Effect of Temperature on the Polymerization and Optical Conductivity of Thin Flexible Polypyrrole/Starch Composites

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Abstract: Conductive PPY/Starch (PS) composites were prepared at varying temperature by in situ polymerization method. These polymerized materials were subjected to various studies viz. UV-Vis, FTIR, and XRD to study their effective interaction with each other. The impact of polymerization temperature on the optical conductivity of all the fabricated materials and individual components were studied, these studies shows the increased amount of conductive PPY in the composites leads towards higher optical conductivity of fabricated composites. The PPY/Starch composite synthesized at 0±1°C was observed to have the optical band gap of 4.9 eV and optical conductivity of ~2.8×10⁸ S⁻¹ at 290 nm, which is decent for a material to be used as an optical conductive and hence the proposed material find its application in diverse field of energy storage.

Introduction: Because of their effective electrical, magnetic, electronic, optical, biomedical etc. properties conjugated polymers such as polypyrrole (PPY), polyaniline (PANI) polythiophene (PTh) and polyindole (PIN) had emerged as promising materials for fabrication of electrode material for energy storage devices [1]. These conducting materials had been the most extensively studied material for their diverse properties and are employed for their various commercial application as in batteries, sensing, energy storage, optoelectronics, solar cells, etc. Band gap is a one of the most important factor for determining the above mentioned application of these material for their diverse field. The excitation of the electrons (from valence to conduction band is important for optical conduction which is significant for measure the band gap [2]. Subjected to its unique properties like facile polymerization, extended conjugation, tunable/engineered conductivity, and physical stability [3], polypyrrole (PPY) is one of the most attracted conducting material between its competitors for optical applications.

Copolymers of PPY along with poly(ε-caprolactone) and poly(ethyl cyanoacrylate) [4, 5] Polypyrrole-polylactic acid blend [6] had also been employed for various studies. Polymer nanocomposites (PNCs) were fabricated in presence of inorganic nanofiller (ZnO nanorods) with sago starch [7]. Similarly the PPY/starch nanowires had been electrochemically transformed to a stable high surface area sustenance for certain catalysts [8]. Antonio J.F. Carvalho also had defined starch as a substrate for synthetic polymers [9], starch along with conducting polymers viz., PANI, PPY etc had been applied for various aspects [10-13]. Similarly conductive composite based on polyaniline and starch were prepared by template polymerization [14].

Effect of application of heat on the optical properties of Sr₇₀₋₇₋₃₋₁₋₄₋₁₋₉₋₁₋₉ was studied by Mohammed et al. 2018, application of variation of the temperature consequences in diminution of the band gap hence increasing the optical performance of the material [15]. Mudila et al. 2014, had investigated the effect of temperature variance on the electrochemical
performance of PPY over stainless steel in 0.1 M KOH electrolyte, suggesting considerable effect of reduced temperature (10±1 °C) on the electrochemical performance of the electroactive material [16]. Similar results were achieved by Kassim et al. 2002, decrease in conductivity (26.26-0.04 S/cm) with increase in polymerization temperature (1.2-59.8 °C) [17]. Thus suggesting pronounced effect of polymerization temperature over properties of the electroactive polymer. This article is an attempt to study the optical conductivity of PPY-starch (PS) composites where PPY were polymerized at varying temperature thus defining the effect of temperature on polymerization as well on the optical conductivity.

Experimental:

Material and Method:

Starting material: Pyrrole (PPY, 99%) was procured from Sigma Aldrich, starch (soluble, corn) was obtained from Oxford Lab. India, Glycerol, H₂O₂ (30%, mol), H₃PO₄) were obtained from Merck.

Preparation of Polypyrrole/Starch Composites: 2g corn starch was gelatinized with 40 ml of water in a beaker at 75±1°C for ½ hr [18], to which Glycerol (as plasticizer, 30% w/w) was poured in the process, this heat-induced breakdown of starch granules in water is termed as gelatinization. To the above obtained slurry pyrrole (PY, 2g, 2.98×10⁻³ mol), H₂O₂ (2ml), H₃PO₄ cat. (10%, w/w) were charged, and were allowed for constant mechanical stirring @ 600 rpm over different condition of reaction temperature (Table-1) [19].

| Composite | Reaction Temperature (°C) | Polymerisation Time (hr) | Inference (Colour) | Optical Conductivity (×10⁻⁸ S⁻¹) |
|-----------|--------------------------|--------------------------|--------------------|---------------------------------|
| PS-1      | 100±1                    | ~½                       | Black              | ~1.2                            |
| PS-2      | 50±1                     | ~2½                      | Black              | ~2.1                            |
| PS-3      | 0±1                      | ~24                      | Black              | ~ 2.8                           |

The obtained polymerized products were poured to mold and were dried in vacuum oven at 50±1°C/400 mm Hg over 24 hr. The flexible films were peeled off and used as electrodes. Stejskal et al. 1998 and Jain et al. 2006, suggest that with increasing temperature the time required for PANI polymerization is reduced which supports the current investigation [20, 21], similar trend was observed in case of insitu polymerization of PPY in starch.

Results and Discussion:

FTIR: ATR-FT-IR of pyrrole, starch and composite were done on JASCO ATR PRO 450-S/470-H spectrophotometer. PPY demonstrate its characteristic peaks. The spectra for all composites shows all the important peaks of PPY and starch. Broad peaks in the region of 3450-3000 cm⁻¹ was regarded to bonded –OH of starch. Peak near 1500 cm⁻¹ tallies to C–N str. vibration present in the PY ring, while broad peak from 1390 - 1240 cm⁻¹ shows the C–H/ C–N in–plane def. styles, while band peaks from 1200 cm⁻¹ and lower are bending vibration of PY ring. While peaks near at 1690 cm⁻¹ are affected by C-O vib. of hydroxypyrrole (fig 1a) [13].
X-ray diffraction (XRD): XRD patterns of samples were studied over Rigaku-Geigerflex X-Ray Diffractometer using Cu-Kα radiation at room temperature. XRD analysis of the as synthesized composites depicts the amorphous nature of the materials. The as prepared composites clearly shows the presence of both the components in them. Addition of PY to starch in the composites doesn’t affect the semicrystalline nature of the later in great manner, however the amorphous behavior was found to decrease with polymerization temperature. Also the multiple peaks present in starch get merge with polymer. Peaks at 2θ=22.5° was prominent for all the prepared composites suggesting polymerization with complete entanglement (fig 1b).

UV-Vis analysis: PPY and PS composites were subjected for UV-Vis studies, PPY show a great hump at ~ 450 nm (π-π* transition) due to transition between bipolaron/polaron energy levels, while a shorter hump is observed at near 310 nm. When PY monomer is polymerized in starch the peak at ~ 450 had shifted to higher wavelength ~ 480 nm showing significant effect of starch on the electronic excitations (fig 2a).

Optical conductivity and energy band gap: Optical conductivity is an intrinsic property of any material, optical conductivity of any material depends upon the optical band gap (measured in eV) between the two levels i.e. conduction band (CB) and valance band (VB). For a particular conducting or semiconducting material band gap plays a key role for application of the material in different fields. To conclude the optical band gap and other optical parameter of the samples the UV-vis spectra were studied. The optical band gap of the samples were ascertained through following relation:

\[ \alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad ----- (1) \]
Fig 2. (a) UV-Vis spectra of PS composite (b) Energy band gap of PS composite

Where “α” represents the absorption coefficient of material, term “\(h\nu\)” represents the energy of incident photon, “A” is a constant and “\(E_g\)” is subjected material’s optical band gap. The optical band gap for a material can be assessed by extrapolation of the graph available by employing equation 1. The optical band gap of the composites was observed to be increasing with increasing polymerization temperature. The photon energy range of various material was found in between 4.9 to 5.3 eV (fig. 2b) which suggest the possibility of generating optical conductance by the as prepared materials so that can be used in various field viz. like blue laser diode, UV LED’s etc.

Fig. depicts the relation between extinction coefficient (\(\varepsilon\), designates the extent of light lost due to scattering) and incident photon energy (\(h\nu\)), \(\varepsilon\) can be estimated by following relation, which is the measure of absorption of light by the material which is in turn related to adsorption coefficient (α) of the material.

**Extinction coefficient:** is the measure of light absorption by and optical active material. extinction coefficient of the material can be assessed by following equation:

\[
K = \frac{\alpha \lambda}{4\pi}
\]  

Where, “K” represents the extinction coefficient, “α” embodies is absorption coefficient while, “\(\lambda\) is wavelength of incident light. It is observed (fig 4) that the extinction coefficient gives a hump at near 4.5 eV, while it decreases afterwards which again increases steeply after 5.2 eV this suggest that the loss of photon due to scattering decreases.
Refractive Index: RI of the prepared samples was extracted by following relation:

\[ n = \frac{1}{T_s} + \left( \frac{1}{T_s} - 1 \right)^{1/2} \]  \hspace{1cm} (3)

Where \( T_s \) is % transmission coefficient and \( n \) is RI, a normal dispersion property was observed for the sample as the RI decreases with increasing photon energy which represent the interaction between photon and \( \pi \) electrons. This corresponds towards the low transmittance and high absorption coefficient thus suggesting the application of the fabricated material in the arena of optoelectronics.

**Dielectric properties**: This represents the dielectric behavior which depends upon the internal property of the material, where the real part (fig 4a) of the dielectric constant tells about the decrease in speed/velocity of the incident light striking the and light, meanwhile the imaginary part (fig 4b) of dielectric constant designates the absorption of the energy from an electric field due to dipole motion present in the material. Following relationship generates the dielectric constants:

\[ \varepsilon_r = n^2 - k^2 \]  \hspace{1cm} (4)

\[ \varepsilon_i = 2nk \]  \hspace{1cm} (5)

Where, “\( n \)” is RI (refractive index), and “\( k \)” is extinction coefficient, “\( \varepsilon_r \) and \( \varepsilon_i \)” are real and imaginary part of dielectric constant of optical active material. The ratio of the two dielectric constant (imaginary : real) provides us the photon loss factor. The real dielectric constant found to get decrease with the increase in photon energy in higher region while in lower region it get reduces steadily, also the imaginary dielectric constant was observed to decreases steadily with rise in the photon energy especially for PS-3.
Following relation is employed for evaluation of optical conductivity ($\sigma$) which suggest the optical response of the as fabricated material.

$$\sigma = \alpha nc/4\pi \quad \text{(6)}$$

where, “c” represents the velocity of light, “n” is RI and, “$\alpha$” represents absorption coefficient. From fig. 5 it can be depicted that PS-2 is having highest optical conductivity (~$2.8\times10^8$ S$^{-1}$ at 290 nm) among all the variants, the optical conductivity was highest for the composite prepared at reduced temperatures, it is observed from the results that the optical conductivity is directly dependent upon refractive index and absorption coefficient, which were again found to be highest for PS-3 composite.

**Conclusion:** Amorphous, conductive, *in situ* polymerized, PPY-starch composite were fabricated at varying temperature condition as to find their optical conductivity and hence their application. XRD analysis was performed to confirm the nature of the fabricated material which suggest its
amorphous nature. Uv-Vis studies shows π-π* electronic transitions, while FT-IR suggest the complete entanglement of both the material in the composite. The studies related to dielectric constant, refractive index and extinction coefficient suggest the superiority of PS-3 over the other two suggesting that low temperature polymerization induces higher degree of polymerization and low band gap (4.9 eV) while an optical conductivity of ~2.8×10^8 S/m at 290 nm was recorded. This material can find its application in optoelectronics and specially LEDs.

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