Chapter 5

Heat Diffusion in Conducting
Polymer Composites

5.1 Introduction

The past few decades witnessed tremendous progress in the synthesis and characterization of conducting polymers. The possibility of synthesizing materials capable of simultaneously presenting the properties of organic polymers and of semiconductors has attracted much interest from both academic and industrial researchers. Of all known conducting polymers, polyaniline, polypyrrole, polythiophene and their substituted forms are the most frequently used in commercial applications. These polymers enjoy long term stability of their conductivity and form composites with optimal mechanical properties. The list of the wide variety of applications of conductive polymers include energy storage devices, sensors, EMI shielding materials, antistatic coatings, displays and radar absorbing materials [1 – 8]. Traditionally these polymers are synthesized by chemical or electrochemical polymerization.

5.1.1 Tailoring processability of polymers

In order to make a polymer technologically viable, the processability and thermal stability of polymers must be improved. The simplest approach to achieve this is copolymerization. The physical properties of conductive
polymers can be tailored by incorporating it into a host polymer so as to form blends, composites or interpenetrated networks. This is a widely used technique to combine the electrical properties of a conductive polymer with the desirable physical properties [9, 10]. Polyaniline and polypyrrole are considered to be the most promising candidates for the fabrication of conductive blends or composites with industrially important polymers [11].

Interpenetrating network conductive composite can be synthesized through in-situ polymerization of monomers of conducting polymers inside the matrices of the conventional linear polymers like polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), etc. Co-processing of conductive polymers with other industrially important polymers can be effected through chemical or electrochemical means. The electrochemical method uses an electrode coated with conventional polymers [12, 13]. Oxidizing agents such as ferric chloride or cupric chloride is introduced into the polymer in chemical polymerization [14 - 16]. The polymer is then exposed to monomer vapour, or to a solution of monomer in appropriate liquid.

Conductive polymer composites and blends have many applications in the field of microwave engineering. They are used as coating in reflector antenna, coating on the frequency selective surface of electronic equipments, electromagnetic shielding material, etc. It is used as a radar absorbing material (RAM) to reduce the radar cross section (RCS) of military aircrafts, so that the vulnerability of the aircraft can be minimized [17]. The microwave absorbing properties of conducting polymers and composites can be tailored by controlling the inter-chain distance and the localization length [18]. The inter-chain distance can be modified by ring substituted monomers or counter anions with different sizes [19, 20]. The localization length can be controlled by changing the defect rates in the polymer [21].
5.1.2 Open Photoacoustic Cell configuration

Photoacoustic (PA) techniques are widely used in material characterization. This non-contact non-destructive technique can be applied to the thermal characterization of a wide variety of conducting polymers. Open photoacoustic cell (OPC) configuration described in chapter 4 is a simple and elegant technique to study thermal properties of materials. The theoretical background of the conventional photoacoustic technique was developed by Rosencwaig and Gersho [22]. The open cell photoacoustic theory was developed by Helander et. al. and was later modified by McQueen et. al. [23 - 27]. In the OPC technique the sample is directly mounted on an electret microphone arranged inside the PA cell, leaving a small volume of air in between the sample and the microphone. Compared to conventional PA methods, large area samples can be analyzed using OPC configuration. The sensitivity and noise immunity is relatively high in this technique.

An outline of the theory of OPC is already given in section 4.1.1 of chapter 4.

5.2 Preparation of Polymer Composites

In this work, the conducting polymers selected for the preparation of polymer composites are polyaniline (PANI) and polypyrrole (PPy). Polyvinyl chloride is selected as the polymer host matrix. Synthesis is carried out so as to form composites of PANI/PVC and PPy/PVC.

5.2.1 Preparation of PANI/PVC

Chemical oxidative polymerization of aniline is carried out using ammonium persulphate as initiator in the presence of 1M HCl and emulsion
grade polyvinyl chloride. The polymerization is carried out for about four hours at room temperature. It is then filtered, washed and dried at room temperature in vacuum for forty eight hours. Different compositions of PANI:PVC composite (3:1, 2:1 and 1:1) are prepared using the above procedure.

5.2.2 Preparation of PPy/PVC

PPy/PVC composite is prepared by polymerization of pyrrole with ferric chloride. The reaction is carried out for twenty minutes at 0 to 5°C. It is then filtered, washed and dried under vacuum for sixteen hours at room temperature. Different compositions (3:1, 2:1 and 1:1) of PPy-PVC composite are prepared as described above.

5.3 Thermal diffusivity measurements

Thermal diffusivity measurements in PANI/PVC and PPy/PVC composites are carried out using OPC technique. The experimental setup of the OPC configuration used in thermal diffusivity measurements is shown in figure 4.2 of chapter 4.

PAN/PVC and PPy/PVC in the powder form are pressed into pellets of diameter 1cm and thickness less than 1mm. Each pellet is mounted on the inlet of the OPC cell using vacuum grease. Intensity modulated radiation (20mW, 632.8nm) from a He-Ne laser (Melles Griot) with beam diameter 0.7mm and divergence 1.2 milliradians is allowed to fall on the sample. A mechanical chopper (Stanford Research Systems SR 540) with a chopping frequency range of 4 Hz to 4 kHz is used for intensity modulation. An electret microphone (Knowles FG 3329) arranged inside the PA cell detects the acoustic waves produced by the PA effect. The microphone output is fed to a lock-in amplifier
(Stanford Research Systems Inc. SR830) for phase sensitive detection of the signal.

The phase of the photoacoustic signal is measured at different values of the modulation frequency. The thermal diffusivity of each sample is computed from the plot of phase versus square root of frequency, taking into account the effect of thermo elastic bending, as already described in section 4.4 of chapter 4.

5.4 Electrical conductivity measurements

In order to study the relation between electrical conductivity and heat transport of the different composites, conductivity measurements are carried out on the composites. For this, polymer samples in the powder form are pelletised to form pellets of about 1cm diameter. Silver paste is coated on either side so as to serve as terminals for applying a DC voltage. V-I measurements are carried out using Keithley Model: 236 Source Measure Unit, keeping the pellets in a conductivity cell. The room temperature electrical conductivity of all the samples are determined from V-I measurements.

5.5 Results and discussion

The dependence of PA phase on frequency for pure PANI is given in figure 5.1. The corresponding plots for the three different compositions of PANI/PVC composite are shown in figures 5.2 - 5.4. The plots for pure PPy and PPy/PVC composites are shown in plots 5.5 – 5.8. The thermal diffusivity values of all the samples computed by curve fitting are listed in table 5.1. As is evident from the table, there is a marked reduction in the rate of heat diffusion for both the composites with increase in the content of PVC.

The values of electrical conductivity computed from V-I measurements for all samples are listed in table 5.2. It is observed that there is a reduction in
electrical conductivity for both PANI/PVC and PPy/PVC composites with increasing content of PVC. Electrical conduction in PANI and PPy takes place through the polarons and bipolarons. The different conduction mechanisms in these polymers are affected by the presence of the host matrix, which is an insulator. As concentration of PVC in the composite increases, conductivity is found to decrease drastically. There is a corresponding reduction in the rate of heat diffusion also. This implies a carrier assisted heat transport mechanism in conducting polymers. Figure 5.9 and 5.10 shows the nature of variations of thermal diffusivity and electrical conductivity with the concentration of PVC in the two composites.

Figure 5.1 Variation of PA phase with frequency for PANI
Figure 5.2 Variation of PA phase with frequency for PANI:PVC = 3:1

Figure 5.3 Variation of PA phase with frequency for PANI:PVC = 2:1
Figure 5.4 Variation of PA phase with frequency for PANI:PVC=1:1.

Figure 5.5 Variation of PA phase with frequency for PPy.
Figure 5.6 Variation of PA phase with frequency for PPy:PVC = 3:1

Figure 5.7 Variation of PA phase with frequency for PPy:PVC = 2:1
Figure 5.8 Variation of PA phase with frequency for PPy:PVC 1:1

Figure 5.9 Variation of thermal diffusivity / conductivity with PVC % in PANI-PVC)
Table 5.1: Effect of composition on thermal diffusivity of PANI/PVC and PPy/PVC.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
<th>Thermal diffusivity (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/PVC</td>
<td>Pure</td>
<td>(3.87 ± 0.02) × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>(1.10 ± 0.01) × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>(7.53 ± 0.02) × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>(5.95 ± 0.03) × 10⁻⁶</td>
</tr>
<tr>
<td>PPy/PVC</td>
<td>Pure</td>
<td>(2.25 ± 0.01) × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>(8.83 ± 0.03) × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>(6.94 ± 0.02) × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>(3.38 ± 0.03) × 10⁻⁶</td>
</tr>
</tbody>
</table>
Table 5.2: Effect of composition on electrical conductivity of PANI/PVC and PPy/PVC.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
<th>Electrical conductivity (Sm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/PVC</td>
<td>Pure</td>
<td>2.04 x 10⁻²</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>2.26 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>4.19 x 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>7.69 x 10⁻⁵</td>
</tr>
<tr>
<td>PPy/PVC</td>
<td>Pure</td>
<td>4.41 x 10⁻²</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>6.20 x 10⁻³</td>
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<tr>
<td></td>
<td>2:1</td>
<td>9.43 x 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>2.41 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Conclusion

Thermal diffusivity measurements of two composites (PANI/PVC and PPy/PVC) synthesized in three different compositions are carried out using the open photoacoustic cell technique. With increasing content of the insulating polymer (PVC) in the conducting polymers (PANI and PPy), the heat diffusion is found to be hindered. Electrical conductivity measurements show a similar reduction in electrical conductivity with increasing content of insulating polymer. Thus it can be concluded that the reduction in thermal diffusivity occurs due to a decrease in the contribution from polaron assisted mechanisms with increasing concentration of the insulating polymer.

References