Synthesis, Characterization and Properties of MgB$_2$ Doped Polyaniline

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ABSTRACT

Present paper reports novel synthesis of MgB$_2$ doped Polyaniline (PAni). PAni is synthesized through oxidative polymerization method using Ammonium Peroxodisulphate and doped by different compositions of MgB$_2$. The DC conductivity of undoped and doped polymers is measured in the temperature range of 300 – 400 K and is found to increase with temperature. An increase in conductivity by five orders of magnitude has been observed after doping. Conduction mechanism was also studied in all of the samples. FT-IR (Fourier Transform Infrared spectroscopy) and Ultraviolet (UV)-Visible studies confirm the occurrence of PAni in conducting emeraldine salt form in the composites. The optical studies signify that absorption mechanism is due to direct allowed transition and the band gap decrease after doping. Thermal stability of all the composites has been explained on the basis of variation in $T_c$–$T_g$ and $\Delta H_c$ by using DSC (Differential Scanning Calorimetry) measurements.

Keywords: Polyaniline, MgB$_2$, Conductivity, DSC, UV-Vis, FT-IR

1. Introduction

As a conducting polymer, Polyaniline (PAni) has showed broad prospect of applications in various fields such as diode, electrochromism, sensor, secondary battery and electromagnetic shielding [1-6]. In spite of various advantages, PAni has received limited applications because it is neither completely soluble nor fusible in organic solvents as well as water. The development of PAni with better solubility in common solvents was first achieved by Cao et al. [7-9]. The chemistry of PAni is generally more complex with respect to other conducting polymers, due to their dependence on both the pH value and the oxidation states. The most important EB form of PAni gives ES form on its protonation by means of H$^+$, which is merely responsible for the strong increment of the conducting properties [10]. Conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in a variety of electric and electronic devices. It has been observed that such composites can exhibit some novel properties such as positive temperature coefficient of resistance (PTC) and piezoresistivity [11], which are not found in the host polymer. In the quest for superior performance, PAni has been combined with different materials to obtain a
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promising performance like PAni/Au, PAni/Ag, and PAni/CNTs etc. Meanwhile the combination of PAni with inorganic materials has also been done in order to obtain organic/inorganic heterojunctions with special combining properties which could be difficult to obtain separately with individual components. MgB$_2$ is of great significance for the practical applications due to its good structural, physical and magnetic properties. Its simple metallic structure with the cheap raw materials makes it highly competitive among the other superconducting materials including conventional ones. MgB$_2$ materials have not only shown great importance for the electronics sector, but also a possible fabrication of many kilometres of wires, tapes and cables because of the lower cost and simpler fabrication process[12]. The combination of PAni with MgB$_2$ may result in enhanced properties of both of the components. We premeditated and successfully synthesized PAni/MgB$_2$ in different compositions at room temperature. In the present article, the synthesis of PAni Composites with bulk MgB$_2$ and their electrical, optical and morphological properties were studied systematically.

2. Materials and Methods

2.1 Materials

Aniline (Mercer India, AR grade) was used after double distillation. Hydrochloric acid (Qualigen Fine Chemicals, India, LR grade), Ammonia solution in water (99%, Merck India), Ammonium peroxydisulfate (APS) (Merck India, AR grade and MgB$_2$ (Mercer India) were used as received without further purification.

2.2 Synthesis and Doping of PAni

PAni was synthesized by chemical oxidation method. In this procedure ammonium peroxydisulphate was taken as an oxidizing agent in aqueous acid solution. After polymerization a green salt (emeraldine salt) was obtained which was the conducting form of PAni. This emeraldine salt was converted into insulating blue emeraldine base by treatment with liquid ammonia [13]. The ultimately dried emeraldine base was then chemically doped with different concentrations of MgB$_2$. MgB$_2$ dissolved in Tetra hydro furan (THF) was added to swollen PAni (Swollen by the effect of solvent) and stirred for 24 h at room temperature in different ratios (80:10, 82:08, 84:06, 86:04, and 88:2 by weight). The doped PAni was then dried and finally ground for making the samples. Samples were prepared in the form of pellets by using hydraulic press at a pressure of 770 kPa.

2.3 Characterization

Scanning Electron Microscopy (SEM) was used to study the morphology of the sample using JEOL JSM 6380 SEM at 10 KV. Conductivity of the composites was measured in the temperature range of 300-400 K. Samples in the form of pellets were mounted between the two steel electrodes, fixed inside a metallic sample holder for conductivity measurements. Annealing of the samples was done before conductivity measurements at a vacuum of $10^{-3}$ Torr for 1h in order to avoid the effect of moisture absorption. The temperature measurements were done through the calibrated chromel alumel thermocouple. The voltage of 1.5V (through regulated dc supply) was applied to the pellet and the resulting current was measured with a Keithley Electrometer model 6157A. The polymer was dissolved in THF to carry out UV-Visible absorption spectra using a Camspec M-550 double beam scanning UV-Visible spectrophotometer. FT-IR spectra of undoped and doped PAni-KBr pellets were obtained by using Perkin-Elmer FT-IR spectrometer in the range from 400 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. Thermal study was carried out by Differential Scanning Calorimeter (DSC) (Model-DSC plus, Rheometric Scientific Co. UK). The temperature precision of this equipment is ±0.1 °C. DSC scans were taken for undoped and MgB$_2$ doped samples at 10°C/min heating rates. The temperature range covered in DSC was from room temperature to 180°C.
3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

SEM micrographs of MgB$_2$ doped PAni are shown in Figure 1. As shown by image a, pure PAni is observed to be irregular and clew like, while for PAni/MgB$_2$ composites, more regular and ball-shaped particles are observed. For instance, when the weight content of MgB$_2$ is about 8%, as shown by image b, more regular and smaller particles are displayed. Interestingly, the smaller size favours the intercalation/de-intercalation process of the MgB$_2$ into PAni and the discharge capacity drops more or less linearly with increasing the particle size. Figure 1 c & d show SEM image of 10 wt% doped sample at different magnifications.

3.2 DC Conductivity Measurements

The doping of conducting polymers implicates charge transfer, the associated insertion of a counter ion and the simultaneous control of Fermi level or chemical potential. Through doping electrical and optical properties of conducting polymers can be controlled over a long range [14]. The Arrhenius plot of conductivity vs. temperature of pure and doped PAni composites with different MgB$_2$ concentrations is given in Figure 2.

![SEM images of MgB$_2$ doped PAni](image)

**Figure 1:** Scanning Electron Micrographs of MgB$_2$ doped PAni; (a) Pristine PAni; (b) 8% (w/w) doped; (c) & (d) 10% (w/w) doped PAni at different magnifications.

**Figure 2:** Temperature dependence of DC conductivity in the temperature range (300-400) K for undoped PAni and PAni doped with different concentrations of MgB$_2$. 
Here the temperature dependence of DC conductivity is measured using the Arrhenius relation

$$\sigma = \sigma_o e^{-\left(\frac{\Delta E}{k_B T}\right)}$$

where $\Delta E$ is the activation energy, $\sigma_o$ is the pre-exponential factor and $k_B$ is the Boltzmann constant. The Arrhenius plots show good straight line behaviour implying that the charge transport is mainly by band conduction. The DC conductivity of undoped PAni (emeraldine base) measured at 350 K was $3.41 \times 10^{-12}$. After doping with different concentrations the conductivity changed and is found to be of the order of $10^{-8}$–$10^{-7}$ S/cm. The value of DC conductivity continues to increase with increase of MgB$_2$ content up to 10% by weight. The DC conductivity and activation energy are plotted against concentration and shown in Figure 3.

The activation energy decreases on increasing the dopant percentage whereas the DC conductivity increases with the dopant percentage. The calculated values of $\sigma$, $\sigma_o$ and $\Delta E$ are calculated and given Table 1.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Samples</th>
<th>DC conductivity $\sigma$ [S cm$^{-1}$]</th>
<th>Activation energy $\Delta E$ [eV]</th>
<th>Pre-exponential factor $\sigma_o$ [S cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Undoped PAni</td>
<td>$3.41 \times 10^{-12}$</td>
<td>0.462</td>
<td>$1.48 \times 10^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>2% doped PAni</td>
<td>$7.16 \times 10^{-8}$</td>
<td>0.305</td>
<td>$1.97 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>4% doped PAni</td>
<td>$7.32 \times 10^{-8}$</td>
<td>0.059</td>
<td>$2.77 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>6% doped PAni</td>
<td>$7.17 \times 10^{-8}$</td>
<td>0.046</td>
<td>$3.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>8% doped PAni</td>
<td>$1.65 \times 10^{-7}$</td>
<td>0.043</td>
<td>$6.85 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>10% doped PAni</td>
<td>$5.35 \times 10^{-7}$</td>
<td>0.028</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

According to the results, the electrical conductivity of PAni/MgB$_2$ composite was elevated by increasing the MgB$_2$ content in samples. A maximum conductivity was obtained for PAni/MgB$_2$ hybrid systems with MgB$_2$ content of about 10 wt% in composite materials. It is well known that the electrical conductivity of PAni depends on molecular weight of chains, oxidation state, and percentage of doping and dopant type [15]. Interchain and intrachain hopping have important effects on the charge carrier transport in polymers. The conformation and arrangement of polymer chains determine the carrier mobility in
polymer. It can be inferred here that under the effect of MgB$_2$, PANi has an extremely oriented structure. Highly oriented PANi chains can reduce the barriers of interchain and intrachain hopping and allow the carrier to move easily because of the high conjugation. The concentration dependent DC conductivity and activation energy values of all samples are shown in Figure 2. An increase in DC conductivity with corresponding decrease in activation energy is found to be associated with a shift of Fermi level in doped samples. From a single value of activation energy, it is clear that the conduction is through the carrier concentration at the Fermi level. But the activation energy ($\Delta E$) alone does not provide any information whether the conduction takes place in extended states or by hopping in localized states. This can be explained on the basis of the values of pre-exponential factor ($\sigma_\circ$) [16]. According to Mott and Davis [17, 18] value of $\sigma_\circ$ in the range $10^3$–$10^4$ S cm$^{-1}$ indicates that the conduction takes place mostly in extended states. In the case PANi/MgB$_2$, the values of $\sigma_\circ$ are found to dwell between the orders of $10^{-5}$–$10^{-7}$. Therefore, the conduction takes place by the hopping process due to wide range of localized states present in the sample. It may be determined from the observations that hopping mechanism is responsible for conduction in all of the composites. An increase in the density of defect states is specified by a smaller value of $\sigma_\circ$, concluding that the conduction mostly takes place by hopping process in all the composites.

3.3. UV-Visible Studies

UV–Visible absorption spectroscopy was performed to evaluate the mid gap state availability of the polymeric composites stimulated by charge transfer. The sample powder was dissolved in THF to record UV-Visible absorption spectra using a double beam scanning UV-visible spectrophotometer. The UV-Visible absorption spectra of the undoped and doped polymer in THF are shown in Figure 4. It showed that absorbance varies with dopant concentration. Band gap can be evaluated from the absorption spectra.

The relation between the optical band gap ($E_g$), absorption coefficient ($\alpha$) and the energy ($h\nu$) of the incident photon is given by [19, 20]-

$$(\alpha h\nu) \propto (h\nu - E_g)^n,$$

where $n = 1, 2, 3$

It was found that all the composites are obeying direct transitions. $(\alpha h\nu)^2$ vs energy of powders at different concentrations have been plotted (Figure 5), which show a very good straight line behaviour and the value of $E_g$ is calculated by taking the intercept on the X-axis. The extinction coefficient $k$ is given by $k = \alpha\lambda/4\pi$, and has been estimated at the wavelength 550 nm. The absorption spectra of all the samples show two absorption peaks, one is near 290 nm and the other is at 360 nm. The peak at 380 nm arises from $\pi \rightarrow \pi^*$ electronic transitions within benzenoid segments of the polymer which has a small red shift with doping concentration. The red shift of above said peaks proved the delocalization of charge through PANi chain, as it is known that the semiconductor materials having dimensions smaller than the Bohr radius of the exciton produce the absorption edge to red shift [21].

![Figure 4: UV-Visible absorption spectra of MgB$_2$ doped PANi at different doping concentrations (w/w) %](image-url)
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Figure 5: \((\alpha h v)^2\) vs photon energy of PAni/bulk-MgB₂ at different doping concentrations

From this the interaction of dopant with PAni is clearly evident. The band gap is found to decrease after doping, but it increases on increasing the dopant concentration. The values of band gap and extinction coefficient are given in Table 2.

Table 2: Optical parameters for PAni/MgB₂ at wavelength 550 nm

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Dopant %</th>
<th>Absorption coefficient</th>
<th>Optical band gap ((E_g)) [eV]</th>
<th>Extinction coefficient ((k))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0% doped PAni</td>
<td>2140</td>
<td>3.5</td>
<td>0.018</td>
</tr>
<tr>
<td>2.</td>
<td>2% doped PAni</td>
<td>3860</td>
<td>2.5</td>
<td>0.033</td>
</tr>
<tr>
<td>3.</td>
<td>4% doped PAni</td>
<td>1965</td>
<td>2.6</td>
<td>0.017</td>
</tr>
<tr>
<td>4.</td>
<td>6% doped PAni</td>
<td>1500</td>
<td>2.8</td>
<td>0.013</td>
</tr>
<tr>
<td>5.</td>
<td>8% doped PAni</td>
<td>2900</td>
<td>2.7</td>
<td>0.025</td>
</tr>
<tr>
<td>6.</td>
<td>10% doped PAni</td>
<td>4466</td>
<td>2.9</td>
<td>0.039</td>
</tr>
</tbody>
</table>

3.4 FT-IR

FT-IR spectra have been obtained for all the samples. The spectra of PAni doped with different MgB₂ levels are shown in Figure 6.
The spectrum of PANi shows five major vibration bands: 1560-1610 (stretching vibration of quinoid ring), 1470-1510 (stretching vibration of benzene ring), around 1300 (stretching vibration of C-N), around 1140 (characteristic vibrational mode of quinoid ring) and around 830 cm⁻¹ (out-of-plane bending vibration of C-H on para-disubstituted rings) [22]. We did not observe splitting of PANi bands after doping. So the observed bands correspond to PANi absorptions only. However, the incorporation of MgB₂ in the polymer leads to small shifts of some FT-IR peaks of PANi with reduced peak intensity. The intensity of the peaks follows the same pattern showed by DC conductivity and band gap measurements. The reduced peak intensity may result from the interaction between PANi and MgB₂ even when there are only small amounts of MgB₂ in the composites.

3.5 DSC Analysis

The glass transition temperature \( (T_g) \), crystallization temperature \( (T_c) \) and enthalpy of crystallization \( (\Delta H_c) \) for the PANi doped with different concentrations of MgB₂ are determined by DSC study under non-isothermal conditions at heating rate of 10 °C/min. In the evaluation of thermal parameters systematic error of instrument has been mooted. Typical DSC curves for different samples are shown in Figure 7. In the DSC thermograms of all samples, two endothermic and one exothermic peaks were observed. The first endothermic hump corresponds to glass transition, which arises due to an abrupt increase in specific heat of the sample.

Figure 7: DSC curves for all samples at heating rate 10°C/min (a) Undoped, (b) 2%, (c) 4%, (d) 6%, (e) 8%, (f) 10% MgB₂ doped PANi samples
The observed exothermic peak has been generally attributed to cold crystallization (T_c) or a cross linking reaction of the polymer. The endothermic peak corresponds to the glass transition temperature T_g and the exothermic peak corresponds to the crystallization temperature T_c. Estimated values of T_g, T_c and ΔH_c are given in Table 3.

Table 3: Thermal parameters of all samples at heating rate 10°C/min

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Samples</th>
<th>T_g [°C]</th>
<th>T_c [°C]</th>
<th>ΔH_c [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0% doped PAni</td>
<td>51.88</td>
<td>109.36</td>
<td>200.22</td>
</tr>
<tr>
<td>2.</td>
<td>2% doped PAni</td>
<td>59.52</td>
<td>120.36</td>
<td>110.06</td>
</tr>
<tr>
<td>3.</td>
<td>4% doped PAni</td>
<td>61.68</td>
<td>124.70</td>
<td>107.07</td>
</tr>
<tr>
<td>4.</td>
<td>6% doped PAni</td>
<td>63.02</td>
<td>128.36</td>
<td>106.05</td>
</tr>
<tr>
<td>5.</td>
<td>8% doped PAni</td>
<td>61.02</td>
<td>131.53</td>
<td>98.45</td>
</tr>
<tr>
<td>6.</td>
<td>10% doped PAni</td>
<td>65.02</td>
<td>136.70</td>
<td>94.97</td>
</tr>
</tbody>
</table>

The second endothermic peak observed for composites, at about 300 °C, is related with the degradation process due to strongly bonded water and/or organic molecules coming from the solvent being removed from the structure of the polymer. It is considered that the shift to higher temperatures observed in this peak by doping may be due to small increase in the crystallinity of undoped PAni, which itself is a semicrystalline conducting polymer. Possible morphological changes (such as changes in the degree of crystallinity and interactions at a molecular level) in the structure of PAni as a result of doping process could be another factor. Thermal stability of the samples has been ascertained through the T_c–T_g difference and the maximum value of T_c–T_g is observed for 10% (w/w) doped samples. Therefore, 10% (w/w) doped PAni/MgB_2 is the most stable composition among all of the composites, which is also confirmed from T_c–T_g plots. The change in enthalpy and T_c–T_g versus dopant concentration is shown in Figure 8.

\[ \Delta H_c = KA/m \]

Where A is the area of crystallization peak, m is the mass of sample and K is the instrument constant which is found to be 1.2. It is observed that ΔH_c decreases with the increase in MgB_2 concentration because the samples being in the metastable state try to minimize their enthalpy as well as Gibbs free energy at every temperature by elementary atomic motion to gain stability. As the most stable composite already possesses a stable atomic configuration, hence it will release the least energy to gain stability. Therefore, the most stable composite will have the least value of ΔH_c. In present case least value of ΔH_c corresponds to 10% (w/w) doped sample. Hence this composition (10% (w/w)) is most stable among all of the composites.

4. Conclusions

PAni/MgB_2 composites have been successfully synthesized in different compositions. Temperature dependence of DC conductivity of all the PAni/MgB_2 samples has been studied. Increase in the conductivity by five orders of magnitude is discovered after doping. The optical studies indicate that the absorption mechanism is due to direct transition and the optical band gap decreases after doping. From FT-IR spectra it was evident...
that the structure of PAni does not change after doping. Thermal stability of all the samples has been explained on the basis of variation in $T_c-T_g$ and $\Delta H_c$, which confirms that 10% (w/w) doped sample is most stable among all the composites.

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**How to Cite this Article:**


**References**


