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Research Article

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Posted Date: October 7th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10802740/v1>

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Additional Declarations: No competing interests reported.

Synthesis-Temperature-Driven Evolution of Structural, Optical and Charge Transport Properties in Polypyrrole–Polyvinyl Alcohol Nanocomposites

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Abstract: This study presents a systematic investigation of the influence of synthesis temperature on the structural, optical and charge transport properties of polypyrrole–polyvinyl alcohol (PPy–PVA) nanocomposites prepared by in situ dispersion polymerisation. Films synthesised at 5 °C, 25 °C and 50 °C were characterised by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, UV–Visible absorption spectroscopy and electrical transport measurements. SEM analysis reveals predominantly spherical nanoparticles with mean diameters of 50 ± 5 nm, 75 ± 6 nm and 92 ± 7 nm at 5, 25 and 50 °C, respectively. The resolved PPy-related diffraction feature becomes progressively sharper with increasing synthesis temperature, and the apparent crystallite size increases from 5.8 ± 0.5 nm for Film 2 to 8.7 ± 0.6 nm for Film 3. FTIR analysis indicates interactions between the PPy and PVA components, with changes in the hydroxyl-related spectral features suggesting the involvement of Fe³⁺-mediated coordination. Tauc plot analysis yields optical band gaps of 2.08 ± 0.03 eV, 1.82 ± 0.03 eV and 1.72 ± 0.03 eV, decreasing monotonically with synthesis temperature. Room-temperature in-plane conductivity increases correspondingly from $(5.6 \pm 0.4) \times 10^{-2}$ S cm⁻¹ to $(19.1 \pm 0.8) \times 10^{-2}$ S cm⁻¹. Statistical analysis of temperature-dependent conductivity using Mott's variable-range hopping (VRH) model reveals a transition in charge transport dimensionality from two-dimensional (2D) VRH at 5 °C to three-dimensional (3D) VRH at 25 °C and 50 °C. These results establish a coherent, quantitative correlation among synthesis temperature, nanoparticle morphology, crystallite size, optical band gap, DC conductivity and hopping dimensionality, underscoring the potential of PPy–PVA nanocomposites for flexible electronics, optoelectronic devices and chemical sensing.

Keywords: Polypyrrole; polyvinyl alcohol; nanocomposite; synthesis temperature; variable-range hopping; Scherrer analysis; optical band gap; charge transport dimensionality.

1. Introduction

Conducting polymers have attracted sustained research interest because they combine the electronic properties of semiconductors with the processability and mechanical flexibility of polymers. Their tunable electrical, optical and electrochemical characteristics have led to applications in flexible electronics, energy storage devices, chemical sensors, electromagnetic interference (EMI) shielding, actuators and biomedical systems [1–5, 30, 33, 41]. In recent years, research has increasingly focused on understanding how synthesis and processing conditions influence the structure–property relationship of conducting polymers, as microstructural evolution during polymerisation plays a decisive role in determining their electrical performance [41, 16].

Among the family of intrinsically conducting polymers, polypyrrole (PPy) is one of the most extensively investigated owing to its facile synthesis, environmental stability, reversible redox behaviour and relatively high electrical conductivity [6, 41]. PPy can be synthesised by either chemical or electrochemical oxidation of pyrrole monomers [7, 8]. Chemical oxidative polymerisation using ferric chloride (FeCl_3) as the oxidant is attractive because of its simplicity, scalability and compatibility with aqueous processing [35, 36, 41]. Despite these advantages, pristine PPy suffers from poor mechanical strength, limited film-forming ability and negligible solubility in common organic solvents, restricting its processability and practical applications [6]. Incorporation of PPy into suitable polymer matrices has therefore emerged as an effective strategy for improving its mechanical integrity while preserving its electrical functionality. Among various host polymers, poly(vinyl alcohol) (PVA) is especially attractive because of its excellent film-forming ability, hydrophilicity and compatibility with oxidative polymerisation [11, 12, 16]. Besides acting as a mechanically robust matrix, PVA functions as a steric stabiliser that regulates particle nucleation and growth, thereby influencing the morphology and dispersion of PPy nanoparticles within the composite. Such characteristics make PPy–PVA nanocomposites an excellent model system for investigating the influence of synthesis conditions on microstructural evolution and electronic transport.

Electrical conduction in PPy-based composites is governed by the combined contributions of carrier transport along conjugated polymer chains and thermally activated hopping between neighbouring conducting domains [13]. Since chemically synthesised PPy possesses a heterogeneous microstructure comprising ordered conducting regions embedded within disordered domains, charge transport is strongly influenced by crystallinity, particle connectivity and structural disorder [13, 27, 41]. Under such conditions, Mott's variable-range hopping (VRH) model provides an effective description of carrier transport, with the hopping dimensionality reflecting the connectivity of the conducting network and the degree of electronic localisation within the material [27]. Consequently, synthesis parameters capable of modifying the microstructure are expected to influence not only the magnitude of electrical conductivity but also the dominant transport mechanism.

Among the various synthesis parameters, polymerisation temperature plays a particularly important role because it directly influences reaction kinetics, particle growth and structural ordering. Recent studies have shown that synthesis conditions such as oxidant concentration, dopant chemistry, pH and polymerisation temperature significantly affect the morphology and electrical properties of PPy-based composites [2,31,32,34,37,41]. Nevertheless, most investigations have focused on optimising conductivity or application-specific performance, while comparatively fewer studies have attempted to establish quantitative correlations between synthesis-induced microstructural evolution and the corresponding charge transport behaviour [2,41]. Systematic investigations linking synthesis-temperature-induced microstructural evolution with crystallite size, optical band gap, electrical conductivity and hopping dimensionality in PPy–PVA nanocomposites remain limited.

Motivated by this gap, the present work investigates the influence of synthesis temperature on the structural evolution, optical response and charge transport behaviour of PPy–PVA nanocomposites synthesised by *in situ* oxidative dispersion polymerisation at 5, 25 and 50 °C. Structural and morphological changes are correlated with optical and

electrical characteristics to establish a comprehensive processing–structure–property–transport relationship. Emphasis is placed on identifying the dominant hopping mechanism through statistical analysis of temperature-dependent conductivity data and relating the observed transport behaviour to synthesis-temperature-induced microstructural evolution. This integrated analysis provides a mechanistic understanding of how synthesis temperature regulates the conducting network in PPy–PVA nanocomposites and offers useful guidelines for designing conducting polymer materials with tailored electronic properties.

2. Experimental

2.1. Materials

Pyrrole monomer ($\geq 99\%$, Sigma-Aldrich) was purified by repeated vacuum distillation immediately before use and stored under nitrogen at $-20\text{ }^{\circ}\text{C}$ to prevent aerial oxidation. Poly(vinyl alcohol) (PVA; $M_w \approx 72\,000\text{ g mol}^{-1}$, degree of hydrolysis $\geq 98\%$, Merck) was used as the stabilising matrix. Ferric chloride (FeCl_3 , anhydrous, $\geq 99\%$), hydrochloric acid (HCl , 37%) and all other reagents were of analytical reagent grade and used without further purification. All solutions were prepared in triple-distilled water with a resistivity of $18.2\text{ M}\Omega\text{ cm}$.

2.2. Synthesis of PPy–PVA Nanocomposite Films

PPy–PVA nanocomposites were prepared by in situ oxidative dispersion polymerisation. In a typical synthesis, PVA was dissolved in 100 mL of deionised water at the concentration specified in the original experimental protocol (reported as 1 M) under continuous magnetic stirring at $60\text{ }^{\circ}\text{C}$ for 1 h and then cooled to the target reaction temperature. Pyrrole (1 M) and HCl (1 M, used as the protonic dopant) were subsequently added to the PVA solution according to the specified 1:1 pyrrole:PVA ratio, and the mixture was equilibrated at the target temperature for 15 min under continuous stirring. In a separate vessel, FeCl_3 (1 M) was dissolved in 100 mL of acidified water ($\text{pH} \approx 2$). Polymerisation was initiated by adding the FeCl_3 solution dropwise to the pyrrole–PVA solution at an approximate rate of 1 mL min^{-1} while maintaining the reaction temperature using a thermostated water bath (accuracy $\pm 0.5\text{ }^{\circ}\text{C}$). The endpoint of polymerisation was identified by the development of a uniform black colour in the dispersion, indicating the formation of PPy. Three syntheses were conducted at 5, 25 and $50\text{ }^{\circ}\text{C}$, and the resulting materials are designated Film 1, Film 2 and Film 3, respectively. Thin films for characterisation were prepared by spin-coating the dispersions onto appropriate substrates at 1500 rpm for 30 s, followed by slow drying under dynamic vacuum (10^{-2} mbar) at room temperature for 12 h to remove residual solvent without inducing thermal artefacts. Film thicknesses, estimated from cross-sectional SEM, were in the range 180–220 nm for all three films. The synthesis procedure is summarised schematically in Figure 1.

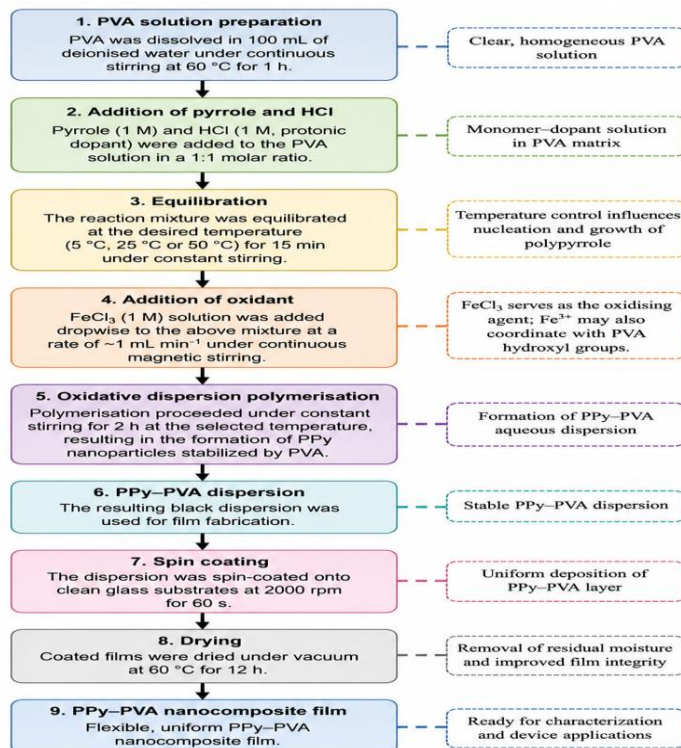


Figure 1: Flowchart of the synthesis of PPy-PVA nanocomposite films by in situ oxidative dispersion polymerisation.

2.3. Characterisation

Surface morphology and particle size were examined by scanning electron microscopy (SEM; JEOL JSM-6360, accelerating voltage 15 kV) using films spin-cast on glass substrates coated with a 5 nm Au-Pd layer to prevent charging. Particle diameters were measured from at least 200 particles per sample using ImageJ software (version 1.54), and the mean diameter and standard deviation were extracted from log-normal fits to the frequency histograms.

Crystal structure was investigated by X-ray diffraction (XRD; Scifert XRD 3000P diffractometer) using Cu K α radiation ($\lambda = 1.5406$ Å) in the 2θ range 5° – 60° with a step size of 0.02° and a counting time of 2 s per step. Crystallite sizes (D) were calculated from the full width at half maximum (FWHM) of the dominant diffraction peaks using the Scherrer equation:

$$D = K\lambda / (\beta \cos \theta) \quad (1)$$

where $K = 0.94$ is the Scherrer shape factor, λ is the X-ray wavelength, β is the FWHM (in radians) corrected for instrumental broadening using a Si standard, and θ is the Bragg angle. The instrumental broadening was determined separately to be 0.10° (FWHM).

Chemical bonding and crosslinking were examined by Fourier-transform infrared (FTIR) spectroscopy (Perkinelmer, Model RV5) using KBr pellets in the wavenumber range 400 – 4000 cm^{-1} at a resolution of 4 cm^{-1} (64 scans averaged). Optical absorption spectra were recorded with a double-beam UV-Visible spectrophotometer (Cary 300

Scan) in the wavelength range 200–800 nm; films were deposited on quartz substrates, and a blank quartz substrate was used as the reference.

For electrical measurements, films were deposited on indium tin oxide (ITO)-coated glass substrates (sheet resistance $8\text{--}12\ \Omega\ \text{sq}^{-1}$) and ohmic contacts were formed with silver paste (contact geometry verified by I–V linearity). In-plane four-probe conductivity was measured at room temperature using a Keithley 220 constant-current source and a Keithley 595 C–V meter. Each conductivity value reported is the mean of five independent measurements on the same film; the standard deviation of these measurements defines the reported uncertainty. Temperature-dependent conductivity was measured over the range 120–340 K by placing the film in an evacuated chamber (pressure $< 10^{-3}$ mbar) equipped with a resistance heater and liquid-nitrogen cooling; temperature was measured with a calibrated Pt-100 sensor (accuracy ± 0.5 K). All data were acquired via a GPIB interface.

3. Results and Discussion

3.1. Colloidal Stability

The colloidal stability of the PPy–PVA dispersions decreases with increasing synthesis temperature: the dispersion at 5 °C remained stable (no visible sedimentation) for more than 72 h, while those at 25 °C and 50 °C settled within approximately 36 h and 12 h, respectively. This trend is attributed to two concurrent effects: (i) increased thermal motion at higher temperatures promotes interparticle collisions and aggregation, and (ii) temperature-dependent PVA–Fe³⁺ coordination may reduce the effective availability of free hydroxyl groups and alter steric stabilization. (evidenced by FTIR, Section 3.4).

3.2. Particle Morphology and Size Distribution

SEM micrographs of Films 1–3 (Figure 2) show predominantly spherical PPy nanoparticles distributed within the PVA matrix at all synthesis temperatures. Particle-size distributions were obtained by analysing at least 200 particles per sample. The mean particle diameters were 50 ± 5 nm for Film 1 (5 °C), 75 ± 6 nm for Film 2 (25 °C), and 92 ± 7 nm for Film 3 (50 °C). The progressive increase in particle size with synthesis temperature indicates enhanced particle growth and aggregation at elevated temperatures. Increased thermal motion may promote interparticle collisions, while temperature-dependent changes in PVA-mediated stabilization can influence particle growth and dispersion stability. Film 2 (25 °C) exhibits a distinctly bimodal particle-size distribution, with a primary population centred near 65 nm and a secondary population near 90 nm. This behaviour suggests the coexistence of primary PPy nanoparticles, and a fraction of larger aggregates formed during dispersion polymerisation [14].

At 5 °C, the particles appear relatively more uniformly distributed within the PVA matrix. With increasing synthesis temperature, the micrographs show progressively larger PPy-rich domains and greater local aggregation, consistent with the temperature-dependent particle growth observed from the size distributions.

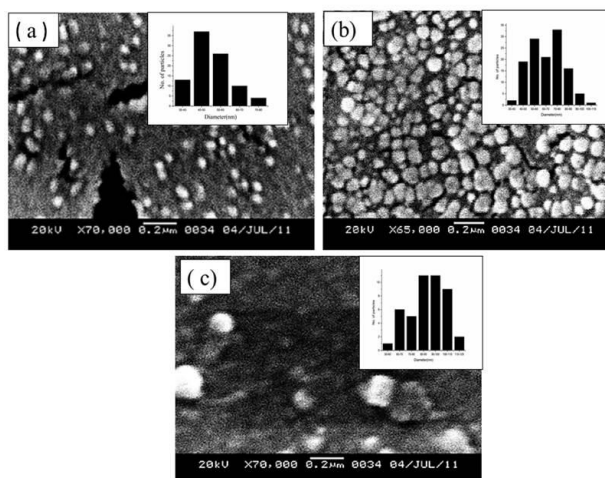


Figure 2. SEM micrographs and particle size frequency histograms (≥ 200 particles per sample) of PPy-PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Solid curves are log-normal fits. Scale bar: 200 nm.

3.3. Crystalline Structure and Scherrer Analysis

All diffraction patterns exhibit a broad peak centred at, characteristic of the semicrystalline PVA matrix and associated with the ordered regions of the PVA chains [16]. For Film 1 (5 °C), no well-resolved PPy-related diffraction peak is observed, although a weak, broad feature is present near $2\theta \approx 42^\circ$. Because of its low intensity and broad profile, this feature is not assigned unambiguously to the PPy phase. With increasing synthesis temperature, a diffraction feature near $2\theta \approx 25.6^\circ$ emerges in Film 2 and becomes more clearly resolved in Film 3, consistent with the broad diffraction feature commonly reported for partially ordered PPy [2]. Additional reflections in the $16^\circ - 18^\circ$ region are also observed for Film 3, suggesting increased structural ordering in the composite at the highest synthesis temperature.

Scherrer analysis was applied to the resolved PPy-related reflection near $2\theta \approx 25.6^\circ$ for Films 2 and 3. The corresponding apparent crystallite sizes were 5.8 ± 0.5 nm and 8.7 ± 0.6 nm, respectively. For Film 1, a reliable Scherrer crystallite size was not determined because not sufficiently resolved PPy-related diffraction peak was observed. The increase in apparent crystallite size from Film 2 to Film 3 is consistent with increased structural ordering at higher synthesis temperature. This structural evolution is consistent with the observed increase in electrical conductivity (Section 3.6) and the change in the best-fitting hopping dimensionality (Section 3.7).

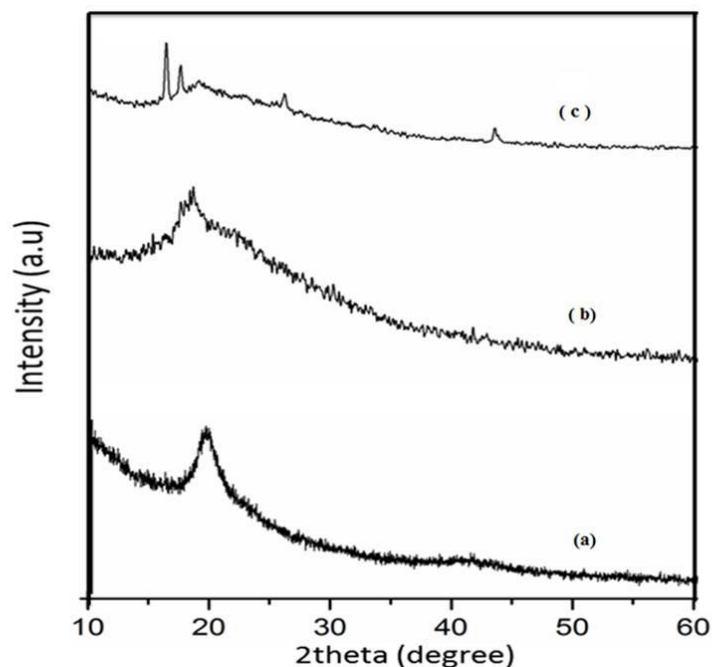


Figure 3. XRD patterns of PPy-PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C.

3.4. FTIR Spectroscopy

FTIR spectra of the three films are presented in Figure 4; and the corresponding band assignments are compiled in Table 1. The spectra of all films display the characteristic vibrational signatures of both PPy and PVA, together with additional features that confirm composite formation and crosslinking. Broad N–H/O–H stretching bands in the range 3452–3753 cm^{-1} are observed in all films and arise from the overlapping contributions of the N–H stretching vibration of PPy, the O–H stretching vibration of PVA and adsorbed moisture. The broadness of this band is consistent with hydrogen-bonding interactions among PPy, PVA and absorbed water molecules, together with the presence of residual dopant species within the polymer network [2]. A weak band in the 2300–2361 cm^{-1} region is assigned to C–H-related vibrational contributions.

The characteristic PPy bands include C=C ring stretching in the 1647–1585 cm^{-1} region [18], ring deformation near 1423 cm^{-1} , C–N stretching in the 1350–1228 cm^{-1} region and in-plane N–H bending near 1091 cm^{-1} [19]. Out-of-plane C–H deformation bands occur in the 918–849 cm^{-1} region, while ring-bending modes appear in the 597–470 cm^{-1} region. The C–O stretching vibration of PVA near 1091 cm^{-1} overlaps with the PPy N–H bending band. A shoulder in this region may be associated with interactions between PVA hydroxyl groups and Fe^{3+} ions [17], consistent with Fe^{3+} –PVA coordination within the composite. However, the FTIR data alone do not establish covalent crosslinking.

The characteristic PVA bands, particularly the O–H stretching vibration near 3300 cm^{-1} and the C–O stretching vibration near 1091 cm^{-1} , progressively decrease in intensity from Film 1 to Film 3. This systematic attenuation suggests a temperature-dependent modification of the PVA chemical environment and may be associated with increased

interactions between PVA hydroxyl groups and Fe^{3+} ions at higher synthesis temperatures. These changes may influence the interfacial interactions between the PVA matrix and the PPy phase and thereby contribute to the observed temperature-dependent structural and electrical behaviour.

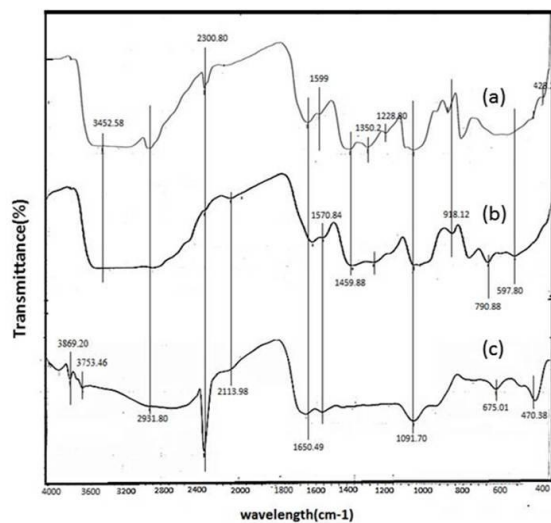


Figure 4: FTIR spectra (KBr pellets, 400–4000 cm^{-1}) of PPy–PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Arrows indicate vibrational bands showing systematic intensity changes with increasing synthesis temperature.

3.5. UV–Visible Spectroscopy and Optical Band Gap

UV–Visible absorption spectra of Films 1–3, recorded over 200–800 nm, are shown in Figure 5. All three films exhibit strong absorption in the UV region, with the principal absorption features occurring between approximately 200 and 350 nm. These features are associated primarily with π – π^* electronic transitions of the conjugated PPy backbone. Films 1 (5 °C) and 3 (50 °C) exhibit absorption maxima near 320 nm, whereas Film 2 (25 °C) shows a red-shifted maximum near 348 nm. The shift toward longer wavelength is consistent with changes in the electronic structure of PPy and the presence of additional localized charge-carrier states associated with oxidation and structural disorder. Polaronic and bipolaronic states are known to introduce electronic levels within the optical gap of PPy and can contribute to enhanced absorption at longer wavelengths. An additional absorption feature near 419 nm is observed for Film 3. This feature may be associated with transitions involving polaronic states in oxidized PPy; however, its assignment should be regarded as tentative because UV–Visible absorption alone does not uniquely distinguish polaronic from other overlapping electronic transitions. The increasing absorption toward the visible region is also consistent with the progressive darkening of the films with increasing synthesis temperature.

Optical band gaps were estimated from Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ (Figure 6), using the direct-transition approximation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap and A is a proportionality constant. The absorption coefficient was calculated from the measured absorbance A_{abs} and film thickness d using $\alpha = \frac{2.303A_{abs}}{d}$. The band-gap values were obtained by linear regression of the appropriate linear region of the Tauc plots, with the extrapolated intercept on the photon-energy axis taken as E_g . The uncertainty in E_g was estimated from the 95% confidence interval of the regression intercept together with the uncertainty associated with the film-thickness measurement (± 5 nm).

The extracted optical band gaps are 2.08 ± 0.03 eV for Film 1, 1.82 ± 0.03 eV for Film 2 and 1.72 ± 0.03 eV for Film 3. The progressive decrease in E_g with increasing synthesis temperature indicates a temperature-dependent modification of the electronic structure of the PPy-PVA composite. This behaviour can be associated with increased structural ordering and changes in the distribution of localized and dopant-related electronic states within the PPy phase. The larger PPy domains and enhanced aggregation observed by SEM, together with the increased structural ordering indicated by XRD, may facilitate greater electronic connectivity within the conducting phase. The reduction in optical band gap is therefore consistent with the simultaneous evolution of morphology, structural ordering and electrical conductivity observed with increasing synthesis temperature.

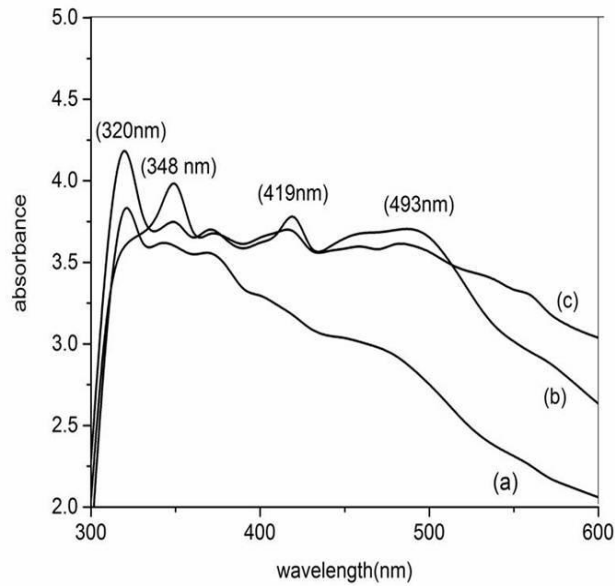


Figure 5. UV-Visible absorption spectra (200–800 nm) of PPy-PVA nanocomposite films synthesised at (a) 5°C, (b) 25 °C and (c) 50 °C.

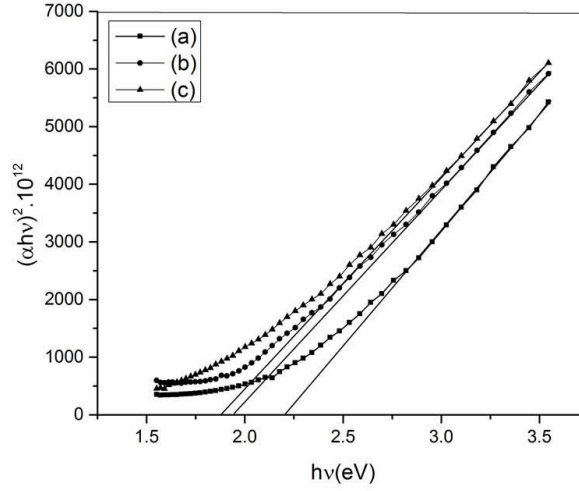


Figure 6. Tauc plots $[(\alpha h\nu)^2 \text{ vs. } h\nu]$ for PPy-PVA films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Dashed lines show linear extrapolations used to determine E_g . Error bars reflect propagated uncertainty from film thickness ($\pm 5 \text{ nm}$) and regression intercept (95% CI).

3.6. Room-Temperature Electrical Conductivity

In-plane I–V characteristics measured at 300 K are presented in Figure 7(a). All three films exhibit highly linear I–V behaviour ($R^2 > 0.9998$), indicating ohmic contact behaviour and linear electronic transport at room temperature. The room-temperature in-plane conductivities (mean $\pm$ SD, $n = 5$ measurements) are $(5.6 \pm 0.4) \times 10^{-2}$, $(12.3 \pm 0.7) \times 10^{-2}$ and $(19.1 \pm 0.8) \times 10^{-2} \text{ Scm}^{-1}$ for Films 1, 2 and 3, respectively (Figure 7(b); Table 5).

The conductivity increases systematically with synthesis temperature. This trend is consistent with the combined effects of increased structural ordering within the PPy-rich domains, growth and aggregation of PPy nanoparticles, and changes in the electronic structure of the composite. The emergence and sharpening of the PPy-related diffraction feature near $2\theta = 25.6^\circ$ indicate increased structural ordering at higher synthesis temperatures, which may facilitate charge transport. The larger PPy-rich domains and increased aggregation observed by SEM may also improve connectivity between neighbouring conducting regions. In addition, the reduction in optical gap is consistent with changes in the electronic-state distribution and enhanced electronic delocalization within the composite.

The conductivity values obtained here are lower than those commonly reported for highly conducting PPy, for which conductivity can vary over several orders of magnitude depending on the dopant, morphology and synthesis conditions [35]. The values are nevertheless comparable with those reported for PVA-based PPy composites and related PVA/PPy systems, where the insulating polymer matrix and conducting-phase fraction strongly influence the resulting transport properties [38, 39]. Recent studies of PPy–PVA-based films and PVA/PPy composites likewise demonstrate that the electrical response depends strongly on the composition, morphology and connectivity of the conducting PPy

phase. The lower conductivity relative to highly conducting PPy is therefore consistent with dilution of the conducting phase by the PVA matrix and the resulting modification of the conducting network.

The activation energy obtained from the temperature-dependent conductivity measurements decreases from Film 1 to Film 3 (Table 5), providing additional evidence for reduced transport barriers at higher synthesis temperatures.

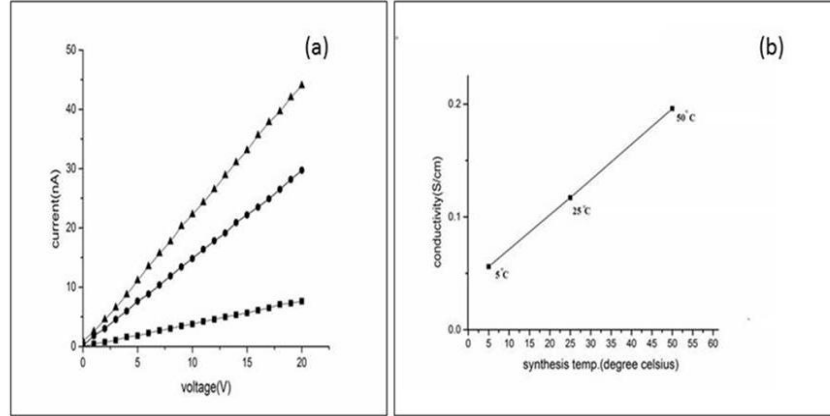


Figure 7. (a) In-plane current–voltage (I – V) characteristics of PPy–PVA films at 300 K: Film 1 (5 °C, ■), Film 2 (25 °C, ▲) and Film 3 (50 °C, ●). Solids lines represent linear fits ($R^2 > 0.9998$). (b) Room-temperature in-plane conductivity as a function of synthesis temperature. Error bars indicate ± 1 SD ($n = 5$ independent measurements).

3.7 Temperature-Dependent Conductivity and VRH Mechanism

Temperature-dependent conductivity was measured over the range 120–340 K. All three films exhibit semiconducting behaviour, with conductivity decreasing monotonically on cooling, consistent with thermally activated charge transport through localized electronic states [27]. To examine the transport mechanism, the conductivity data were analysed using Mott's variable-range hopping (VRH) relation,

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/(d+1)} \right]$$

where σ_0 is the pre-exponential factor, T_0 is the characteristic temperature and d represents the effective dimensionality of the hopping network. The corresponding linear forms were evaluated for $d = 1, 2$ and 3 using plots of $\log \sigma$ against $T^{-1/2}$, $T^{-1/3}$ and $T^{-1/4}$, respectively. An Arrhenius model was also evaluated for comparison using a plot of $\log \sigma$ against T^{-1} . Least-squares regressions were performed over the full 120–340 K temperature range, and the Pearson correlation coefficient and coefficient of determination (R^2) were used to compare the quality of different fits. The quality of each fit was assessed by the Pearson correlation coefficient r and the coefficient of determination (R^2); results are tabulated in Tables 2–4.

For Film 1 (5 °C), the best linearity is obtained for the 2D VRH ($T^{-1/3}$) plot, with $r = -0.9981$ and $R^2 = 0.9962$, compared with $r = -0.9923$ ($R^2 = 0.9847$) for 1D representation and $r = -0.9944$ ($R^2 = 0.9888$) for 3D VRH. For Film 1

(5 °C), the 2D Mott representation gives the highest linearity among the tested Mott exponents, with and, compared with for the 3D representation and for the representation. These results provide the strongest support for a 2D Mott-type hopping description among the models examined.

For Films 2 (25 °C) and 3 (50 °C), the 3D Mott representation provides the highest linearity, with $R^2 = 0.9956$ and 0.9982, respectively. The stronger 3D-VRH fit at these temperatures is consistent with the increased particle size, aggregation and structural ordering observed by SEM and XRD. These microstructural changes may increase the connectivity of the PPy-rich conducting domains and provide a more three-dimensionally connected hopping network. The present results therefore support a change from predominantly 2D-type to 3D-type Mott hopping behaviour as the synthesis temperature increases.

For all three films, the Arrhenius representation ($\log \sigma$ versus $1000/T$; Figure 9) also gives relatively high linearity, with R^2 values ranging from 0.9783 to 0.9912. Thus, simple thermally activated transport cannot be excluded solely based on linearity. However, the higher R^2 values obtained for the corresponding Mott-VRH representations provide stronger statistical support for VRH within the present fitting framework. A more rigorous discrimination among transport models would require additional statistical criteria and/or independent transport analysis. The activation energies obtained from the Arrhenius fits are 148 ± 6 , 121 ± 5 and 98 ± 5 meV for Films 1, 2 and 3, respectively (Table 5). The progressive decrease in activation energy (E_a) indicates a reduction in the effective thermal barrier for charge transport with increasing synthesis temperature.

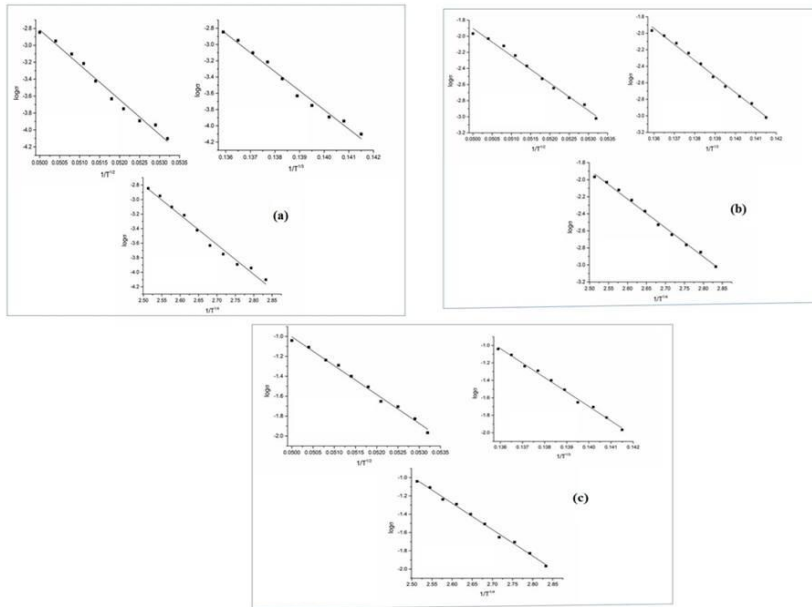


Figure 8. Mott VRH fitting plots [$\log \sigma$ versus $1000/T$, where $d = 1, 2$ and 3] for PPy–PVA films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. The asterisk (★) indicates the best-fitting Mott model for each film. Solid lines represent least-squares fits over 120–340 K.

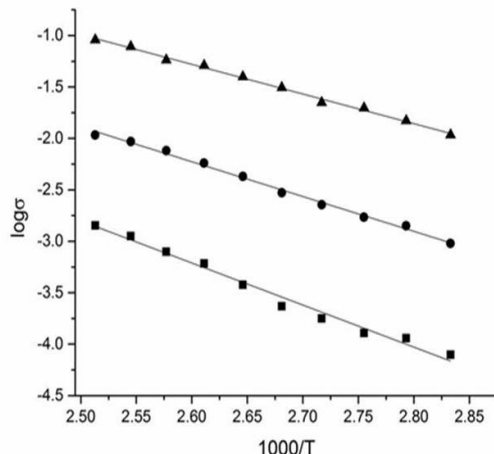


Figure 9. Arrhenius plots of $\log \sigma$ versus $1000/T$ for PPy-PVA films synthesised at 5 °C (■), 25 °C (▲) and 50 °C (●). Solid lines represent linear fits. The corresponding activation energies are listed in Table 5.

4. Conclusion

This study demonstrates that synthesis temperature provides an effective means of tuning the morphology, structural ordering, optical response and charge-transport behaviour of PPy-PVA nanocomposite films prepared by in situ dispersion polymerisation. Increasing the synthesis temperature from 5 to 50 °C resulted in a systematic increase in the mean PPy nanoparticle diameter from 50 ± 5 to 92 ± 7 nm, accompanied by increased particle aggregation and the development of larger PPy-rich domains.

XRD analysis revealed enhanced structural ordering with increasing synthesis temperature. A reliable Scherrer crystallite size could not be determined for the 5 °C film because not sufficiently resolved PPy-related diffraction peak was observed, whereas apparent crystallite sizes of 5.8 ± 0.5 and 8.7 ± 0.6 nm were obtained for the 25 and 50 °C films, respectively. FTIR analysis confirmed the presence of both PPy and PVA and indicated temperature-dependent interactions between the two components, including changes in hydroxyl-related vibrational features.

The optical band gap decreased from 2.08 ± 0.03 eV for Film 1 to 1.72 ± 0.03 eV for Film 3. In parallel, the room-temperature electrical conductivity increased from $(5.6 \pm 0.4) \times 10^{-2}$ to $(19.1 \pm 0.8) \times 10^{-2}$ S cm⁻¹. These changes are consistent with the combined influence of particle growth, increased structural ordering and modification of the electronic structure of the composite.

Temperature-dependent conductivity measurements further showed that the 2D Mott representation provided the best fit for Film 1, whereas the 3D Mott representation gave the best fits for Films 2 and 3. The change in the best-fitting Mott dimensionality is consistent with the temperature-dependent evolution of particle size, aggregation and structural ordering observed by SEM and XRD. Although the Arrhenius representation also showed good linearity, the higher (R^2) values obtained for the corresponding Mott-VRH fits provide stronger statistical support for VRH within the present fitting framework.

Overall, the results establish a consistent relationship between synthesis temperature, microstructural evolution and charge transport in PPy–PVA nanocomposites. The study demonstrates that controlling the polymerisation temperature can be used to tailor the structural and electrical characteristics of these materials, providing a useful basis for further optimisation of PPy-based composite films for electronic and sensing applications.

Acknowledgements

The authors acknowledge the Department of Science and Technology (DST) and the University Grants Commission (UGC), Government of India, for equipment support through various grants. The authors thank Sophisticated Analytical Instrument Facility (SAIF), North-Eastern Hill University (NEHU), for SEM measurements, and SAIF, USIC and the Department of Chemistry, Gauhati University, for XRD, UV–Visible spectroscopy and FTIR measurements. The authors declare no conflicts of interest.

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Table 1. Assignments of FTIR absorption bands observed in PPy–PVA nanocomposite films. Band intensities: s = strong, m = medium, w = weak.

Wavenumber (cm ⁻¹)	Intensity	Assignment	Component
3452–3753	b, s	N–H and O–H stretching	PPy N–H; PVA O–H
2300–2361	m	C–H stretching	PPy backbone C–H
1647–1585	s	C=C benzenoid stretching	PPy conjugated ring
1423	m	Ring deformation	PPy five-membered ring
1350–1228	m	C–N stretching	PPy C–N bond
1091	s	C–O stretching; N–H in-plane bend; Fe–O–C bridge	PVA –OH/Fe ³⁺ ; PPy N–H
918–849	w	Out-of-plane C–H deformation	PPy C–H wagging
597–470	w	Degenerate bending modes	PPy ring deformations

Table 2. Pearson's correlation coefficient (r) and coefficient of determination (R²) for least-squares VRH and Arrhenius fits of Film 1 (synthesized at 5 °C). Best-fitting model is highlighted.

Model / Plot	Exponent	r	R ²
1D Mott VRH ($T^{-1/2}$)	$T^{-1/2}$	–0.9923	0.9847
2D Mott VRH ($T^{-1/3}$) ★	$T^{-1/3}$	–0.9981	0.9962
3D Mott VRH ($T^{-1/4}$)	$T^{-1/4}$	–0.9944	0.9888
Arrhenius (1000/T)	1/T	–0.9891	0.9783

Table 3. Pearson's correlation coefficient (r) and coefficient of determination (R²) for least-squares VRH and Arrhenius fits of Film 2 (synthesized at 25 °C). Best-fitting model is highlighted.

Model / Plot	Exponent	r	R ²
ES-VRH (1D Mott, $T^{-1/2}$)	$T^{-1/2}$	–0.9901	0.9803
2D Mott VRH ($T^{-1/3}$)	$T^{-1/3}$	–0.9935	0.9870
3D Mott VRH ($T^{-1/4}$) ★	$T^{-1/4}$	–0.9978	0.9956
Arrhenius (1000/T)	1/T	–0.9912	0.9825

Table 4. Pearson's correlation coefficient (r) and coefficient of determination (R²) for least-squares VRH and Arrhenius fits of Film 3 (synthesized at 50 °C). Best-fitting model is highlighted.

Model / Plot	Exponent	r	R ²
ES-VRH (1D Mott, $T^{-1/2}$)	$T^{-1/2}$	–0.9876	0.9753
2D Mott VRH ($T^{-1/3}$)	$T^{-1/3}$	–0.9947	0.9894
3D Mott VRH ($T^{-1/4}$) ★	$T^{-1/4}$	–0.9991	0.9982
Arrhenius (1000/T)	1/T	–0.9956	0.9912

Table 5. Summary of physical parameters for PPy–PVA nanocomposite films as a function of synthesis temperature. Values are mean ± SD; conductivity SD from n = 5 measurements; particle-size SD from log-normal fit to ≥ 200 particles; E_g uncertainty from propagated regression and thickness errors; crystallite size uncertainty from FWHM fitting.

Temp. (°C)	Particle Size (nm)	Crystallite Size (nm)	E _g (eV)	σRT (10 ⁻² S cm ⁻¹)	E _a (meV)
5 (Film 1)	50 ± 5	ND	2.08 ± 0.03	5.6 ± 0.4	148 ± 6
25 (Film 2)	75 ± 6	5.8 ± 0.5	1.82 ± 0.03	12.3 ± 0.7	121 ± 5
50 (Film 3)	92 ± 7	8.7 ± 0.6	1.72 ± 0.03	19.1 ± 0.8	98 ± 5

N.D.: not determined because not sufficiently resolved PPy-related diffraction peak was available for reliable Scherrer analysis.

Figure Captions

Figure 1. Flowchart of the synthesis of PPy–PVA nanocomposite films by in situ oxidative dispersion polymerisation.

Figure 2. SEM micrographs and particle size frequency histograms (≥ 200 particles per sample) of PPy–PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Solid curves are log-normal fits. Scale bar: 200 nm.

Figure 3. XRD patterns of PPy–PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C.

Figure 4: FTIR spectra (KBr pellets, 400–4000 cm^{-1}) of PPy–PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Arrows indicate vibrational bands showing systematic intensity changes with increasing synthesis temperature.

Figure 5. UV–Visible absorption spectra (200–800 nm) of PPy–PVA nanocomposite films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C

Figure 6. Tauc plots [$(\alpha h\nu)^2$ vs. $h\nu$] for PPy–PVA films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. Dashed lines show linear extrapolations used to determine E_g . Error bars reflect propagated uncertainty from film thickness (± 5 nm) and regression intercept (95% CI).

Figure 7. (a) In-plane current–voltage (I–V) characteristics of PPy–PVA films at 300 K: Film 1 (5 °C, ■), Film 2 (25 °C, ▲) and Film 3 (50 °C, ●). Solids lines represent linear fits ($R^2 > 0.9998$). (b) Room-temperature in-plane conductivity as a function of synthesis temperature. Error bars indicate ± 1 SD ($n = 5$ independent measurements).

Figure 8. Mott VRH fitting plots [$\log \sigma$ versus $1000/T$, where $d = 1, 2$ and 3] for PPy–PVA films synthesised at (a) 5 °C, (b) 25 °C and (c) 50 °C. The asterisk (★) indicates the best-fitting Mott model for each film. Solid lines represent least-squares fits over 120–340 K.

Figure 9. Arrhenius plots of $\log \sigma$ versus $1000/T$ for PPy–PVA films synthesised at 5 °C (■), 25 °C (▲) and 50 °C (●). Solid lines represent linear fits. The corresponding activation energies are listed in Table 5.