Thermal characterization of doped polyaniline and its composites with CoPc

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Thermal diffusivity of the composites of camphor sulphonic acid (CSA) doped polyaniline (PANI) and its composites with cobalt phthalocyanine (CoPc) has been measured using open cell photoacoustic technique. Analysis of the data shows that the effective thermal diffusivity value can be tuned by varying the relative volume fraction of the constituents. It is seen that polaron assisted heat transfer mechanism is dominant in CSA doped PANI and these composites exhibit a thermal diffusivity value which is intermediate to that of CSA doped PANI and CoPc. The results obtained are correlated with the electrical conductivity and hardness measurements carried out on the samples.

I. INTRODUCTION

The discovery of the fourth generation of polymeric materials, viz., conducting polymers, has created a new area of research on the boundary between chemistry and condensed matter physics.[1] The structural, electrical, and optical properties of these materials can be tuned using various doping techniques such as chemical, electrochemical, photodoping, etc.[2] This versatility makes them ideal candidates for the fabrication of several devices such as polymer batteries, electrochemical windows, and light emitting electrochemical cells.[3] Polyaniline (PANI), the conducting polymer available in metallic form, after postdoping with sulphonic acid, has emerged as a useful material both for research as well as industrial purpose due to its high stability, simpler polymerization procedure with high yield, availability of inexpensive monomer, etc.[1,4] Also among the many conducting polymers, PANI is a good candidate for preparing conducting polymer composites since it is stable, both thermally and environmentally. Conducting polymer composites based on PANI and cobalt phthalocyanine (CoPc) is a suitable candidate for making rechargeable batteries.[5]

The past two decades have witnessed the emergence of photoacoustic and related photothermal techniques as effective analytical tools for the evaluation of transport and optical properties of materials with considerable accuracy.[6] In this Brief Report the measurement of thermal diffusivity of camphor sulphonic acid (CSA) doped PANI using open cell photoacoustic technique is reported for the first time. As the composite allows tunability in thermal properties of the parent compound, a systematic study of its compositional variation on effective thermal diffusivity was performed. The experimentally obtained results are correlated with electrical conductivity and hardness measurements performed on all these samples. Analysis of our observations reveals that phonons play a dominant role in the heat transport mechanism in these materials. CoPc possesses a planar structure and has the highest electrical conductivity amongst the other metallic phthalocyanines. Hence the evaluation of the thermal properties and its correlation with electrical and me-

chanical properties of the composites of these materials with CSA doped PANI have great physical and practical significance, especially from the device point of view.

II. SAMPLE PREPARATION

In order to prepare the samples under investigation, initially the monomer aniline and aqueous percholoric acid were kept at $4\,°C$ and ammonium per sulphate was added drop by drop to these starting materials. This mixture was stirred for 2 h and then filtered and washed with water and methanol. Subsequently, PANI doped with percholorate was transformed into insulating polyaniline emarldine base using hydrazine hydrate. The resulting compound was doped with 50% CSA in nitrogen atmosphere to produce an emeraldine salt form of this material which is then purified and dried in vacuum.[5,7] The tetramer of cobalt phthalocyanine was prepared, purified, and characterized by the solution method, wherein cobalt sulphate, pyrometallic dianhydride, excess urea, ammonium chloride, and ammonium molybdate were homogenized well and heated at $180\,°C$ in nitrobenzene ambient for 12 h. The reaction mixture was then cooled and washed with methanol repeatedly to remove nitrobenzene. This crude product was further boiled with 2N sodium hydroxide containing sodium chloride and then filtered. The residue was acidified with hydrochloric acid, washed severally and then dried to obtain the final product, viz., phthalocyanine tetramer.[8] The composites of these materials were prepared as follows. The powdered PANI doped with CSA was blended with tetrameric cobalt phthalocyanine by mixing them homogenously in agate mortar. The materials were finally prepared in the following volume fractions: 90% PANI:CSA - 10% CoPc, 50% PANI:CSA - 50% CoPc, and 10% PANI:CSA - 90% CoPc. All these samples were palletized and are black in color.

III. EXPERIMENTAL SETUP AND THEORETICAL BACKGROUND

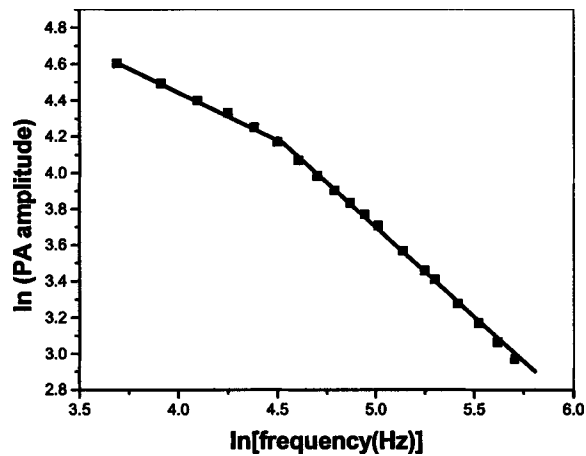In the present investigation, optical radiation at 488 nm and at 50 mW power from an Argon ion laser is chopped

FIG. 1. The amplitude spectrum of the sample PANI:CSA.

FIG. 2. Phase spectrum of all the samples under investigation.

(Stanford Research Systems SR 540) before it impinges on the surface of the sample, which is fixed to the photoacoustic cell cavity with vacuum grease. The output amplitude and phase of the PA signal generated in the cavity was detected using a sensitive electret microphone (Knowles BT 1754) and measured using a dual phase lock-in amplifier (Stanford Research Systems SR 830). Details of the experimental setup are described elsewhere.[9] All the samples under investigation have a thickness of ~600 μm.

According to the theoretical background suggested by Rosencwaig and Gersho on the basis of the thermal piston model,[10] at low frequencies, thermal diffusion is the major mechanism of heat transport in materials. In the low frequency range (f), the thermal diffusion length, $\mu = \sqrt{\alpha_s/\pi f}$ (where α_s is the thermal diffusivity of the specimen under investigation) is greater than the sample thickness and the specimen is said to be thermally thin. It becomes thermally thick with increase in modulation frequency and is characterized by a critical frequency (f_c) in the amplitude spectrum of the PA signal. Figure 1 shows the PA amplitude spectrum for CSA doped PANI. By taking into account the thermoelastic bending of the specimen, due to the temperature gradient existing within the sample, the phase of the PA signal under heat transmission configuration varies as[11]

$$\Phi_{el} \approx \frac{\pi}{2} + \arctan\left[\frac{1}{x-1}\right] \qquad (1)$$

where $x = l_s(\pi f/\alpha_s)^{1/2}$, with l_s as the sample thickness. Thus by using α_s as the fitting parameter in the PA phase spectrum, the thermal diffusivity value of the specimen under investigation can be evaluated.

IV. RESULTS AND DISCUSSION

The present experimental setup is calibrated by evaluating the thermal diffusivity value of aluminium and GaAs. The measured values (0.98 cm^2 s^{-1} and 0.26 cm^2 s^{-1}, respectively, for Al and GaAs) are found to be in agreement with earlier reported values of these specimens (0.99 cm^2 s^{-1} and 0.26 cm^2 s^{-1}, respectively).[12] Thermal diffusivity value essentially determines the rate of heat diffusion through the
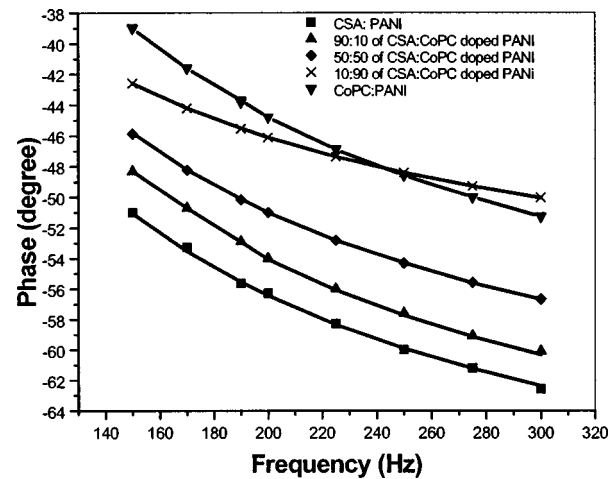
sample and the inverse of thermal diffusivity yields a measure of the time required to establish thermal equilibrium in systems for which a transient temperature change has occurred.[6,9] Figure 2 shows the phase spectrum of all the specimens under investigation. The values obtained for the best fit between the experimental and the theoretical spectrum suggested by Eq. (1) are tabulated in Table I.

From Table I is obvious that CSA doped PANI exhibits maximum value for thermal diffusivity. This can be understood in terms of carrier assisted heat transport mechanism in these materials. Recent studies on conducting polyaniline and other polymers have created a debate on whether its structure is homogenous or inhomogeneous.[13] In general, the conduction processes in conducting polymers is taking place through either hopping or tunneling processes.[14] It has already been reported that the conduction processes in the polyaniline protonated partially with emeraldine can be explained on the basis of interpolaron hopping mechanism.[15] The conduction phenomena in samples protonated with emeraldine base can be explained on the basis of granular polaron model.[16] However, for highly doped polyaniline, as in the present case, the density of charge carriers is approximately equal to the density of protonated charge sites. In such cases, the increase in conductivity (diffusivity) occurs due to three factors; the increased "metallic" content of the sample, a reduction in tunneling/hopping distance between the metallic regions, and the increased charge-carrier density.[4] Polyaniline doped with a sulphonic acid such as

TABLE I. Thermal diffusivity values of the samples under investigation.

Sample	Thermal diffusivity (cm^{2}s^{-1})
PANI:CSA	0.760±0.0004
PANI:CSA (90%) and CoPc (10%)	0.404±0.0003
PANI:CSA (50%) and CoPc (50%)	0.356±0.0002
PANI:CSA (10%) and CoPc (90%)	0.289±0.0003
Co-Pc	0.241±0.0002

camphor sulphonic acid can be classified as an inhomogenously disordered metal comprising of "metallic islands" separated by insulating barriers (metallic island model).[17] However, doping of polyaniline with CSA at this high level (50%) results in interchain coupling and consequently an enhanced ordering between crystalline regions (metallic regions) as well as on the chains bridging the metallic regions. Such an ordering results in the increase of localization length of electronic wave function and hence allows the coherent transport of both heat and electricity. Transport models for three-dimensional amorphous semiconductors have often been used to account for the charge delocalization phenomena in conducting polymers, despite fundamental differences.[18] In conducting polymers the dopant ions are positioned interstitially between chains, whereas in conventional semiconductors they are usually substituted directly into the host lattice.[18] Further, covalent bonding along polymer chains and weak bonding between them result in a quasi-one-dimensional morphology which has an important role in the charge delocalization of these systems.[19] In a relatively ordered crystalline material, as in the present case, protonation of polyaniline with sulphonic acid results in a decrease in hopping distance and consequently enhances the hopping mechanism (phonon-assisted tunneling between electronic localized states centered at different positions).[20] It is difficult to distinguish between different conduction mechanisms such as quasi-1D variable range hopping mechanism,[21] 3D hopping with electron-electron interaction,[22] tunneling between mesoscopic metallic islands [23] or correlated hopping between polaronic clusters in polyaniline.[24] Nevertheless, experimental investigations show that results can be explained very well in terms of the metallic content as well as in terms of dominant hopping/tunneling mechanism. In addition to that, previous x-ray analysis shows that there is a significant degree of crystallinity in PANI:CSA.[25] In these crystalline regions of the polymer, a precise phase order exists between adjacent polymer chains and this is expected to allow coherent carrier transport along and between individual chains. This means that carrier delocalization can occur in more than one dimension, on a scale larger than the average interchain separation.[4] Therefore, the mean-free-path is limited not by scattering at interchain transfer events but by phonon scattering due to thermal motion of the crystal lattice, or by molecular vibrational modes and it become apparent in bulk conductivity of the specimen at room temperature.[4] Therefore, 50% CSA doped polyaniline can be considered as a heterogeneous conductor in which two transport mechanisms such as metallic diffusion within the crystalline regions and temperature activated transport in the disordered region contribute to the conduction mechanism. Hence the increase in mobility of charge carriers with protonation of polyaniline with sulphonic acid results in strong interaction between electrons and phonons due to lattice vibration, especially at room temperature, which in turn results in coherent transport of thermal energy via electron-phonon interaction (polarons). As a result, 50% CSA doped PANI, exhibits highest value for thermal diffusivity.

The effective thermal diffusivity value of composite materials has been reported to depend on the thermal conductivity as well as thermal diffusivity of its constituents.[26] The thermal properties of all the composites are discontinuous functions of the location and consequently neither Fourier's law nor heat conduction equation can be applied.[26] However, the effective thermal parameters, i.e., the properties of equivalent homogeneous material that produces the same physical effects of the specimen under investigation, is of great significance and has wide applications in device fabrication. Eventhough the effective heat capacity follows the mixture rule, it has already been reported that the effective thermal diffusivity of composites depend on the thermal diffusivity of constituents as well as on their relative volume fraction.[26] In the present case also, the composites of CSA doped PANI and CoPc exhibit a thermal diffusivity value, which is intermediate to that of CSA doped PANI and CoPc. This can be ascribed to the existence of interfacial thermal contact resistance between the different constituent phases in a composite as well as on their thermal expansion mismatch.[27] The existence of such thermal barriers results in a lowering of the effective thermal diffusivity of the composite. It is evident from our observations that introduction of 10% CoPc results in large inhomogeneties in the sample, which consequently lowered its thermal diffusivity in a substantial manner. However, further increase in volume fraction of CoPc does not cause considerable variation in their already inhomogeneous distribution and is evident in their thermal diffusivity values. The present analysis shows that the combination of a good thermal diffuser with a bad diffuser can result in composites of intermediate thermal diffusivity value. The measured thermal diffusivity value of CoPc falls in the typical range of the thermal diffusivity of phthalocyanines.[28]

In order to ensure the effective charge transport mechanism in these materials, both dc and ac electrical conductivity measurements were carried out by employing the two probe technique on the specimen placed in a conductivity cell under high vacuum, (10^{-5} Torr) using Keithley Voltage source. The results obtained are tabulated in Table II. It is seen from the table that the variation in electrical conductivity of the samples also follows the thermal diffusivity measurements. However, the order of variation is small in the case of thermal diffusivity as compared to electrical conductivity.[29] This is due to the fact that thermal energy transport mechanism in conducting polymers is dominated by phonon assisted mechanism, whereas electrical conduction is dominated by the variable range hopping process and metallic diffusion of electrons.[30]

The effective thermal parameters of composites depend on the thermal properties of its constituents as well as on the microstructural parameters such as volume fraction of each phase, shape, size, and distribution of the particles. Hence a study on the correlation between thermal diffusivity and hardness of the material was carried out, wherein, the surface hardness of all the specimens under investigation were measured using the indentation technique (Shore D hardness technique). The values obtained for the hardness of the samples under investigation are given in Table II. It is seen from the Tables I and II that there exists an inverse relation between thermal diffusivity and hardness of the specimen, as observed by other researchers.[31] The increase in relative vol-

TABLE II. Electrical conductivity and hardness of the samples under investigation.

Sample	ac conductivity ($\times 10^2$S/m) 100 kHz & 300 K	dc conductivity ($\times 10^2$S/m)	Shore D hardness
PANI:CSA	1.3565	27.892	10
90% PANI:CSA: 10% CoPc	1.0125×10^{-1}	20.484	15
50% PANI:CSA: 50% CoPc	5.4238×10^{-2}	9.6763	18
10% PANI:CSA: 90% CoPc	2.519×10^{-2}	5.9871×10^{-1}	22
CoPc	1.115×10^{-2}	4.1109×10^{-3}	25

ume fraction of CoPc increases the hardness of the material while the increase in interface thermal resistance and thermal barrier resistance causes a decrease in the effective thermal diffusivity value. The present investigation also shows that the variation in volume fraction of the composites allows tunability in their mechanical properties and a correlation of various thermophysical properties of such heterogeneous systems is possible.

V. CONCLUSIONS

In conclusion, a study on the measurement of the thermal diffusivity value of CSA doped PANI and its composites with CoPc using open cell photoacoustic technique are presented. From the present investigation it is clear that, with proper choice of the volume fraction of specimens having different thermal diffusivity, we can modify the effective thermal parameters of the composites. The electrical conduc-tivity measurements substantiate the thermal diffusivity experiment and suggest a decrease in effective carriers for transport of thermal energy with the increase in relative fraction of CoPc in the composite.

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