Thermal stability of polyaniline

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Summary

Among conducting polymers with metallic characteristics, polyaniline (PANI) is claimed to have one of the highest environmental stability. From an industrial point of view it would be useful to be able to thermally process this material into useful products using conventional techniques such as extrusion, stretching, rolling, etc., which generally are carried out at elevated temperatures. Somewhat surprisingly, relatively few studies have addressed the thermal stability of PANI, in particular that of the non-protonated emeraldine base form. Therefore, a study of the thermal properties was performed to examine the thermal stability of this material and to identify the optimum processing and maximum application temperatures.

Introduction

It has been argued that emeraldine base shows a high heat stability, with thermal decomposition commencing at a temperature as high as 400°C (1-3). It has also been reported that the protonated polyaniline is significantly less stable than the emeraldine base form, and that the stability of the former varies with the protonic acid (1,2).

Several studies have been devoted to the time-temperature dependence of the electrical conductivity of PANI in both the protonated and non-protonated state (1,4-6). It has been reported that the temperature, particular protonic acids, and the solvents used for preparation of, for example, films and fibers can significantly affect the electrical conductivity (7,8). All studies indicate that protonated PANI displays a slow decrease in electrical conductivity when treated at temperatures below 200°C. At temperatures exceeding 200°C, the electrical conductivity decreases very rapidly and the material eventually becomes an insulator (1,6).

In order to gain a better understanding of the origin and kinetics of conductivity degradation of protonated polyaniline, the effect has also been analyzed through structural studies (9-12). These studies, which were conducted on materials treated in various atmospheres, indicate that conductivity decay is associated with different chemical degradation mechanisms such as oxidation, chemical cross-linking and deprotonation. In a morphology-based attempt to account for the observed effects, virgin, electrically conductive PANI has been depicted as a heterogeneous structure in which highly conducting crystalline "islands" are separated by less conducting, amorphous parts (13). The degradation of conductivity has been explained in terms of the size of conducting "islands", which is argued to decrease with aging time, in parallel with broadening of intergrain barriers (12-14).

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In order to study the reversibility of the thermal annealing process, heat-treated acid-treated polymer samples have been reprotonated with the same protonating agent. It has been reported that the conductivity of heat-treated polymer increased significantly upon reprotonation, but never reached that of virgin material (10,15,16). This incomplete recovery of the conductivity of "aged" PANI samples is unsatisfactorily explained by the above mechanism. Therefore, there appear to be other processes involved during thermal aging, which evidently requires development of further knowledge.

The problem addressed here is the stability of polyaniline in its base form. Surprisingly little is known about thermal behavior of this interesting form of PANI, which is a most important intermediate and end-product as, e.g., in electrochromic applications. Here, we present a comprehensive study of thermally treated polyaniline, which allowed us to develop an understanding of stability of this unique polymer.

Experimental

Chemically synthesized polyaniline of the emeraldine base (EB) form (Neste Chemicals) was used for the aging experiments. The polymer in powder form was heated in air to different temperatures ranging from 50°C to 200°C during different periods of time ranging from 10 min to 24 h.

The heated samples were dissolved in concentrated H_2SO_4 to prepare 1 w/w % solutions. The solutions were then centrifuged at 4000 rpm for 30 min and the liquid phase was carefully removed by a Pasteur pipette. Only those powders, which virtually completely dissolved under the above conditions were analyzed by viscosity measurements. The inherent viscosities of these samples were determined at 25°C in 0.1 w/w % solutions in concentrated sulfuric acid using an Ubbelohde viscometer; average molecular weights were calculated according to the method in reference (17). Fourier-Transformed Infrared spectra (FTIR) of air aged samples were recorded on a Bruker IFS66v spectrometer in the range of 400-4000 cm^{-1}. Pressed pellets were prepared of the powder samples ground with KBr (Fluka IR grade) for this purpose. Thermogravimetric analysis (TGA) was performed using a Netzsch TGA209 instrument, at a heating rate of 20°C/min, under nitrogen, from 25°C to 500°C.

Further, the different, aged EB powder samples were mixed at room temperature with (±)-10-camphersulfonic acid (CSA, Aldrich) in a molar ratio of 0.5:1 (CSA to phenyl-N repeat unit of PANI). The resulting mixture was subsequently mixed with purified formic acid using an ultrasonic bath for 24 h. Viscous dark-green solutions, thus obtained were cast on cleaned glass substrates and dried at room temperature for 24 h to yield uniform, defect-free emereldine salt films. All films used in subsequent experiments were vacuum dried overnight to minimize the effect of moisture on conductivity measurements. Four-point in-line conductivities were determined using a Keithley 237 digital multimeter. The sample thickness was measured by a Tencor (alpha step 200) profilometer.

Results and Discussion

Elementary analysis of the as-received base form of polyaniline yielded the following results: C: 74.13%; H: 5.39%; N: 14.26% and O: 6.52%. The customary chemical formula of emeraldine base gives theoretical values of C: 79.56 %; H: 4.97 %; and N:

15.47%. After heat treatment, elementary analysis indicates less oxygen, which we attribute to the loss of approximately 10.8 mol% H_2O per repeat unit.

Thermogravimetric analysis under nitrogen atmosphere of PANI-EB shows two major weight loss processes: one (about 3.5 % w/w) until 200°C and an additional at starting around 400°C as shown in Figure 1. The weight loss at 400°C is attributed to structural decomposition of the polymer, which will not be discussed in this paper. Here we focus on the thermal processes that occur at the lower temperatures. The weight loss commencing at around 100°C is assigned to the loss of initially present water molecules. From the data in Figure 1, we conclude that some water molecules are extremely strongly bound to the polymer.

DSC of PANI-EB powder samples does not exhibit any pronounced specific thermal transitions below 200°C. This observation also seems to indicate that PANI is thermally stable up to 200°C, with little, if any, weight loss other than H_2O.

In order to more quantitatively evaluate the thermal processes at and below 200°C, thermal aging experiments were performed in air at various temperatures for different time periods. The heat-treated powders were subsequently analyzed in terms of, among other things, their solubility.

Previous studies have shown that carefully synthesized PANI base can be completely dissolved up to polymer concentrations of more than 20 w/w% in several concentrated strong protonic acids such as H_2SO_4, CH_3SO_3H and CF_3SO_3H (18). Here, we observed that the solubility of EB powder dramatically decreased, when the material is thermally treated at elevated temperatures. In fact, we found that PANI no longer dissolves in any solvent after treatment at temperatures exceeding 125°C (Table 1). Clearly, heat treatment of PANI-EB in air leads to cross-linking of the polymer.
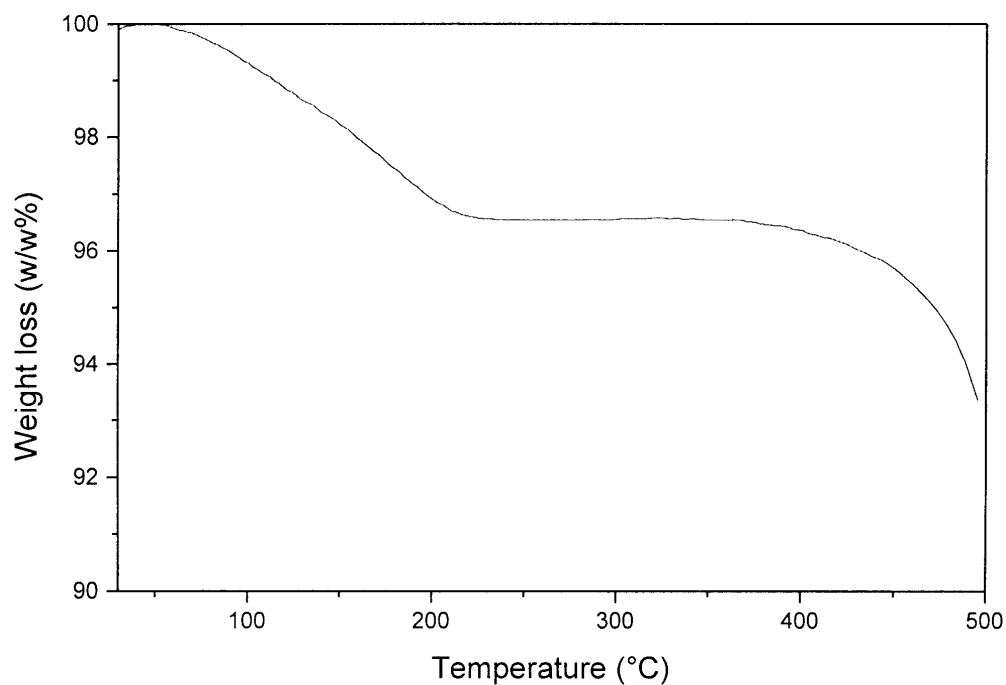

Figure 1   Thermogram of emeraldine base form of polyaniline.

Table 1   Solubility at room temperature in concentrated H_2SO_4 of PANI-EB heat-treated at different temperatures during various periods of time.

Heating Temp. / Heating Time	50°C	75°C	100°C	125°C	150°C	175°C	200°C
10 min	--	--	--	--	*	↑	↑
30 min	--	--	--	--	*		
1 h	--	--	--	--	*	Gel	Completely insoluble
2 h	--	--	--	--	Gel		
5 h	--	--	--	--			
24 h	--	--	--	*	↓	↓	↓

--   completely dissolved
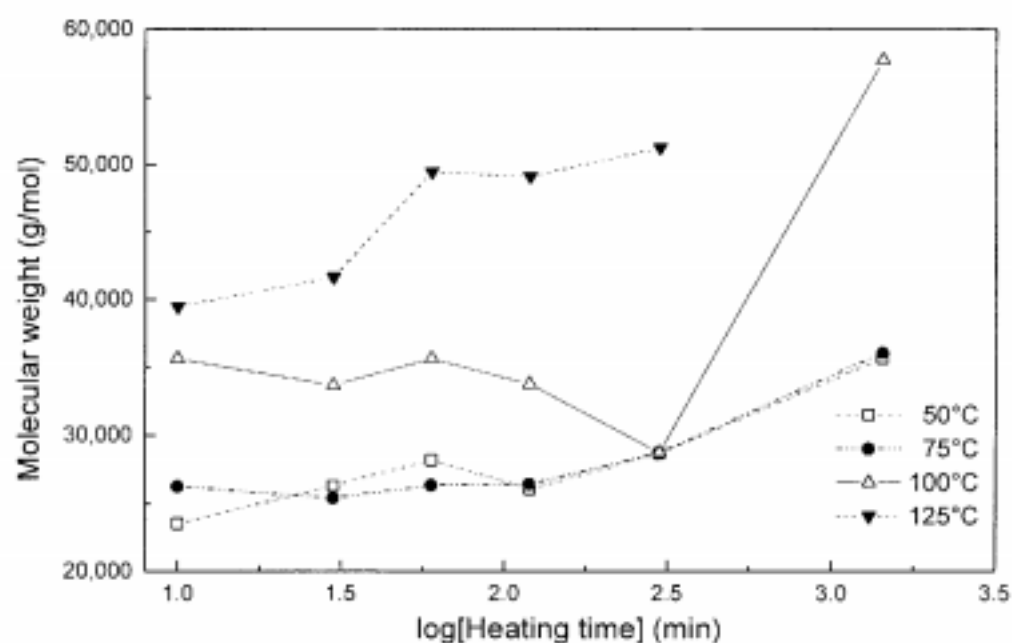*   partially dissolved
Gel; forms swollen gel

Figure 2   Variation of molecular weight of PANI-EB as a function of heating time.

The aged polymer samples also were analyzed by inherent viscosity measurements. For this purpose, the viscosity of the soluble fraction of the polymer in concentrated sulfuric acid was used as an indicator of its molecular weight.

Figure 2 shows the molecular weight variation of samples aged at different temperatures starting at time periods of 10 min. Non-aged PANI-EB exhibited an inherent viscosity about 0.72 dl/g at 25°C which corresponds to a viscosity average molecular weight of 28,000 g/mol (17). The molecular weights of aged samples were observed to strongly depend on both aging temperature and time. It is seen in Figure 2 that the molecular weight increased with increasing heating time as well as temperature. These observations are consistent with our conclusion that during heating the material cross-links and that the degree of cross-linking increases with heat treatment.

Chemical changes associated with the observed reduced solubility were investigated by Fourier-transform infrared spectroscopy (FTIR) of the aged samples. The major peaks and their positions were found to remain essentially the same in all spectra. However, some of the absorption peaks were less intense for powders aged in air above 150°C for 24 hours, and almost absent for those treated for 24 hours at 250°C.

Figure 3 shows various spectra of PANI after different heat treatments. Both aged and non-aged powder spectra displayed five major absorption peaks. The peak assignments of PANI-EB are summarized in Table 2. The vibrational bands characteristic of the polymer backbone (in the base form) at 1587, 1494, 1306, 1164 and 830 cm^{-1} were observed to be shifted to 1600, 1504, 1298, 1173, and 823 cm^{-1} after heating at 250°C. The bands at ~1590 and ~1494 cm^{-1} were still prominent in the IR absorption of all samples after heat treatment. The spectra appear to indicate that the intensity ratio of these two peaks decreased as temperature of heat treatment increased.
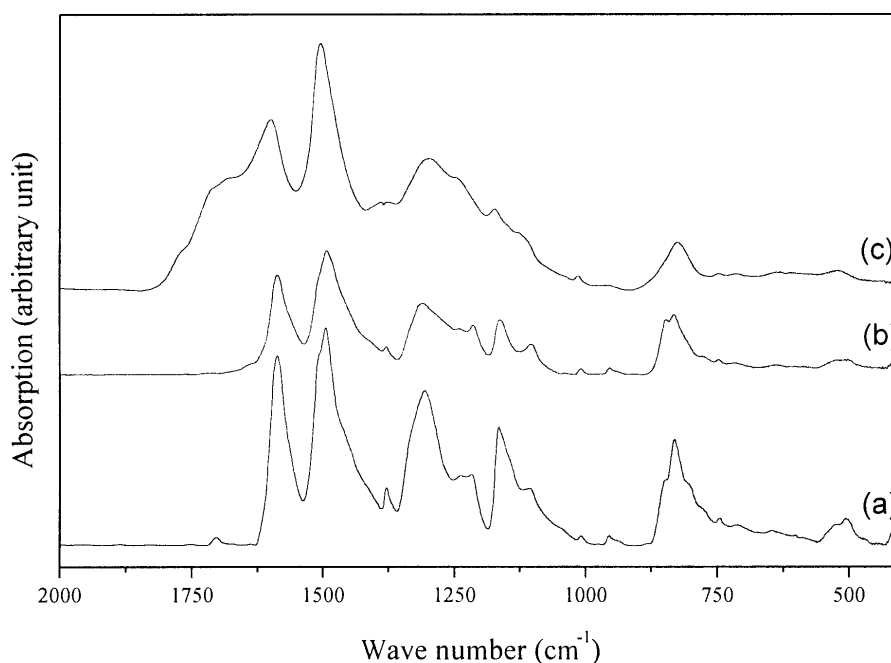

Figure 3   FTIR spectra of PANI-EB heat-treated at (a) 50°C for 24 h (b) 150°C for 24 h and (c) 250°C for 24 h.

Table 2   Assignment of the FTIR spectra of PANI-EB

Wave number (cm^{-1})	Peak assignment
1586	str. of N=Q=N
1494	str. of N-B-N
1378	C-N str. in QB$_t$Q
1306	C-N str. of QB$_c$Q, QBB and BBQ
1164	mode of N=Q=N
830	C-H out of plan bending on 1,4-ring

Abbreviations: str-stretching, Q-quinoid unit, B- benzenoid unit, B$_t$- trans benzenoid unit, B$_c$- cis benzenoid unit

Earlier studies (19-21) suggested that the band near 1590 cm^{-1} is related to quinoid ring stretching and the one near 1500 cm^{-1} is associated mainly to benzenoid ring stretching of PANI. The spectrum in Figure 3(c) exhibits a very low 1590/1500 cm^{-1} intensity ratio and, hence, the peak assignments support a structure rich in benzenoid units in PANI-EB heat treated at 250°C. Main absorption peaks at 1160 cm^{-1} and 830 cm^{-1}, and some weak bands were observed in the region between 1260 and 500 cm^{-1}. Also, a change can be seen in the band at 1164 cm^{-1} of the heat-treated material. The intensity of this peak is decreasing relative to that of the peak at around 1494 cm^{-1}. This region has been assigned to in and out of plane bending of the C-H bonds of aromatic rings. The 1160 cm^{-1} band has been referred to by MacDiarmid et al. as the electronic like band (22). It has also been shown that the intensity of this band changes almost proportional to that of the 1587 cm^{-1} peak. Therefore, it appears likely that the former band is associated with another mode of the nitrogen quinoid group.

Our results indicate the occurrence during heat-treatment of a reaction involving the conversion of quinoid rings to benzenoid rings. We suggest, therefore, that the cross-linking reactions that take place during the thermal aging involve reactions of amine and imine groups. It can be envisioned that the cross-linking reaction may have resulted from coupling of two neighboring N=Q=N moieties giving rise to two N-B-N moieties; through a link of the N atom with its neighboring quinoid ring, as was earlier suggested by Scherr et al. (23).

Conductivity measurements were carried out on films prepared from heat-treated PANI powder subsequently protonated with CSA. The room temperature conductivity of films of pristine EB.CSA$_{0.5}$ cast from formic acid was 0.038 S/cm. This value is comparable with that reported in reference (24). The conductivity data of films prepared from heat-treated PANI are presented in Figure 4. It appeared that also the DC conductivity depended on the heating temperature and aging time of nonprotonated polymer. As shown in the figure, powders heated at 50°C, displayed a rapid initial drop in conductivity, which somewhat slowed down after treatment for a few hours. By contrast, aging at temperatures of 100 and 125°C, lead to continued rapid decrease of the conductivity of post-protonated material. Not unexpectedly, at longer aging time, the decay of the conductivity was increasingly dramatic. These results strongly suggest that the cross-linking process occurring during thermal aging lead to a deterioration of the amount of sites along the PANI-EB chain can be protonated; i.e. the quinoid moieties.
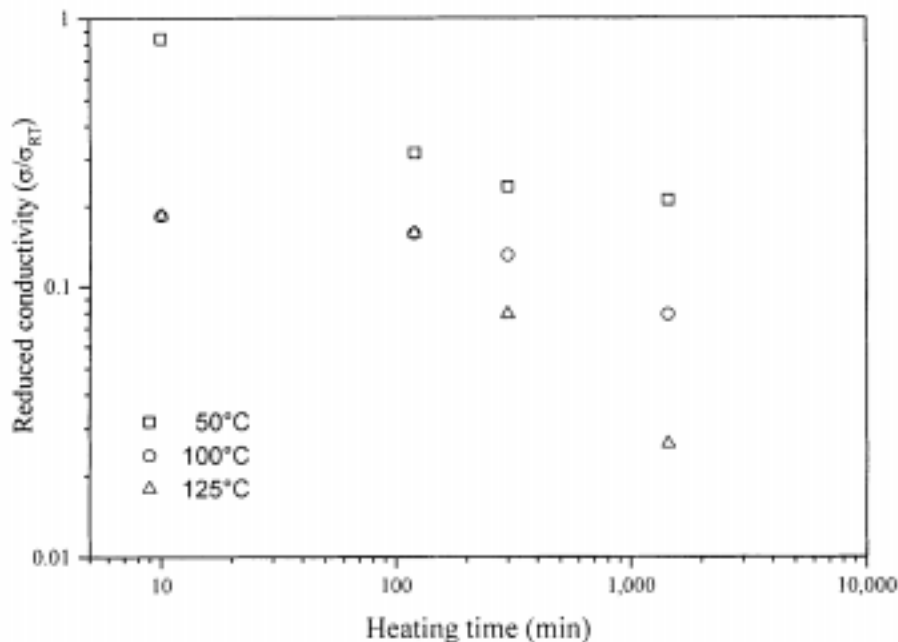
Figure 4   Variation of conductivity of EB.CSA$_{0.5}$ films as a function of heating time.

Conclusion

The cross-linking process of PANI-EB occurs during heat treatment. Longer heat treatment time lead to more pronounced cross-linking which, in turn, lead to reduced solubility of the polymer and to reduced electrical conductivity of post-treatment protonated polymer.

The present work conclusively indicates that the non-reversible part of the observed loss conductivity originates in fewer imine nitrogen atoms being available for re-protonation of the polymer after the thermal aging due to cross-linking of the former moieties.

Acknowledgments

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