Thermal behaviour of synthetic metals: Polyanilines

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Polyanilines have been synthesized by chemical polymerization technique using ammonium persulphate as an oxidant. These polymers have been doped using an inorganic dopant, i.e., HCl and an organic dopant like p-toluene sulphonic acid (PTSA). Thermal behaviour of polyanilines has been studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. The thermogravimetric analysis shows a three-step decomposition of the polymer corresponding to loss of water molecules, dopant, and degradation of the polymer backbone respectively. The morphological behaviour has also been studied using scanning electron microscopy (SEM) technique.

The advent of polymers represents one of the important industrial revolutions of the current century. An important fundamental property, i.e., electrical conductivity distinguished polymers from metals. Polymers possessing high electronic conductivity are also referred as synthetic metals or conducting polymers offer a lot of very important advantages over the metals. These newly developed materials will not only replace metals in many areas but also infiltrated our day-to-day life with a wide range of products extending from most common consumer goods like batteries to highly specialized applications in space and aeronautics. Among conducting polymers, polyaniline family has attracted much attention of scientists world-wide because of their ease of synthesis, unique conduction mechanism, high environmental stability in the presence of oxygen and water, low cost, light weight and good sensing capability. These polymers also exhibit highly reversible redox behaviour, which is very important for many applications. To make polyanilines more technologically viable polymers, the processability of these polymers needs more attention.

Thermal stability is one of the key factors for successful blending of conducting polymers with conventional thermoplastics, wherein polyanilines exist as in dispersed phase. Conventional thermoplastics are melt processed, usually several degrees above their melt point or glass transition temperature. Therefore, conducting polyanilines have to be stable under the processing condition of the host polymer. Flynn and Wall have reviewed methods of kinetic analysis placing emphasis on the thermogravimetry of polymers. In addition to TGA, DSC technique could be employed to investigate phase transitions like glass transition $T_g$ and melting temperature $T_m$. Besides this, thermal relaxation associated with a particular physico-chemical change can be studied through measurement of loss molecules, storage molecules and tan delta. To study the thermal behaviour of polymers, Meggie reviewed the thermal analysis particularly, TGA, DSC and thermochemical analysis, while Gedde reviewed DSC, DTA, TGA, thermal mechanical analysis (TMA) and thermal optical analysis. Chacko et al. reported the melting transition of polyaniline. A perusal of literature reveals that the thermal behaviour of conducting polyanilines had not yet been studied systematically. Therefore, we report the synthesis of polyaniline (PANI), poly(o-toluidine) (POT) and poly(aniline-co-o-toluidine) copolymer and their characterization using TGA, DSC and SEM techniques.

Experimental Procedure

All chemicals of analytical grade procured from Sigma were used for the measurements. The polymerization of freshly distilled monomer (anilines) to polymer is carried out by chemical oxidative method using ammonium persulphate as an oxidant in non-oxidizing protonic acid such as 1.0 M...
HCl solution. To a 0.2 M solution of monomer in 1.0 M HCl at 0-2°C, 0.2 M solution of aqueous ammonium persulphate was added drop by drop. A constant stirring for 4-5 h resulted the stabilization of temperature of reaction mixture till the completion of reaction. The dark-green precipitate so obtained was filtered and washed repeatedly with distilled water and then by 1.0 M HCl solution and finally with diethyl ether until the disappearance of colour of the filtrate. The precipitate was dried under vacuum at 40°C for 24 h. To get an undoped polyanilines, the precipitate was treated with 0.5 M aqueous ammonia solution. Now leached polyanilines can be doped either with 1.0 M HCl or PTSA dopant by stirring the mixture for 3-4 h at room temperature. Upon doping the polyanilines, the doped form of polymers green in colour, is filtered, washed and finally vacuum dried. Actually, synthesis has been carried out with similar method reported earlier 13. Both doped and undoped samples of polyanilines were then characterized by means of TGA, DSC and SEM techniques.

Thermogravimetric analysis (TGA) gives informations about the thermal stability including degradation kinetics of materials. Upon heating a polymer sample at a specific heating rate, the loss in weight due to thermal reaction or degradation is measured with a thermobalance as a function of temperature using thermal analyzer (Du Pont). A constant stream of nitrogen gas (flow rate 150 mL/min) was monitored around the sample chamber to minimize heat dissipation during measurements. The weight loss is plotted as a function of temperature or time to get thermogram. Samples were also analyzed using a precalibrated Perkin Elmer DSC (model DSC-7). Indium (melting temperature 158°C) is the best standard material to check the calibration mark of DSC thermogram. The sample (10 mg) and reference materials are kept in an aluminium sample holder at the same temperature through the use of an automatic compensator that senses any difference in temperature and makes appropriate adjustment14. The heat compensation value is recorded as a function of heat flow rate. A cooling device is used to cool down the temperature of the system. A constant stream of nitrogen gas (75 mL/min) was maintained around the sample chamber to minimize heat dissipation during measurements. The heating rate during each thermogram maintained at 10°C/min and thermogram were recorded on a Hewlett-Packard graphic plotter. The JEOL fine coat-ion sputter (model JFC 1100) has been used for the gold coating on polymeric samples prior to run through the JEOL scanning electron microscope (model JSM 840).

Results and Discussion

Chemical oxidative polymerization of predistilled anilines to polyanilines were carried out using ammonium persulphate as an oxidant in non-oxidizing protonic acid such as HCl. Polymerization steps are shown in the following chart while the reaction mechanism of polymer growth is given in Scheme 1.

![Scheme 1 — Reaction mechanism of polymer growth.](image-url)
Precooled 1.0 M HCl solution at 0-5°C
Add 0.2 M monomer (anilines)
↓
Slow addition of oxidant at constant stirring for 4-5 h
↓
Dark-green precipitate
(Emeraldine salt form)
↓
Filtered, washed and dried
↓
Polyanilines powder ($\sigma = 0.1-10$ S/cm)
↓
Chemically undoped with aqueous ammonia solution at pH 12 and stirred for 3-4 h
↓
Blue violet precipitate
(Emeraldine base)
↓
Filtered, washed and then dried
↓
Undoped polyanilines powder ($\sigma = 10^{-11}$ S/cm)

Thermal analysis permits fast determination of heat capacities, heat of transitions and weight of polymeric materials undergoing a physico-chemical change. In order to evaluate fully thermal properties of polyanilines, a number of experiments like TGA and DSC have been performed on doped and undoped polymeric samples. The thermogram of emeraldine base (Fig. 1a) of PANI shows a negligible weight loss up to 428°C and from 428 to 584°C, the loss in weight is 30% possibly due to the decomposition of the polymeric backbone. However, the thermogram of leached form or base form of POT (Fig. 2a) shows a negligible weight loss up to 410°C and a continuous loss in weight is observed up to 600°C which is again possibly due to the degradation of POT matrix. This implies that base form of PANI is thermally more stable than undoped POT and substitution at ortho position of PANI brings about thermally less stable polymer. However, the TGA of copolymer of aniline with $\alpha$-toluidine shows a thermally stable copolymer up to 370°C (Fig. 3a) and a continuous loss in weight is observed up to 450°C. Thus, thermograms of undoped polyanilines show a two-step decomposition pattern. The first step is attributed to the loss of water molecules trapped in the polymer matrix, which is followed by the breakdown of polymer chain due to the decomposition of polymeric backbone.

The thermograms of HCl doped PANI, POT and poly(aniline-co-$\alpha$-toluidine) copolymer (curve b of Figs 1, 2 and 3) show rather very interesting behaviour. The doped polymers are thermally less stable than their undoped counterparts. All the doped polymers show a three-step decomposition. The first
doped polyanilines respectively. The first step is attributed to the loss of water molecules trapped in the dopant. It is also observed that at while that for inorganic acid doped sulphonate ions). The last step involves the total elimination of counter ions (i.e., chloride or
level is 18 %. In general, thermograms show a two and three-step decomposition pattern for undoped and doping level as a function of temperature can be estimated from the weight loss in the second step of doped polymer. In the PTSA doped PANI, weight loss begins at 234°C and continues up to 320°C. Thus, the weight loss is 40% corresponding to the weight of dopant. It is also observed that at 234°C the doping level of an organic acid doped PANI remains at 40% while that for inorganic acid doped PANI, the doping level is 18%. In general, thermograms show a two and three-step decomposition pattern for undoped and doped polyanilines respectively. The first step is attributed to the loss of water molecules trapped in the polymer matrix followed by a weight loss due to the elimination of counter ions (i.e., chloride or sulphonate ions). The last step involves the total breakdown of polymer chain.

DSC measures the difference in the heat flow between the sample to be tested and a known standard reference like indium and zinc whose melting temperatures are 158 and 425°C respectively. The results of DSC measurements conducted at the rate of 20°C/min on samples of POT and copolymer are given in Figs 4 and 5 respectively. Fig. 4a shows the thermogram of undoped POT. An endothermic peak appears at 100-120°C followed by exothermic peaks at 235 and 310°C. A transition is also observed at 190°C, which may be attributed to some change in softening of the polymer chain. The peak at 235°C may be assigned due to the occurring of some oxidation or cross-linking in polymer chain whereas the change at 310°C onwards may be assigned due to the degradation of polymeric backbone. However, the HCl doped POT sample shows entirely different DSC thermogram. Two strong endothermic peaks appear at 100°C and 155°C whereas a broad exothermic peak appears at 300°C onwards. The endothermic peak at 100°C in the thermogram may be attributed to the loss of water molecules present in the polymer matrix. Another endothermic peak at 155°C may be assigned to the dopant present in POT and release of HCl molecule from the doped polymer. In the present case, onset of transition at 220°C may also be assigned to the softening of the polymeric backbone. However, it is difficult to say with certainty that this is the glass transition temperature of the doped POT polymer. The continuous rise in exothermic peak from 300°C may be assigned to the decomposition of polymer chain.

Fig. 5 shows the DSC thermogram of undoped and doped copolymer. The copolymer shows an endothermic peak at 70-80°C and an exothermic

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**Fig. 4** — DSC thermogram of undoped POT (curve a) and HCl doped POT (curve b).

**Fig. 5** — DSC thermogram of undoped copolymer (curve a) and HCl doped copolymer (curve b).
transition at 240°C and continuous trend from 330°C indicating degradation of copolymer backbone. An exothermic peak at 240°C is probably due to the oxidation or crosslinking in copolymer matrix. An onset of transition at 160°C in the present case may also be assigned to the softening temperature of copolymer backbone. However, the doped copolymer (curve b) shows a strong endothermic peak at 90°C and a very weak small endothermic peak at 240°C. It is very difficult to say at this juncture whether this endothermic peak is due to the release of dopant present in the copolymer. Therefore, more experiments are underway to ascertain the nature of this peak.

SEM technique is applied primarily for the visualization of organic surfaces, especially for the study of surface morphology, domains, pinhole defects and patterns. The images are formed by the interaction of electrons with sample, in vacuum (10⁻⁴ torr). The images are built up, point, and in a way similar to that used in a TV display. The contrast in the images is a result of differences in scattering from different surface areas as a result of geometrical differences. The conducting copolymer synthesized by chemical oxidative method has been examined for the morphological studies by scanning electron microscopy. It can be clearly seen that the micrographs of poly(aniline-co-o-toluidine) copolymer (Fig. 6) are smooth and homogeneous. After doping with HCl and PTSA, the growth of a microcrystalline structure can be seen with grain size. Thus, a change in the surface morphology as a consequence of doping / dedoping has been observed. A uniform distribution of dopants in the polymer matrix has also been observed with both types of dopants, i.e., an organic dopant and inorganic dopant whereas the symmetrical distribution is not present in the undoped polymeric samples.

**Conclusion**

The undoped polyanilines / emeraldine base form is highly thermal stable polymer with thermal stability upto 370-428°C whereas the doped forms are stable upto 100-234°C depending upon the type of dopant used. The thermal stability of the doped polyanilines is highly dependent on the dopant anion attached to the polymer backbone. Polyanilines doped with an organic dopant, i.e., PTSA is more stable than polymer doped with an inorganic dopant like HCl. Doped and undoped polymer shows a three and two-step decomposition respectively. The first step corresponds to the loss of water followed by the loss of dopant anion and the third step corresponds to the decomposition of polymeric backbone. The doping level can be estimated from the weight loss in the second step decomposition of doped polymer. It has

Fig. 6 — SEM micrographs of poly(aniline-co-o-toluidine) copolymer (undoped form and HCl & PTSA doped forms with magnification 5000, 2500 and 2500 respectively).
also been observed that polymer doped with certain proprietary organic dopants is thermally stable upto 234°C which may find applications in the formation of conducting composites with the conventional thermoplastics.

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References