Journal of Thermal Analysis, Vol. 54 (1998) 171-175

THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)/POLYANILINE CONDUCTING BLENDS

K. Pielichowski

Department of Chemistry and Technology of Polymers, Technical University, ul. Warszawska 24
31-155 Cracow, Poland

Abstract

A series of blends of poly(vinyl chloride) (PVC) and polyaniline (PANI) was prepared by solution casting and investigated by methods of thermal analysis, namely thermogravimetric analysis (TG), coupled with Fourier transform infrared spectroscopy (TG-FT/IR) and differential scanning calorimetry (DSC). It was found that the thermal stability of this polymer system depends on the composition of blend; the main product of prevailing PVC decomposition process – hydrogen chloride – seems to play specific role during degradation since it can react with PANI structures, characterized by different protonation degree.

Keywords: blends, polyaniline, PVC, thermal properties

Introduction

Polymer blending is a useful technique for designing materials with a wide variety of properties. An important commercial advantage is that polymer blends offer a way to produce new materials by using already existing materials, which thus reduces development costs [1–4]. Among different class of polymers PANI is one of the most investigated conducting polymers, due to its easy synthesis and good conductivity [5–6]. However, its intractability resulting from the stiffness of backbone and hydrogen-bonding interaction between adjacent chains limits not only industrial applications but also complete understanding of the properties of this polymer. Thermal properties of polyaniline has been the subject of some recent studies. From the thermogravimetric results it can be found that the degradation process of PANI proceeds in two or three steps being attributed to the evolution of water, loss of dopants and eventually breakdown of the polymer backbone. Some kinetic studies performed so far were, according to the author's knowledge, limited only to methods assuming a given order of reaction (*n*). This rather simple approach does not allow drawing any conclusions if the condensed phase decomposition exhibit fractional reaction order or if the (apparent) activation energy (E_{app}) is changing with the degree of conversion. Such an effect is

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

often observed in reaction systems where factors limiting the global reaction rate are either mixed together (diffusion – reaction) or of different internal nature (e.g. 2 or 3D-diffusion). In this case each reaction pathway is described by another activation threshold leading to changes in the global E value.

Another interesting question concerns applicability of TG studies for providing some information about the structure of PANI subjected to a controlled heating program. Up to now the knowledge about the structure of PANI is rather little. There were some studies on the crystals of ClO^{4-} and BF^{4-} salts of 'tetramers' and 'dimers' of PANI and on other PANI forms but without a profound explanation. More detailed investigations by X-ray technique revealed that two different crystalline forms of the emeraldine base and its HCl salt occur. The latter contains more crystalline phase (X_c is app. 50%) with the crystalline domain length, L, equal to 30–70 Å and the d spacings in the 2–10 Å range. Such dimensions of the crystalline domains exclude some methods whose resolution is not high enough. For example, the measurements by DSC is known to be sensitive to domain structures of the size range between ca. 25–30 nm. A similar problem still to be solved concerns the fine microscale structure of PVC which was first identified by wide-angle X-ray diffraction (WAXD) method in 1956. Later other observations were made, indicating that two crystal populations, denoted as A and B, occur in solution-cast films [7]. Type A crystals are hypothesized to represent folded-chain lamellar crystals formed by arrangement of syndiotactic sequences. Type A crystals are the more perfect, and hence have a slightly smaller d-spacings and lattice parameters. They also tend to not align with the stretch directions as the micellar type B crystals do, but rather with their chains perpendicular to the drawing direction. Type B crystals are thought to correspond to

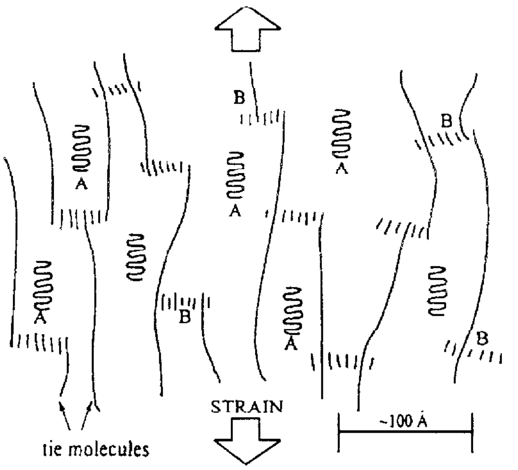


Fig. 1 Microdomain model of crystallinity in PVC, showing the behaviour of type A and B crystallites in a uniaxial strain field [8]

fringed micelle crystals, formed by the bounding of adjacent chains with short stereoregular segments [8]. If strain is applied (Fig. 1) different behaviour of A and B crystallites can be observed.

To improve the mechanical and processing properties of PANI a series of blends with PVC was prepared; this study shows results of an investigation of PANI/PVC blends in respect to their thermal behaviour and stability, determined on the basis of TG, TG/FT-IR and DSC studies.

Experimental

Synthesis of PANI

Polyaniline was synthesized by chemical oxidation in an acidic medium following a previously described procedure [9]. Aniline (POCh Gliwice, Poland) was distilled under nitrogen prior to use; ammonium peroxydisulphate (POCh Gliwice, Poland) was used without further purification.

Preparation of blends

Polymer blends of PVC (from Zakłady Azotowe w Tarnowie-Mościcach SA, M_n=52600) and PANI (m/m [%]: 99/l; 97/3 and 95/5) were prepared by solution casting from THF; di-*n*-butyl phosphate (DnBHP) was used as solubilizing and doping agent. 3-(4-Bromophenylazo)-9-(2,3-epoxypropane)carbazole was added (1 m/m%) as secondary thermal stabilizers.

The well-mixed solution was transferred to a glass dish and dried under vacuum at 40°C for 3 days.

Techniques

DSC measurements were performed on a Netzsch DSC 200, operating in a dynamic mode, with the following conditions: sample mass ~4 mg, heating rate–10 K min^{-1}, atmosphere – argon (30 cm^3 min^{-1}), sealed aluminium pan. The heating rate of 10 K min^{-1} was chosen as the best possibility to ensure high resolution of the DSC curves. The calorimeter was calibrated with an indium reference; an empty aluminium pan was used as reference. The measurements were run in triplicates.

TG was performed on a Perkin-Elmer TGA 7 thermal analyser, operating in a dynamic mode at a heating rate of 10 and 50 K min^{-1}. The conditions were: sample mass ~10 mg, atmosphere – argon or air. Fourier transform infrared (FT/IR) spectra were recorded using a Perkin-Elmer 1725X FT/IR spectrometer. The thermogravimetric analyser (P-E 7) and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimise secondary reaction or condensation on cell walls.

Results and discussion

DSC analysis has shown that pristine PANI in its emeraldine base form is characterised through a broad endothermic transition, starting at app. 55°C and centered at app. 105°C (Fig. 2).

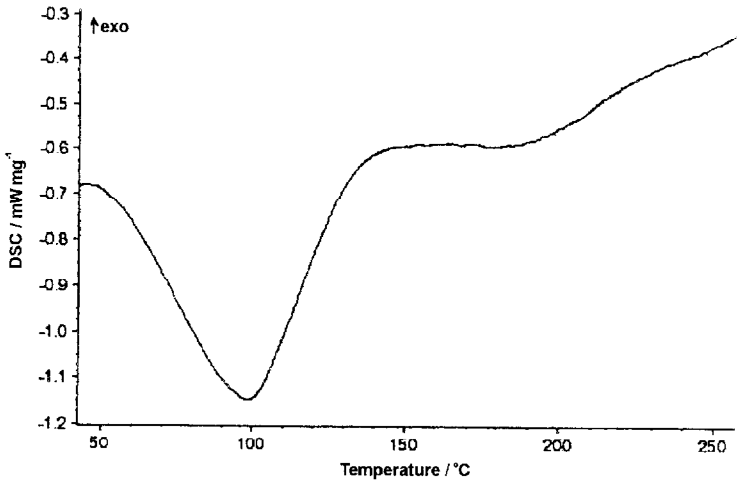
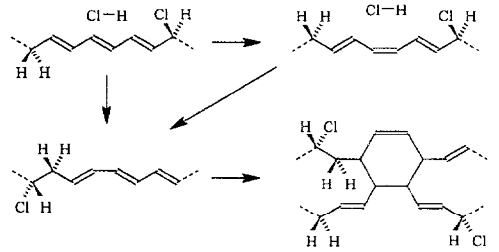


Fig. 2 DSC trace of PANI at 10 K min^{-1}

This result agrees with other studies and indicates evaporation of water molecules from the polymer matrix. In the temperature region of 150–220°C there is no substantial deviation of the baseline.

TG results of PANI in its protonated form show [9] a three-step mass loss process, with the first step indicating a 2–3% mass loss at temperatures up to 120°C. This step can be attributed to the loss of water molecules (although the coevolution of other species such as free acids and oxidant cannot be ruled out), followed by thermal degradation of the skeletal polyaniline chain structure.



Scheme 1

TG analysis of the PVC/ PANI blends at a heating rate of 10 K min^{-1} shows that up to 150°C the first degradation step is completed. Above this temperature a rapid mass loss occurs – the main stage of decomposition can be attributed the dehydrochlorination process (investigated by TG-FT/IR) since it was reported that the evolution of HCl starts at temperature of ca. 100°C followed by several simultaneous polyene rearrangement reactions, leading mostly to aromatic moieties (Scheme 1).

Under the catalytic effect of hydrogen chloride one or more double bonds may isomerize to *cis*-configurations. If those *cis*-double bonds are not isolated at the end of a polyene sequence they can not continue its growth, but they may participate in a series of secondary reactions. If one double bond is isomerized and through double bond migration generates a cisoid diene, a Diels-Alder condensation with another polyene sequence can cross link the polymer. The same cisoid diene may be formed by rotation around a single bond.

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