Measurement of thermal properties of polyaniline salt from room temperature 30 to 140°C

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The thermal transport properties of polyaniline (doped with HCl) have been measured using transient plane source (TPS) technique. Cl- doping is confirmed by FTIR spectroscopy. In the temperature range from room temperature 30 to 140°C both effective thermal conductivity (λe) and effective thermal diffusivity (ke) increase with increase in temperature from 30 to 60°C and become almost constant in the temperature range 60 - 100°C. For further increase in temperature, the values of λe and ke decrease. This behaviour of thermal transport properties in the above mentioned ranges of temperature is due to decrease in moisture content and conversion of single-phase crystalline structure into multiphase crystalline structures, respectively. It has also been found that the values of thermal transport properties are much higher for salt as compared to its base form. This is suggestive of the fact that a change of -NH- group of base form into –[N+H]Cl- group in salt form takes place by doping of chloride ions.

Keywords: Conducting polymers, Transient plane source, Effective thermal conductivity, Effective thermal diffusivity

1 Introduction

Conducting polymers have recently attracted attention because of their many applications in lightweight batteries, solar cells, electro-chromic switching, variable transmission window, sensors and non-linear optical materials1. Within the group of conducting polymer materials, there has been much interest in polyaniline (PANI), the most versatile of the conjugated polymers, because of its excellent stability under ambient conditions. In addition, a wide range of optical, electrical and electrochemical properties make PANI an attractive material for a number of applications such as displays, biosensors, and batteries. The PANI system possesses many unusual and attractive chemical aspects, including dopability by both oxidation and derivatization with a wide variety of substituents. These features play an increasingly important role in studies aimed at understanding the transport, magnetic and optical properties of PANI2,3.

The basic chain structure in PANI exists in three insulating states, Leucomeraldine base (LB), Emeraldine base (EB), and Pernigraniline base. The general formula of PANI is [(B-N=Q=N-)y (B-N=Q=NH2)1-y]x, in which B and Q denote the C6H4 rings in the benzenoid and quinoid form, respectively. The intrinsic oxidation state of PANI can range from the fully oxidized Pernigraniline (y = 0), through 50% oxidized Emeraldine (y=0.5), to fully reduced Leucomeraldine (y=1.0). PANI can achieve its highly conductive state either through the protonation of the imine nitrogen (=NH-) in its Emeraldine state or through the oxidation of the amine nitrogen (-NH-) in it’s fully reduced leucoemeraldine state4.

When EB is equilibrated in a large excess of aqueous acid solution, protonation occurs at the imine repeat units to produce the emeraldine salt of PANI, which is believed to have the following composition

\[\left[\left(C_6H_4-NH-C_6H_4-NH\right)_y\left(C_6H_4-N^+H-C_6H_4=N^+H\right)_{1-y}\right]_x\] 

A- A-
where A⁻ is the anion and it consists of equal number of reduced \((\text{C}_6\text{H}_4-\text{NH}\text{-C}_6\text{H}_4\text{-NH})\) and \((\text{C}_6\text{H}_4\text{-NH}\text{=C}_6\text{H}_4\text{=N})\) repeat units. The positively charged nitrogen portion is related to the doping level, in other words protonation level of the polymer. This results in increased thermal and electrical conductivity. However conductivity is affected by the amount of protonation, level of oxidation, moisture content and polymerization condition.

In the present study, the variation in effective thermal conductivity and effective thermal diffusivity of PANI salt (doped with HCl) in the temperature range 30 to 140°C at normal pressure using the transient plane source (TPS) technique is studied.

### 2 Experimental Details

The polyaniline (PANI) is prepared by redox polymerization of aniline using ammonium peroxydisulphate \(\text{[(NH}_4\text{)}_2\text{S}_2\text{O}_8\text{]}\) as an oxidant. For this double distilled aniline \((.01\text{M})\) is dissolved in 250 ml of precooled HCl \((1\text{M})\) solution. A calculated amount of ammonium peroxydisulphate \((.01\text{M})\) is dissolved in 250 ml of HCl \((1\text{M})\) precooled to 0°C. Now this aqueous solution of ammonium peroxydisulphate is added dropwise to, the stirred solution of aniline dissolve in HCl. The temperature of this solution was maintained at 3-4°C for 2 h of mixing time. The dark green precipitate resulting from this reaction is kept in HCl solution for 24 h. After keeping overnight the precipitate was washed by distilled water and methanol until the green colour of filtrate disappears. Now this precipitate is dried under dynamic vacuum for 8 h at 60 °C temp, to obtain PANI salt. Such prepared PANI salt (doped with HCl) is characterized with the help of FTIR spectra shown in Fig. 1.

Pellets (2 mm thick, 12 mm diam) were prepared from the powdered material (PANI salt) with a load of 5 ton. The sample holder (Fig. 2) containing these samples is placed in a furnace that has a sensitivity of 1 K. After achieving isothermal condition in the sample, a constant current pulse of width 10 s and height 0.0736 Amp is passed through the heating element. The measurements reported in this paper were performed with a TPS element of the type shown in Fig. 3. It is made of 10 μm-thick nickel foil with an insulating layer made of 50 μm-thick kapton on each side of the metal pattern. The evaluation of these results was performed as obtained by Gustafsson. No influence was recorded from the electrical connections, which are shown in Fig. 4.

![Fig. 1—FTIR spectra of PANI salt (doped with HCl).](image)

![Fig. 2—Sample holder diagram with TPS sensor.](image)

![Fig. 3—Schematic diagram of TPS sensor.](image)

![Fig. 4—Schematic diagram of bridge circuit.](image)
These connecting leads had the same thickness as the metal pattern of the TPS element. Each TPS element had a resistance at room temperature of about 3.26 Ω and a temperature coefficient of resistance (TCR) about 4.6×10⁻³ K⁻¹. Because of the change in average temperature of the sensor, the potential across it changes. The transient potential difference across the terminals is recorded by a digital multimeter and the current through the TPS sensor is supplied by a digital power supply. The current in the circuit is adjusted according to the nature of the sample material. Multiple readings at appropriate intervals are taken to ensure the accuracy of the results. The TPS program used here is capable of recording the temperature of the sample through the TPS sensor itself. In addition, a sensitive thermometer is kept just above the sample pieces inside the furnace to monitor the temperature of the sample.

3 Transient Plane Source Theory

The TPS method consists of an electrically conducting pattern (Fig. 3) in the form of a bifilar spiral, which also serves as a sensor of the temperature increase in the sample. The sensor is sandwiched between the thin insulating layers of kapton. The temperature ΔT increase because the flow of current through the sensor gives rise to a change in the electrical resistance ΔR(t) that is given as

\[ ΔR(t) = α R_0 ΔT(t) \]  

where \( R_0 \) is resistance of TPS element before the current has been switched on, \( α \) is the temperature coefficient of resistance (TCR) of the material of the sensor and \( ΔT(t) \) is the mean value of the time dependent temperature increase of the TPS element which has been calculated in a proper way and is given by

\[ ΔT(τ) = \frac{P_0}{π^{3/2} a λ} D_s(τ) \]  

and

\[ ΔT(y, z, τ) = \frac{1}{4π^{3/2} a λ} \frac{z}{dσ} \right) \]  

where \( P_0 \) is the lead resistance, \( R_s \) is a standard resistance with a current rating that is much higher than \( I_0 \), which is the initial heating current through the arm of the bridge containing the TPS-element. \( γ \) is the ratio of the resistance in two ratio arms, of the bridge circuit, which is taken to be 100 in the present case.

4 Characterisation

The FTIR spectra of polymer powder obtained in KBr pallet is shown in Fig. 1. The C-Cl stretching peak arises at 650 cm⁻¹. This confirms Cl⁻ doping of the chemically synthesized polyaniline. The peak near 800 cm⁻¹ is due to the N-H out-of-plane bending absorption. The strongest band observed near 1140 cm⁻¹ is due to the C-C stretching of the alkyl chain. The peak at 1320 cm⁻¹ is due to C-N stretching of the polymer and peak at 1380 cm⁻¹ is because of C-N + stretching doublet band. The C=C stretch absorption of aromatic compounds generally occur in the range of 1475-1625 cm⁻¹, in the present study this peak was obtained at 1610 cm⁻¹. The peak due to N-H banding can be seen at 1640 cm⁻¹. Amine (-NH₂) group can be recognized by absorption due to N-H stretching in the region 3300-3500 cm⁻¹. The two bands at 3380 and 3400 cm⁻¹ are due to symmetric and asymmetric N-H stretching.
5 Results and Discussion

The values of \( \lambda_e \) and \( k_e \) of PANI salt doped with HCl in the temperature range 30 to 140 ºC have been plotted in Figs 5 and 6.

From these figures it can be observed that the values of \( \lambda_e \) and \( k_e \) for this sample increase from 30 to 60ºC and remain almost constant in the temperature range 60 to 100ºC. Again in the temperature range 100 to 140ºC a continuous decrease is observed in the values of \( \lambda_e \) and \( k_e \).

The initial increasing behaviour of \( \lambda_e \) and \( k_e \) can be explained on the basis of decrease in moisture content in the sample with the increase of temperature. With the increase of temperature the sample becomes more and more dry and the intermolecular distance decreases owing to loss of water molecules, which in turn increases the values of \( \lambda_e \) and \( k_e \). In the temperature range 60 to 100 ºC the sample becomes almost moisture free and the PANI salt in pure form is in its optimize position with stable values of \( \lambda_e \) and \( k_e \).

The values of \( \lambda_e \) and \( k_e \) are higher for PANI salt (doped with HCl) as compared to PANI base. This can be understood on the basis of their structures. First the base form of PANI is neither charge conjugation symmetric because neither the Fermi level nor the band gap are formed in the center of the \( \pi \) bond, thus making the valence and conduction bands asymmetric. When PANI base is doped with HCl the protonation occurs which adds H\(^+\), so that holes are added to the imine groups around the quinoid ring which can be looked upon as a charge delocalization of holes in the valence band.

Another interesting fact is that conducting polymers in their original form can be polycrystalline or amorphous or combination of inorganic and organic classes of materials. Here this sample is prepared at low temperature (3-4ºC) by the sol-gel technique, which upon heating at high temperature initially gives rise to single-phase crystalline or multiphase crystalline ceramics. Initially single phase crystalline structure tends to increase the values of \( \lambda_e \) and \( k_e \) and after that multiphase crystalline structure contribute in decreasing the values of thermal diffusivity because of increase in cross-linking of polymer chains. Furthermore, the sides branching which starts forming at slightly higher temperature of preparation of polymer, with the formation of multiphase crystalline structure, give rise to lower values of thermal conductivity and diffusivity.

Second both carbon rings and nitrogen atoms are within the conjugation path, forming a generalized polymer AB as shown in the Fig. 7.

Third when PANI base is protonated by HCl then (-N=) sites become (-N\(^+\))

\[
\text{Cl}^- \\
^1 \\
\text{Cl}^-
\]

Sites with (+)ive and (-)ive centers may produce dipole structure. In this type of structure there is good possibility to transfer thermal energy and hence an
increase in the values of $\lambda_e$ and $k_e$ is observed. The change of (-NH-) group in (-N$^+$H-) group with the Cl$^-$ formation of polarons and bipolarons, produces interruption of the order of polaron lattice$^{14}$. That may be the reason for the higher conductivity of HCl doped PANI.

Finally the doping procedure differs from the conventional ion implantation used for three-dimensional semiconductors, typically being carried out by exposing the polymer powder (PANI base) to solution of dopant. The polymer backbone and dopant ions form new three-dimensional structure. Due to this doping there is a rich variety of these structures, which play a significant role in the thermal transport properties. Moreover, the size of ordered/disordered regions in conjugate macromolecular [(B-NH-B-NH-)$x(B-N=Q=N-)$]$_y \text{ system}$ can vary from nanoscopic to macroscopic level, which to a large extent is dependent upon the sample preparation and processing conditions. This complex relationship between structure/morphology and thermal properties has made the understanding of thermal transport properties in conducting polymers quite difficult with respect to conventional systems.

6 Conclusions

It can be concluded that the variation of the effective thermal conductivity ($\lambda_e$) and thermal diffusivity ($k_e$) of the PANI salt (doped with HCl) with temperature is due to decrease in moisture content and conversion of single-phase crystalline structures into multiphase crystalline structures, respectively. Also higher values of thermal transport properties in the salt form of PANI over the base form are because of the change of (-NH-) group in (-N$^+$H-) Cl$^-$ group by doping of chloride ions. FTIR spectra confirm the Cl$^-$ doping in the PANI sample.

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