mass. For the Pani synthesized in APP the thermal stability decrease comparative with the Pani obtained in HCl, for example for Pani-HCl obtained at aniline/acid ratio 1/1, aniline/oxidant molar ratio 1.33 and 2 the temperature corresponding to $\Delta m = 50\%$ was 988.1°C, and for Pani-APP was 489,2°C. Furthermore, the influence of aniline/oxidant molar ratio and synthesis temperature upon thermal stability wasn't so important.

The weight loss of Pani-DVB-APP is continuous starting from 80°C, due to the decomposition of DVB. The temperatures where decomposition rate is maximum is closely to the sample synthesized in APP without DVB.

All Pani samples indicate the first endothermic transition at ca. 130°C as can be seen in Figure 5. These peaks correspond to the evaporation of water trapped inside the polymer or bonded to the polymer chain. The second and the third peaks correspond to the endothermic transitions due to the loss of acid dopant (HCl and APP) respectively to the decomposition of polymer chain starting around 400°C.

Comparing TG data with DSC data, only for the Pani-APP and Pani-DVB-APP samples obtained at 0°C, it was noticed the appearance of an additional peak at about 240°C (Fig. 5 curve C, E, F, G) which do not corresponds to the weight loss recorded on termograms.

The presence of this peak can be assigned to the interaction of Pani and dopant, in this case APP, because in the Pani-HCl samples this additional peak was no observed. The weight loss observed on termograms, corresponding to the maximum decomposition rate overlays with endothermic peaks from DSC which correspond similarly to the maximum decomposition rate.

CONCLUSIONS

The electrical conductivity of Pani–DVB doped with APP (Pani-DVB-APP) were lower than Pani doped with HCl (Pani-HCl) and Pani doped with APP (Pani-APP).

From thermogravimetric data the following conclusions can be drawn.

For Pani synthesized in HCl, with the increase of the aniline/oxidant molar ratio, the temperature where the decomposition process occurs became higher. At higher concentration of oxidant with the increase of temperature at which synthesis was performed, the control of aniline/oxidant ratio upon thermal stability decrease. For the sample synthesized at a higher temperature, 25°C, the weight loss corresponding to 50% ($\Delta m = 50\%$) appears at a lower temperature compared with the sample synthesized at 0°C. Pani obtained in HCl at aniline/acid ratio 1/1, aniline/oxidant molar ratio1.33 and 2 at 0°C, presents the higher thermal stability.

The Pani samples synthesized in APP and both in APP and DVB gels present a thermal stability lower comparative with the Pani obtained in HCl.

The influence of aniline/oxidant molar ratio and synthesis temperature upon thermal stability of Pani synthesized in APP was not so significant.

The continuous weight loss starting from 80°C, of Pani-DVB-APP samples are due to the decomposition of DVB gels.

In general, the thermal behavior of all Pani samples shows a characteristic "three step" weight loss, as can be seen from DSC. Only for the Pani-APP and Pani-DVB-APP samples obtained at 0°C, an additional peak appears at about 240°C which no longer corresponds to the weight loss recorded on termograms, and was assigned to the interaction of Pani and acid dopant, in this case APP.

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