

# Elucidating the Effects of Stirring Time on Chemical and Electrochemical Properties of Polyaniline Salt Dispersion in Tetrahydrofuran

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## ABSTRACT

*Polyaniline (PANi) salt was synthesized using the oxidative polymerization method with ammonium persulfate (APS) as an initiator. The dispersibility of the prepared samples in tetrahydrofuran (THF) at different stirring durations (30 minutes, 8 hours, and 24 hours) was studied by elucidating their chemical and electrical properties. Fourier Transform Infrared (FTIR) spectroscopy was employed to determine the composition of PANi salt, while electrical properties were studied using UV-Vis spectroscopy to calculate the absorbance and optical band-gap energy of the PANi salt dispersion. The results show that the best dispersibility of PANi salts occurs at 8 hours, as indicated by FTIR and UV-Vis spectroscopy investigations that detect the highest absorption peaks characteristic of quinoid and benzenoid units, respectively. It was observed that dispersing PES in THF for 8 hours improves the bandgap of PANi from 3.10 eV to 2.41 eV. Thus, this study underlines the critical significance of stirring time in increasing PANi dispersibility and understanding its spectroscopic properties, providing insights for its practical use in various applications, including organic electronics, sensors, and actuators.*

*Keywords: Polyaniline (PANi); Polyemeraldine Salts (PES); Dispersion; Band-gap*



## INTRODUCTION

Polyemeraldine salts (PES) are polyaniline (PANi) in its salt form and are conducting polymers known for their exceptional electrical conductivity and versatile applications. PES can be synthesized through a doping process involving oxidative polymerizations of aniline monomers with acids. PES exhibits unique properties determined by its chemical structure and the dopant. Comprising repeating phenylene units linked by nitrogen atoms, the polymer achieves enhanced electrical conductivity. PES typically appears as a dark green powder, and its physical properties, including color and conductivity, can be modified by adjusting the doping conditions [1]. These distinct characteristics make PES a focus of research for applications ranging from sensors to electrical components in electronic devices.

Most applications of polyaniline (PANi) in electrical components involve its use in paste or film form [2-3]. This means that PANi must be dispersed in a solvent for these purposes. Thus, the importance of dispersion in PANi applications is crucial, as it directly influences the performance of PANi-based materials as electrical components. Achieving uniform dispersion is essential for optimizing electrical, mechanical, and thermal properties, thereby enhancing overall functionality. Tailoring dispersion to meet the specific requirements of diverse applications is important to ensure that PANi can effectively contribute to various fields. The dissolution of PANi in solvents is often associated with its chemical structure, the types of solvent used, and the interactions between PANi and the solvent. Additionally, understanding dispersion is essential for maximizing the performance and applicability of PANi-based materials.

Few researchers have studied the dispersion of PANi in various solvents. Dash *et al.* [4] used dimethylformamide (DMF) to prepare a PANi dispersion for 6 hours. Other organic solvents, such as N-methyl-2-pyrrolidone, NMP [5], chloroform [6], and tetrahydrofuran, THF [7-8], are also used to disperse PANi. However, the dispersibility of PANi in solvents often presents a problem, as PANi particles, whether in base or salt form, tend to aggregate easily. To address this issue, Wang *et al.* [9] incorporated a clay mineral known as palygorskite to prevent the aggregation of polyaniline. However, the technical parameters during the dispersion process, such as the effects of stirring time, are not fully discussed.

Thus, this study focuses on finding the optimal stirring time for achieving uniform dispersion of PANi in THF solvent. It is believed that stirring time can affect the solubility and dispersion of PANi in the reaction medium. Efficient stirring helps break down any agglomerates, ensuring better interaction between monomers and the oxidizing agent. This is particularly important for achieving a homogeneous distribution of PANi in the solvent, which can influence the film-forming properties and overall performance of the polymer in various applications. A short stirring time may lead to partial dissolution, while longer stirring time allows further chain propagation, enhancing polymer-solvent interactions. On the other hand, prolonged stirring enables maximum interaction, which shorter times cannot achieve. Most researchers stirred PANi in a solvent for 30 minutes to 24 hours to produce a homogeneous dispersion of PANI. However, there is limited research discussing the effect of stirring time variations on the properties of PANI. Thus, this research investigates different stirring time; 30 minutes [10-11], 8 hours [12], and 24 hours [13] to better understand the influence of a short and long stirring time on the spectroscopic and electrical properties of PANi.

In summary, characterization using spectral and optical analysis, such as Fourier-transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy, was employed to elucidate the effects of different stirring times on the PES dispersion in THF, focusing on its chemical and electrical properties, including bandgap calculation. Additionally, spectral and absorption analyses of polymers contribute to a fundamental understanding of the relationship between the molecular structure of polymers and their optical properties.

## **EXPERIMENTAL METHODOLOGY**

### **Synthesis of PES**

Aniline monomer with a purity of  $\geq 99.0\%$  was distilled prior to use. Ammonium persulfate (APS) served as the initiator, while hydrochloric acid (HCl) and dimethyl sulfoxide (DMSO) were employed as acid dopant and solvent. All other reagents used were of analytical grade and were

used without further purification. The in situ oxidative polymerization of PANi was carried out as described previously [14]. The polymer produced in this procedure is a dark-green colored powdered polymer, known as polyemeraldine salt (PES).

### **Preparation of PES Dispersion**

0.02 g of PES was accurately weighed and placed in a small container. 8 mL of THF was slowly added to the container containing the PES. The solution was stirred continuously using a magnetic stirrer on a stir plate for 30 minutes, 8 hours, and 24 hours. The PES dispersion was then placed in a tightly sealed container to prevent solvent evaporation and contamination.

### **Spectral Analysis**

The PANi dispersion was cast into a petri dish and left to dry in an oven at 70 °C overnight. The product produced after drying process was PES in film form. The PES film was characterized over a spectral range of 4000 to 500  $\text{cm}^{-1}$  wavenumbers. The spectral analysis was acquired using a Nicolet 6700 FTIR (Thermo Scientific, Waltham, MA, USA) spectrometer.

### **Optical Analysis**

A cuvette was filled with the prepared PES solution at a concentration of 100 ppm and the THF solvent was used as the blank sample. The solvent baseline was measured separately. A UV-Vis spectrophotometer (Shimadzu, UV-1800) was then used to record the absorbance spectrum across the UV and visible regions. The spectrum was examined for characteristic peaks, particularly focusing on the electronic transitions of the sample. The maximum absorbance of each sample was determined to understand the transition wavelengths.

### **Band Gap Energy**

The band gap of material defines whether the material is an insulator, semiconductor, or conductor. Conducting materials often have a smaller bandgap due to the lower energy needed for electrons to transition from the valence band to the conduction band. The Tauc plot method was used to determine the band gap of PES. This method involves plotting the absorption

coefficient ( $\alpha$ ) as a function of photon energy, as obtained from the UV-Visible absorption curve. The band gap is estimated from the intercept of the linear portion of the Tauc plot with the energy axis using Equation (1).

$$\alpha h\nu = A (h\nu - E_g)^n \quad (1)$$

where:

A = absorbance

$\alpha$  = absorption coefficient

$h\nu$  = photon energy

$E_g$  = bandgap energy

## RESULTS AND DISCUSSION

### FTIR Analysis

Figure 1 shows the FTIR spectra of PES dispersion for stirring times of 30 minutes, 8 hours, and 24 hours, respectively. The broad peak at  $3440 \text{ cm}^{-1}$  corresponds to N-H stretching, the peak at  $1651 \text{ cm}^{-1}$  represents C=N stretching, and the peak at  $804 \text{ cm}^{-1}$  and  $1305 \text{ cm}^{-1}$  are attributed to C-H out-of-plane vibrations and aromatic C-N stretching [15]. As the stirring time increases the absorption of polyaniline-related functional group peaks also increases, with the C=N and N-H stretching peaks narrowing and showing lower transmittance values. This indicates an increase in the number of these functional groups.

At 30 minutes of stirring time, C=N stretching shows the lowest absorbance, likely due to the slower reaction kinetics required for the formation of these specific bonds. Slower reaction kinetics cause inefficient interaction between the polymer and solvent molecules [16]. The solvent does not have enough time to penetrate and interact with the PANi chains. As a result, the C=N stretching bond may not be properly aligned or fully dispersed in the solvent to form a stable, well-defined structure. However, after 24 hours of stirring, the N-H peaks show slight broadening, indicating overoxidation [17]. Overoxidation caused partial breakdown of the polymer structure, leading to the formation of smaller oligomeric fragments that

resulted in broader FTIR peaks [18]. A research by Xie *et al.* [19] reported that prolonged stirring causes excessive oxidation of the PES structure, resulting in reduced molecular weight and disordered polymer chain packing.

From this experiment, the optimal stirring time for PES in THF solvent was determined to be 8 hours. At this duration, there were no signs of chain breakage, as indicated by the highest absorption and low transmittance in the FTIR spectrum of the sample. Compared to the PANi sample stirred for 24 hours, the reduction in the intensity of the PANi peaks indicates that the amine-related groups of PANi have been cleaved from the polymer backbone.

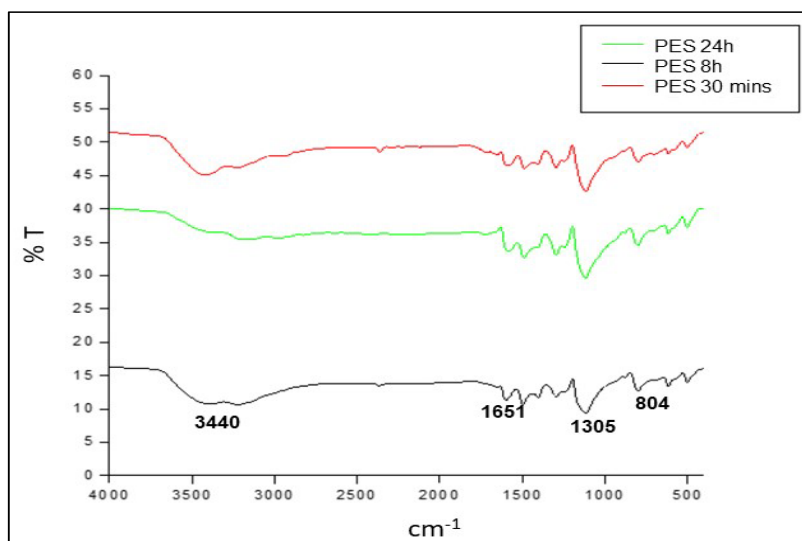


Figure 1: FTIR spectra of PES dispersions with different stirring times.

## UV-Vis Absorbance

Figure 2 shows the absorbance spectrum in the UV and visible regions for a PES dispersion with different stirring times: 30 minutes, 8 hours, and 24 hours. For a stirring of 30 minutes, the peak intensity for  $\pi$ - $\pi^*$  absorption is the lowest, with maximum absorption at 282 nm. At higher energy levels, the energy difference between the excited and unexcited states is slightly

lower, resulting in a small red shift. For 8 hours of stirring, the peak intensity is the highest, with maximum absorption at 300 nm. UV-Vis absorption by organic compounds requires that the absorbed energy corresponds to a transition from an occupied orbital to an unoccupied orbital of higher energy. These transitions between molecular levels result in the most pronounced band spectra. For 24 hours of stirring time, the peak intensity is reduced, with maximum absorption at 299 nm. The lower intensity observed in this sample is due to differences in attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states [20]. The difference in absorbance might also be caused by changes in the PES structure, particularly related to the conjugated bonds of PES. At the shortest stirring time, the flow of electrons in these conjugated bonds might be insufficient, while too long stirring time might destroy the conjugated bonds. Insufficient electron flow causes lower intensity of  $\pi$ - $\pi^*$  transitions because the conjugation of the polymer backbone is not fully developed, leading to lesser electronic transitions between the conjugated  $\pi$  orbitals.

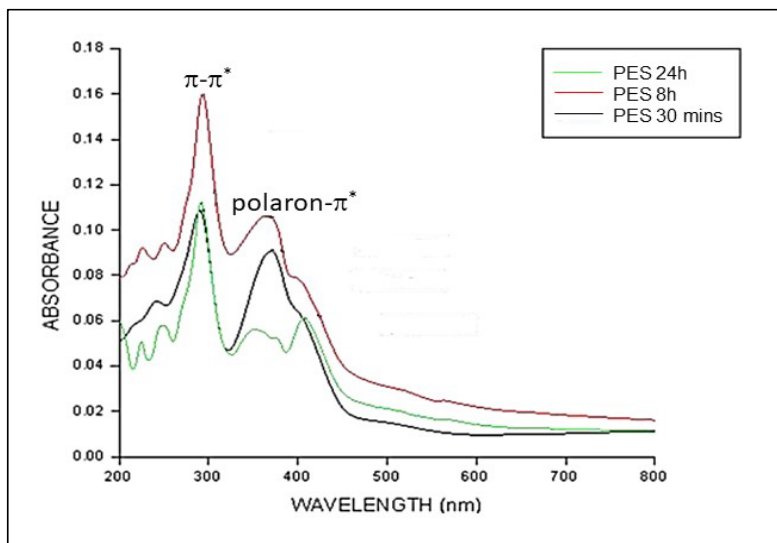


Figure 2: UV-Vis absorbance of PES dispersions in THF at different stirring times.

## Band-gap Energy

The band gap energy is defined as the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), while  $\pi$ - $\pi^*$  transitions in UV-Vis absorption involve the excitation of an electron from the HOMO, which is typically a  $\pi$  orbital, to LUMO, another  $\pi$  orbital. Figure 3 demonstrates a clear correlation between the band gap energy of emeraldine salt dissolved in THF and the duration of stirring. At the initial stirring period of 30 minutes, as indicated in Figure 3 (a), the measured band gap falls within the range of 3.10 eV, indicating a relatively high energy gap. This result is consistent with the understanding that a short stirring time may be insufficient for the complete dissolution of PES in THF. The limited interaction between molecules during this period leads to a less conductive state, as evidenced by the higher band gap [21].

As shown in Figure 3 (b), as the stirring time is extended to 8 hours, a significant change is observed. The band gap decreases to a range of 2.41 eV, reflecting a notable decrease compared to earlier stirring times. This suggests an improvement in dissolution and polymerization processes. The effect of stirring time on the alignment of polymer chains can depend on specific conditions and the nature of the polymer being synthesized. In the case of PES, optimum stirring times typically contribute to better chain alignment, facilitating the formation of longer conjugated segments. Therefore, the reduction in band gap signifies enhanced conductivity [22], indicating a transition toward a more ordered and crystalline structure of conjugated segments of PANi. The increased stirring duration to the optimum level facilitates a more comprehensive interaction between emeraldine salt and THF molecules, promoting the formation of well-aligned polymer chains. Consequently, the band gap decreases, indicative of improved charge transport properties within the material [23]. This trend aligns with the lowest absorption energy observed in UV-Vis results, considering the similar electronic transitions occurring in the material.

However, as shown in Figure 3 (c), after 24 hours of stirring, the band gap energy increases to a range of 2.48 eV. The extended duration of stirring due to too long stirring time allows for the breaking of PES chains in acidic condition [24], which disrupts chain alignment and crystallinity,



which consequently reduces conductivity. In this case, overoxidation cause PANi chains to undergo chain scission, disrupting the conjugation in the polymer chain.

In conclusion, the optimal stirring time for PES dissolved in THF appears to be 8 hours as this duration resulted in the highest absorbance of the PANi functional group, as observed in both FTIR and UV-visible spectra.

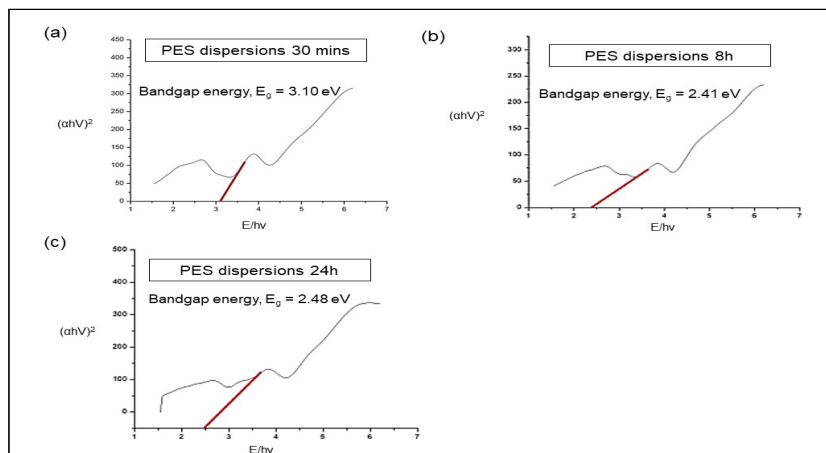


Figure 3: The band gap energy of PES dispersions after (a) 30 minutes, (b) 8 hours, and (c) 24 hours of stirring.

## CONCLUSION

In conclusion, this research investigated the effects of stirring time specifically, 30 minutes, 8 hours, and 24 hours on the solubility of polyaniline in THF. Spectroscopic analysis using Fourier transform infrared (FTIR) and UV-Vis spectroscopy, elucidated the relationship between stirring duration and the properties of PES. The characterization analyses reveal that the optimal stirring time for PES dispersions in THF is 8 hours, as this duration resulted in the most significant functional groups associated with PANi salts. Additionally, the study explored the impact of the estimated optimal stirring duration on the band gap of PES. Consistent with the characterization analysis, the band gap study indicates that an 8 hour stirring time results in the lowest band gap energy, which corresponds to improved electronic properties due to a better structure of PES.

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