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Measurement of thermal transport and optical properties of conducting polyaniline

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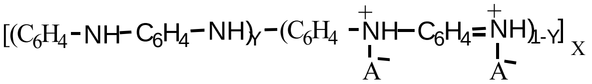
Measurements of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of twin pellets of conducting polyaniline, prepared under a load of 5 ton were carried out from room temperature to 170°C at normal pressure using transient plane source (TPS) technique. The values of λ_e and χ_e by the use of an empirical relation at various fixed temperature in the above mentioned range have been calculated. The calculated values are in good agreement with the experimental results over the entire range of temperatures of investigation. Besides, the optical band gap of the sample is determined using reflection spectra in the wavelength region 300-800 nm. From the analysis of reflection spectra, polyaniline is found to have energy band gap 3.1 eV. The results indicate that band gap values are dependent on annealing temperatures of the samples and λ_e and χ_e vary with annealing temperature in the range from room temperature to 170°C. The effective thermal conductivity and effective thermal diffusivity are maximum at about 100°C, whereas the optical band gap is minimum for the sample annealed at 100°C as compared to other annealing temperatures.

Keywords: Polyaniline, Effective thermal conductivity, Effective thermal diffusivity, Transient plane source technique
IPC Code: G01N25/18

1 Introduction

Polyaniline (PANI) in its emeraldine oxidation state has attracted considerable interest due to its environmental stability, electrical conductivity and thermal conductivity and has emerged as promising materials for application in various states[1,2]. Unlike other conducting polymer, PANI can also be reversibly modified by *p*H change (with the conducting emeraldine salt being doped by base to the insulating emeraldine base form) as well as oxidized and reduced to pernigraniline and leucoemeraldine forms. Chemical formula of PANI is $[(-B-NH-B-NH)_Y(-B-N=Q=N-)_{1-Y}]_X$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinoid forms, respectively. When emeraldine base is equilibrated in a large excess of aqueous-acid solution, protonation occurs at imine repeat unit to produce emeraldine salt of polyaniline (PA-ES) believed to have the composition



$$[(C_6H_4-NH-C_6H_4-NH)_Y-(C_6H_4-\underset{A^-}{\overset{+}{N}}H-C_6H_4=\underset{A^-}{\overset{+}{N}}H)_{1-Y}]_X$$

where A^- is the anion and consists of equal number of reduced $[C_6H_4-NH-C_6H_4-NH]$ and $[C_6H_4-N=C_6H_4=N-]$ repeat units. This results in the increased thermal as well as electrical conductivity. However, conductivity is affected by the protonation, level of oxidation, moisture contact, and polymerization conduction[3,4]. Due to their chemical stability, their high conductivity upon doping and their non-linear optical properties, polypyrrole (PPy) and polythiophene (PTh) are among the most widely studied conducting polymers, experimentally and theoretically. Since PPy and PTh have relativity large band gaps, 2.85 and 2.0 eV, respectively, the neutral forms are insulator[5]. Further, some of the physical properties such as effective thermal conductivity, effective thermal diffusivity and optical band gap are also discussed.

2 Experimental Details

Polyaniline is usually prepared by redox polymerization of aniline using ammonium perdisulphate, $(NH_4)_2S_2O_8$, as on oxidant. Distilled aniline (0.02 M) is dissolved in 300 ml of precooled HCl (1.0 M) solution, maintained at 0.5°C. A calculated amount of ammonium perdisulphate (0.05 M) dissolved in 200 ml of HCl (1.0 M), precooled to 0-5°C, is added to the solution. The dark green precipitate (ppt) resulting from this reaction is washed with HCl (1.0 M) until the green colour disappears. This ppt is further extracted with tetra hydrofuran and NMP (N-methyl pyrolidinone) solution by soxhlet extraction and dried to yield the emeraldine salt. Emeraldine base can be obtained by heating the emeraldine salt with ammonia solution. This composite is then dried in an oven at high temperature

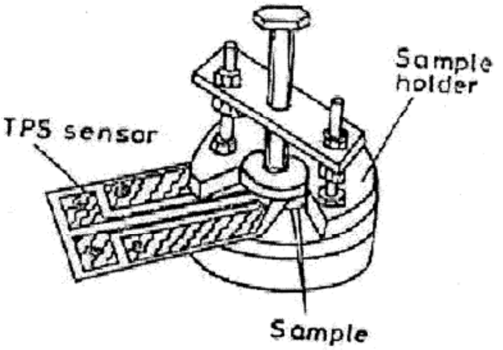


Fig. 1—Sample holder

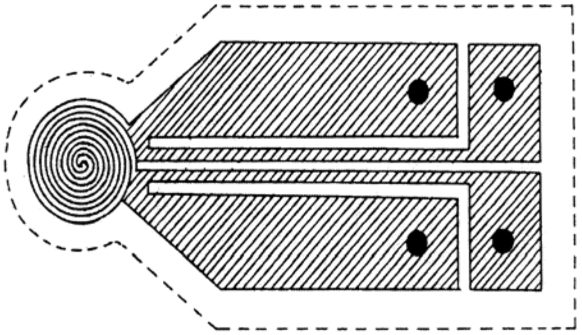


Fig. 2—Schematic diagram of TPS sensor

to get the conducting polymer in powder form. The powder so obtained can be used for device fabrication. The pellets of thickness 2 mm and diameter 12 mm were prepared from the powdered materials by a pressure of 4.33×10^8 Pascal.

The sample holder (Fig. 1) containing these samples is placed in a furnace having sensitivity of 1 K. After achieving the isothermal conditions in the sample, a constant current pulse is passed through the heating element.

3 Characterisation of Sample

3.1 Optical characterisation

The energy band gap of these materials is determined by the reflection spectra. According to the Tauc relation, the absorption coefficient α, for direct band gap material is given by[6]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad \ldots(1)$$

where E_g is the energy gap and constant A, are different for different transitions, ($h\nu$) is energy of photon and n is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the reflection. Also absorption coefficient α is directly proportional to ln $\{(R_{\max}-R_{\min})/(R-R_{\min})\}$ and is given by:

$$2\alpha\, t = \ln\,[(R_{\max} - R_{\min})/(R - R_{\min})] \quad \ldots(2)$$

where t is the thickness of the sample, $R_{\max}$ and $R_{\min}$ are maximum and minimum values of reflectance, respectively, R the reflectance at a given photon energy, $h\nu$. When graph is plotted between $(\alpha h\nu)^2$ or $[h\nu \ln\{(R_{\max}-R_{\min})/(R-R_{\min})\}]^2$ versus $h\nu$ (as abscissa), a straight line is obtained. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the band gap of the sample.

3.2 Transient plane source (TPS) theory

The measurements reported in this paper were performed with a TPS element. It is made of a 10 μm thick nickel foil (having a resistance of about 3.26 Ω and a TCR around 4.5×10^{-3} k^{-1}) with an insulating layer made of 50 μm thick kapton on each side of the metal pattern (Fig. 2).

Evaluation of these measurements was performed in a way that was outlined by Gustafsson[7,8].

4 Results and Discussion

Simultaneous measurements of effective thermal conductivity and effective thermal diffusivity of pellets of polyaniline sample, prepared at an ambient pressure of 4.33×10^8 Pa or an equivalent load of 5 ton, were carried out at room temperature to 170°C. It is seen that the λ_e and χ_e of the sample show a linear increasing trend with temperature to a peak value. The peak value is observed at around 100°C for polyaniline sample.

The values of λ_e and χ_e then decrease with the further increase in temperature and finally obtained a temperature independent value at 170°C. The variation of these two thermal transport properties with temperature is shown in Figs 3 and 4. Figure 3 shows the variation of effective thermal conductivity with temperature of polyaniline. Figure 4 shows the variation of effective thermal diffusivity with temperature. It is observed that at a room temperature value of λ_e and χ_e for polyaniline sample are 0.20 W/m-K and 0.11 mm^2/s, respectively. The maximum values of λ_e and χ_e for polyaniline sample are 0.36 W/m-K and 0.24 mm^2/s. The structure scattering, which is temperature dependent, plays an important role in the variation of the thermal conductivity with temperature. The observed variation in thermal conductivity is explained on the basis of various phonon scattering mechanisms[9] viz structural scattering, stray scattering and chain defect scattering.

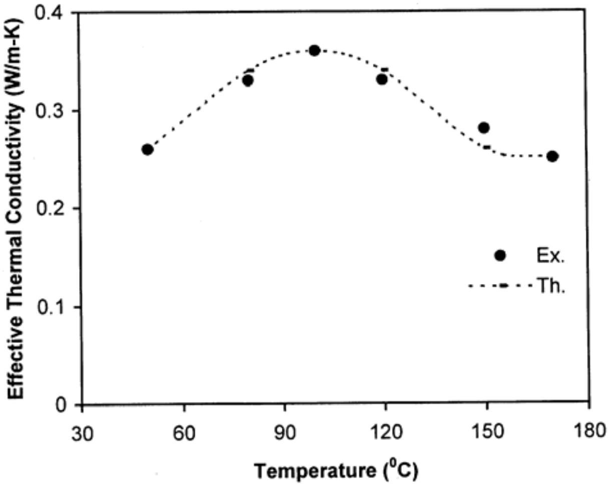


Fig. 3—Temperature variation of theoretical and experimental value of λ_e of polyaniline sample

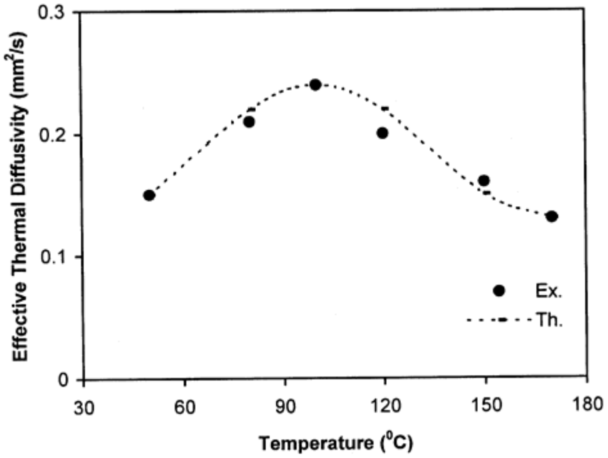


Fig. 4—Temperature variation of theoretical and experimental value of χ_e of polyaniline sample

Polyaniline is a typical phenylene base polymer having a chemically flexible -NH-group in a polymer chain flanked either side by a phenylene ring. The protonation and deprotonation and various other physico-chemical properties of polyaniline can be said to be due to the presence of the -NH- group. At the molecular level, a polymer is an ordered sequence of monomer units. The degree of unsaturation and conjugation influence charge transport via the orbital overlap within a molecular chain. The charge transport becomes obscured by the intervention of chain folds and other structural defects[10].

By means of a least squares fit to the experimental data of effective λ_e and χ_e as a function of temperature, as plotted in Figs 3 and 4 for polyaniline sample, empirical relationships have been established for the calculation of λ_e and χ_e. These are given as:

$$\lambda_e = A + B\,(T-T_o)^2 + C\,(T-T_o)^3 \qquad ...(3)$$

$$\chi_e = a + b\,(T-T_o)^2 + c\,(T-T_o)^3 \qquad ...\ (4)$$

where A, B, C, a, b and c are constants calculated by experimental conditions. T is the temperature of the composite in absolute temperature units. The observed variation in λ_e and χ_e with temperature can be explained by considering the effect of temperature on structural units in a phenomenological manner. In the temperature range below T_o, the temperature dependence of λ_e and χ_e is controlled by the variation of phonon mean free path due to structure scattering, stray scattering and chain defect scattering. The first term A and a in both empirical equations represent the contribution to thermal resistance of structure scattering. For temperatures below T_o, structure scattering become predominant besides chain defect scattering, scattering due to defects introduced by blends and relatively smaller length of chain segments. With rising temperature, the polymeric chain straighten out more and more. Therefore, mean free path increases and thus the contributions to the corresponding thermal resistance decrease linearly with the rise of temperature, resulting into the increase of λ_e and χ_e in this temperature range. The chain defects are effectively identical to stacking faults and hence, are expected to show similar temperature dependence for thermal resistance. The constant B in Eq. (3) represents the thermal resistance by chain-defect scattering. The constant C can also be attributed to represent the contribution to thermal resistance by other possible stray scattering mechanisms. The constants A, B, C, a, b and c are polymer dependent parameters and their values are $A = 0.36$ W/m-K, $B = -4.73\times10^{-5}$ W/m-K^3, $C = 1.46\times10^{-7}$ W/m-K^4, $a = 0.24$ mm^2/s, $b = -4.16\times10^{-5}$ mm^2/s-K^2 and $c = 1.13\times10^{-7}$ mm^2/s-K^3. Figures 4 and 5 also show the variation of λ_e and χ_e with temperature as predicted by empirical relation given in Eqs (3) and (4) for polyaniline sample. It is clear from Figs 3 and 4 that the agreement between the predicted values of λ_e and χ_e using empirical relation and the results of experiment is very good.

In light of these observations, the optical properties of these samples have also been measured. The reflection spectra of polyaniline samples annealed at temperature 100 and 170°C have been recorded by a Hitachi spectrophotometer, which is shown in Fig. 5. The reflection decreases with the decrease in wavelength (Fig. 5). Sudden fall present at a

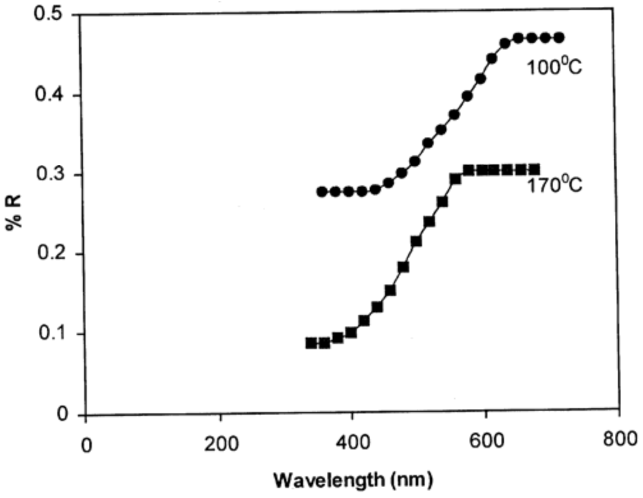


Fig. 5—Reflection spectra of polyaniline samples annealed at 100°C (●) and 170°C (■)

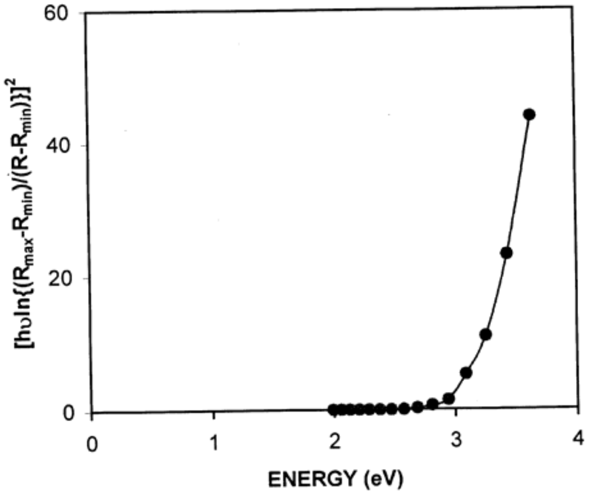


Fig. 6—Energy band gap determination of polyaniline sample at room temperature

particular wavelength, indicates the presence of optical band gap in these samples. Tauc relation as given in Eq. (2) is used for the determination of energy band gap in the polyaniline sample at room temperature.

Graphs between $[h\nu \ln (R_{\max} - R_{\min}/R - R_{\min})]^2$ versus $h\nu$ have been plotted in Fig. 6. It is observed that energy band gap of polyaniline sample in pellet form at room temperature is 3.1 eV. The pellets were annealed at 50, 80, 100, 110, 120, 150 and 170°C for two hours. The energy band gaps of these samples using above technique were measured. Fig. 7 shows the variation of energy band gap with annealing temperature.

The minimum value is observed at around 100°C for polyaniline sample. Thermophysical studies on these samples suggest that at 100°C effective thermal conductivity and effective thermal diffusivity are maximum. Thus, it may be expected low energy band of this material annealed at 100°C. Figure 7 confirms our observation. Similar to relation given in Eqs (3) and (4), an empirical relation for the variation of energy band gap with the annealing temperature has also been developed. The relation is given by

$$E_g(\tau) = E_g(\tau_o) + D(\tau - \tau_o)^2 + E(\tau - \tau_o)^3 \quad \ldots(5)$$

where D and E are constants calculated by experimental conditions and their values are $D = 8.4\times10^{-5}$ eV/K^2 and $E = -4.8\times10^{-7}$ eV/K^3. τ is the different annealing temperature of the polyaniline samples. $E_g(\tau_o)$ is the minimum value of energy band gap, where $\tau_0 = 100$°C. This temperature is

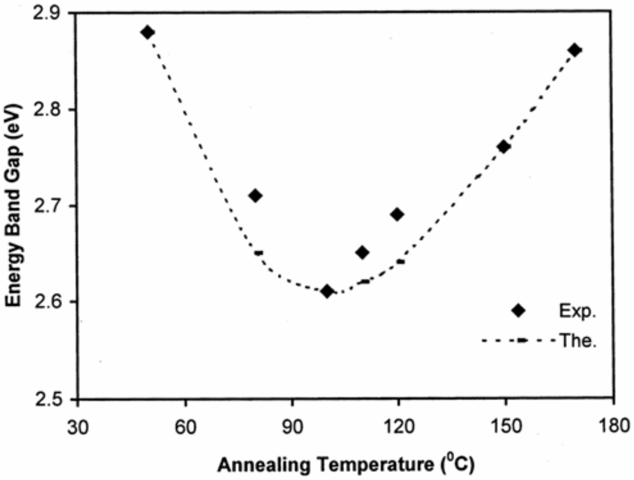


Fig. 7—Variation of energy band gap versus annealing temperature

corresponding to the maximum of λ_e and χ_e. As the structural changes in the samples take place on annealing, similar to the thermal conduction an increase in electrical conductivity is expected up to 100°C. This may be attributed to the increase in carrier concentration, hence, decrease in energy band gap. At temperature above 100°C, the fall in conductivity can be explained by increase in the energy band gap. Thus, the empirical relation given in Eqs (3) and (4) can be used to explain the variation of energy band gap with annealing temperature.

5 Conclusion

In conducting polyaniline, the minimum of energy band gap at 100°C annealing temperature and maximum of λ_e and χ_e at 100°C, suggests that an irreversible structural change has occurred on heating the sample. Although, the sample after annealing was brought to room temperature but the measured values of energy band gap were different then the values obtained at room temperature. This indicates that annealing brings out a permanent change in the structure of the samples as also confirmed through the thermal transport measurements.

References

1 Byun S W & Im S S, *J Appl Polym Sci,* 56 (1995) 425.
2 Kalaycloglu E, Akbulut U & Toppare L, *J Appl Polym Sci,* 61 (1996) 1067.
3 Hennig C, Hallmeier K H & Szargan R, *Synth Met*, 92 (1998) 161.
4 Umare S S, Borkar A D & Gupta M C, *Bull Mater Sci,* 25 (2002) 235.
5 Salzner U, Lagowski J B, Pickup P G & Poirier R A, *Synth Met,* 96 (1998) 177.
6 Kumar S, Sharma S K, Sharma T P & Husain M, *J Phys & Chem of Solids,* 61 (2000) 1809.
7 Gustafsson S E, *Rev Sci Inst,* 62 (1991) 797.
8 Gustafsson S E, Suleiman B, Saxena N S & Haq I U, *High Temp-High Press,* 23 (1991) 289.
9 Saxena N S, Pradeep P, Mathew G, Thomas S, Gustafsson M & Gustafsson S E, *Eur Poly J,* 35 (1999) 1687.
10 Trivedi D C, *Handbook of organic conductive molecules and polymers: 2. Conductive polymers: Synthesis and electrical properties (*Wiley. New York), 1997.