Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 559–564

THERMOGRAVIMETRIC STUDY ABOUT PVC-POLYANILINE BLENDS

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(Received April 15, 2002)

Abstract

By dissolution of PVC and polyaniline in dimethylformamide, a series of blends PVC-polyaniline were produced which were studied by scanning electron microscopy and thermogravimetry. Special attention is focused on the kinetic study of the thermal degradation steps by using non-isothermal thermogravimetric data. The results show that the thermal stability of the synthesized blend is decreased as the total amount of polyaniline is enhanced. Furthermore, the Brønsted acid doped blend is more stable than the corresponding undoped one. PVC and the PVC-polyaniline blends exhibit two mass loss steps which activation energy values are in the range from 176 to 283 kJ mol^{-1} and 306 to 322 kJ mol^{-1}, respectively.

Keywords: blends, kinetic, polyaniline, poly(vinylchloride), thermogravimetry

Introduction

Polyaniline (Pani) is a concuting polymer [1] which can be synthesized by chemical or electrochemical routes [2], exhibiting considerable chemical and mechanical stability [1]. Polyaniline has been employed for the synthesis of new materials, such as intercalation compounds, pH measurements devices and artificial muscles [3–5]. It has also been shown that adsorption of polyaniline on oxides surfaces can exerts remarkable effects on the redox properties [6, 7] and thermal stability [8] of the oxides. On the other hand, poly(vinylchloride), PVC, is a polymer used for wire and cable insulation, for example [9].

The synthesis of polymer blends has been sucessfully used to produce new and improved materials, which exhibits simultaneously properties of the isolated polymers involved [9]. On the other hand, the thermogravimetric study of the degradation of solids, with special attention on the non-isothermal kinetic study, has been recently

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1418–2874/2002/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

used for several applications, such as the study of the metal-aminoacid interactions [10] and the correlation between thermogravimetric and solution calorimetry data for lamellar phosphates [11].

The aim of this publication is to report the synthesis and thermogravimetric study of PVC-polyaniline blends, performing a kinetic study of the degradation processes.

Experimental

The PVC samples were from Aldrich Chemical Co. Polyaniline was chemically [6–8] obtained from an initial homogeneous solution formed by 0.5 mol dm^{-3} of bidistilled aniline (Aldrich) in 1.0 mol dm^{-3} HCl (Aldrich). In the next step, to this solution, maintained at 278 K, was added dropwise 100 cm^3 of a 0.8 mol dm^{-3} $(NH_4)_2S_2O_8$ solution during 2 h. After the complete addition of the oxidant solution, the mixture was stirred for 10 h, to allow completion of the polymerization. The obtained polymer was washed several times with distilled water and acetonitrile, to remove oligomers as well as other possible secondary products. The final product was then treated with a 1.0 mol dm^{-3} NH_4OH solution to promote deprotonation.

The PVC-Pani blends were synthesized by dissolution of stoichiometric amounts of PVC and Pani in dimethylformamide (dmf). The obtained solutions were mixed and the solvent evaporated at room temperature. The obtained films were exhaustively washed with bidistilled water and dried at room temperature for 48 h. Blends with three different mass(PVC)/mass(Pani) ratios were synthesized: 2:1 (PVCPani1), 4:1 (PVCPani2) and 17:1 (PVCPani3). The blend PVCPani2 was also studied after doping [1] with HCl, producing the blend PVCPaniDOP.

FTIR spectra were obtained in a Bomem apparatus, using pressed KBr pellets with 25 scans for each run, and 4 cm^{-1} of resolution. The thermogravimetric (TG) curves were obtained in a Shimadzu TGA-50, under argon atmosphere with a heating rate of 5°C min^{-1}. The SEM micrographs were obtained by using a Jeol microscope, model JSM T-300, with an accelerating voltage of 15 kV.

Results and discussion

The obtained infrared data, confirms that the synthesized Pani is in the emeraldine form [1]. The spectra of the blends exhibits bands from both, PVC and Pani, as expected. None new bands, band shifts or variations in the relative absorbance were observed, suggesting that there are not chemical interactions between the components of the blend.

The SEM micrograph obtained for the PVCPani2 blend is shown in Fig. 1. As can be observed in Fig. 1, the synthesized films shown a porous morphology. The mapping images (EDS) obtained for all films (not shown) confirms the homogeneity of the synthesized blends, since the chlorine atoms (from PVC) are homogeneously distributed on all samples.

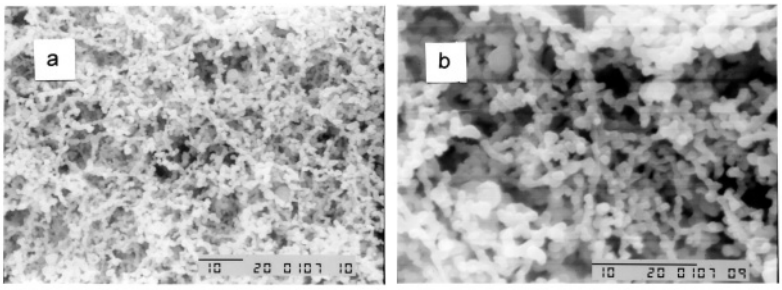

Fig. 1 SEM micrographs for PVCPani2 a – (1500×) and b – (3500×). The scale bar is in micrometers

The thermogravimetric and derivative curves for PVC are shown in Fig. 2b. For comparison, the thermogravimetric curve for Pani is shown in Fig. 2a. The first mass loss step for PVC (60%), is associated with the release of HCl [9, 12]: $-[CH_2CHCl]- = -[CH{=}CH]- + HCl$, with the second mass loss been attributed to the thermal degradation of the $-[CH{=}CH]-$ polymer, giving a final residue of 10%.

The thermogravimetric curves for PVC and the synthesized blends are shown in Fig. 3. Based on these curves, the following sequence of thermal stabilities can be pointed out: PVC (a)>PVCPani3 (b)>PVCPaniDOP (e), PVCPani2 (d)>

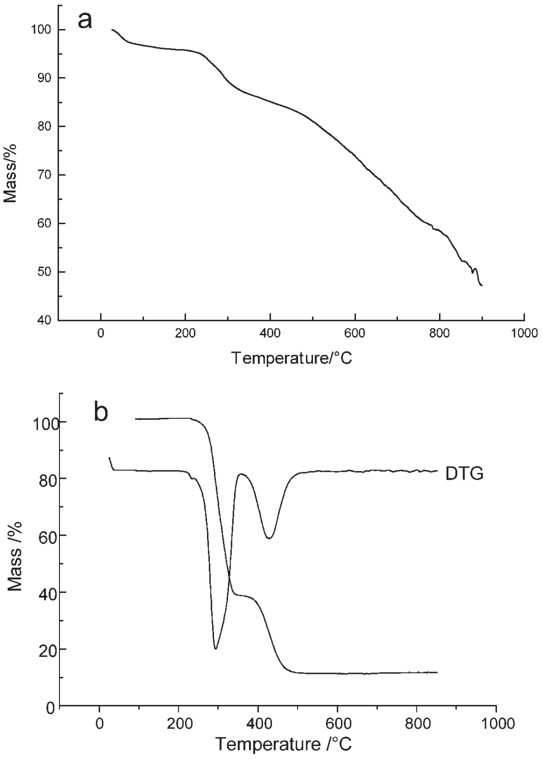

Fig. 2 Thermogravimetric curve for a – Pani and thermogravimetric and derivative curves for b – PVC

PVCPani1 (c). So, it is verified that the blends with a higher amount of PVC are those most stable. Furthermore, comparing the blends PVCPani2 and PVCPaniDOP, can be proved that the doping process increases the thermal stability of the blend. Taking into account that the doping process also increases by several times the conducting properties of Pani [1], it can be stated that blends with higher conductivity and thermal stability can be synthesized by doping process.

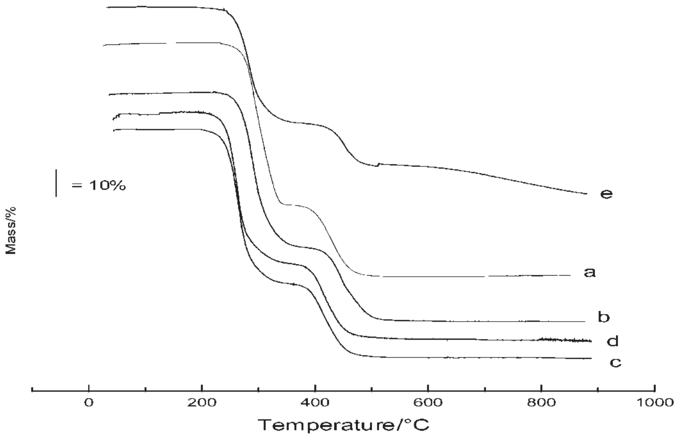

Fig. 3 Thermogravimetric curves for: a – PVC, b – PVCPani3, c – PVCPani1, d – PVCPani2 and e – PVCPaniDOP

Since the product of the first thermal degradation step is HCl [9, 12] it could be supposed that the increased thermal stability observed for the doped sample is a consequence of the presence of HCl in the blend, changing the chemical equilibrium. It is also possible suppose that by controling the degree of doping one could control the thermal stability of the blend. The obtained results are in good agreement with those observed for Brønsted acid doped Pani samples [13, 14] for which the increase of the thermal stability depends on the nature of the doping agent, with the doping species promoting a stabilization of the macromolecule structure.

The kinetic parameters calculated through the Coats–Redfern method [15] by using the non-isothermal thermogravimetric data are summarized in Table 1. As can be observed, for the three non-doped blends, the activation energy values for the two thermal degradation steps increase with the increased amount of PVC: E_a (3)>E_a (2)>E_a (1). On the other hand, for the PVCPani3 blend, the activation energy values are higher than for PVC.

The blend PVCPaniDOP exhibits the lower activation energy value for the first thermal degradation step, despite the fact that this is not the less stable blend. So, it can be concluded that there is not a so straightforward relationship between activation energy for the thermal degradation step and thermal stability. On the other hand, the activation energy value for the second mass loss step is higher for PVCPaniDOP than that calculated for PVCPani1 and PVCPani2. This fact is in agreement with the observation that, despite the elimination of the HCl molecules in the range 230–350°C be almost complete, their influence on the thermal degradation process is observed at higher temperatures for polyaniline [14]. The non-complete agreement between the thermal stability sequence and the activation energy values for the first thermal degradation step for the studied blends, could be attributed to factors such as the preparation conditions of the samples and the diffusion of the gaseous products through the solid residues [16].

Table 1 Kinetic parameters calculated for PVC and its blends with polyaniline by using non-isothermal thermogravimetric data, through Coats–Redfern method. E_a is the activation energy, *n* is the other of reaction, *A* is the frequency or pre-exponential factor, *r* is the coefficient of correlation and Δt is the temperature range considered for calculations

Sample	Step	E_a/kJ mol^{-1}	*n*	*A*	*r*	Δt/°C
PVC	1	273	3.9	$1.1 \cdot 10^{25}$	0.999	281–304
	2	318	2.7	$4.9 \cdot 10^{23}$	0.998	403–450
PVCPani1	1	235	2.4	$6.8 \cdot 10^{22}$	0.999	246–286
	2	266	2.2	$8.3 \cdot 10^{19}$	0.999	400–447
PVCPani2	1	247	2.3	$1.5 \cdot 10^{24}$	0.999	240–280
	2	306	2.5	$9.4 \cdot 10^{22}$	0.999	398–445
PVCPani3	1	283	3.3	$2.5 \cdot 10^{26}$	0.999	272–320
	2	322	2.9	$1.5 \cdot 10^{23}$	0.999	429–480
PVCPaniDOP	1	176	1.5	$2.5 \cdot 10^{16}$	0.999	259–292
	2	310	1.8	$1.6 \cdot 10^{22}$	0.999	432–467

Taking into account that the second mass loss step is associated with the thermal degradation of the residue –[CH=CH]–, it is possible to understand the higher activation energy values for the second steps in comparison with the first ones, since in the first step are observed [17] the rupture of C–H (413 kJ mol^{-1}) and C–Cl (338 kJ mol^{-1}) bonds, with the formation of H–Cl (–431 kJ mol^{-1}) bonds, and also the incorporation of HCl to the blend (doping) which is also an exothermic process. On the other hand, for the second thermal degradation process the rupture of C=C (612 kJ mol^{-1}) [17] bonds it is observed, with none exothermic process to compensate this endothermic value. So, could be supposed that in the thermal degradation of PVC-Pani blends, the kinetic parameter (activation energy) is dependent on the thermodynamic one (bond dissociation enthalpy).

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