Chapter III

Experimental results of polythiophene (PTh) thin films

3.1 Introduction

The experimental techniques used for the preparation and characterization of polythiophene (PTh) thin films were explained briefly in the previous chapter. The synthesis of PTh powder was also explained briefly in chapter II.

This chapter describes the results of polythiophene (PTh) thin films. The PTh thin films have been deposited by using vacuum evaporation technique and chemical bath deposition technique. Due to extensive experimentation, this chapter has been divided in two sections.

SECTION A deals with vacuum evaporated polythiophene thin films using the synthesized powder. These thin films were deposited for three different thicknesses (~150 nm, 200 nm and 250 nm) by means of resistive heating at $10^{-3}$ Torr.

SECTION B deals with chemical bath deposited polythiophene thin films. The polythiophene thin films were deposited by free radical polymerization on the glass substrates, using FeCl$_3$ as an oxidizing agent and CHCl$_3$ as solvent. The polythiophene thin films were deposed with different concentrations of oxidizing agent (FeCl$_3$).

The vacuum evaporated thin films (includes vapor chopped and nonchopped) and chemical bath deposited thin films were studied for structural and surface morphological properties. The optical properties such as optical band gap and refractive index of the thin films were also investigated. The study of mechanical properties such as intrinsic stress and adhesion were measured using interferometric method and direct pull off method (DPO) respectively. The optical
transmission loss was studied with prism coupling method. For the optical, mechanical and waveguiding properties 5 identical films for each thickness was used. The nonchopped and vapor chopped thin films were compared, where as in chemical bath deposited PTh thin films the effect of oxidant concentration on the various properties of thin film was studied.

**Section 3.A: Vacuum evaporated polythiophene (PTh) thin films.**

3. A.1 Structural properties

The structural properties of vapor chopped (VC) and nonchopped (NC) thin films were studied by FTIR spectroscopy. The FTIR spectra of vapor chopped (VC) and nonchopped (NC) thin films is shown in the figure 3.A.1

The FTIR spectra of the PTh thin films of thickness 150 nm the peak at 3411 cm\(^{-1}\) and 3405 cm\(^{-1}\) in nonchopped and vapor chopped thin films may be due to humidity in KBr [1]. The peaks at 2921 cm\(^{-1}\) in nonchopped (NC) and 2928 cm\(^{-1}\) in vapor chopped (VC) thin films correspond to C-H symmetric vibrations. The peaks at 2858 cm\(^{-1}\) in nonchopped (NC) and 2850 cm\(^{-1}\) in vapor chopped (VC) thin films and C-H asymmetric stretching [1]. The peaks at 1634 cm\(^{-1}\) and 1452 cm\(^{-1}\) in NC films were found to be slightly shifted to 1662 cm\(^{-1}\) and 1438 cm\(^{-1}\) in VC films representing C=C symmetric and C=C asymmetric [2]. The band in between 1130 cm\(^{-1}\) and 1000 cm\(^{-1}\) represents C-H out of plane deformation and C–H bending modes in the thiophene ring. The C–S stretching was observed around 809 cm\(^{-1}\) in NC and 822 cm\(^{-1}\) in VC thin films [3].

The slight shifting in the bands was observed in vapor chopping. The absorption peaks found slightly shifted in both nonchopped and vapor chopped thin films with respect to increase in the film thickness i.e. for (200nm and 250 nm). The cross-linking of short chain oligomers during evaporation may be one of the reasons for the shifting of the absorption peaks in FTIR [4]. The intensity of the peaks was found to increase in vapor chopped thin films.
Fig. 3.A.1 FTIR spectra of vapor chopped and nonchopped polythiophene thin films (150 nm, 200nm and 250 nm are the thickness of the thin film).
3. A.2 XPS studies

Figure 3.A.2 and 3.A.3 show the XPS spectra of vapor chopped and nonchopped PTh thin films of thickness (~ 250 nm) respectively.

- The survey scans Fig. 3.A.2 (a) and fig. 3.A.3 (a) illustrate the presence of distinct bands at binding energies corresponding to Si2p, C1s, S2s, S2p and O1s core levels [5].
- In both nonchopped and vapor chopped thin films the peak at 284.5 eV corresponds to C1s, shows good agreement with the signal of standard carbon known to be 284.5 eV [6].
- In nonchopped thin films Si2p, C1s, S2s, C1s and O1s were observed at 101 eV, 284.5 eV, 163.1 eV, 164.2 eV, 228 eV and 531 eV respectively.
- The evolution of C1s core level spectra is shown in Fig. 3.A.2(b) and 3.A.3(b), the main signal at 284.5 eV associated with α and β carbon atoms in the polymeric chains [7].
- The peaks at 285.7 eV and 285.8 eV in nonchopped and vapor chopped thin films presents C-S bonds [6].
- The low intense peaks located at 287.3 eV and 288.9 eV in nonchopped thin films and 288 eV and 289.3 eV due to satellite structure (π-π* transitions) [8].
- The corresponding S2p core level spectra shown in Fig. 3.A.2(c) and 3.A.3(c), for nonchopped thin films the energy difference between S2p_{3/2} 163.12 eV, (FWHM 0.37 eV) and S2p_{1/2} 164.25 eV (FWHM 0.62 eV) is 1.12 eV is nearly close to accepted value 1.17 eV [9].
- The vapor chopped thin films shows nearly similar binding energies as in nonchopped thin films i.e. Si2p~ 102.2 eV, C1s ~284.3 eV, the difference between S2p_{3/2} 163.0 eV (FWHM 0.5 eV) and S2p_{1/2} 164.1 eV (FWHM 0.37 eV) is 1.1 eV.
Fig 3.A.2 XPS of vapor chopped PTh thin films.
Fig 3.A.2 XPS of nonchopped PTh thin films.

3. A.3 Surface morphology

The surface morphological study of vacuum evaporated PTh thin films were carried out by scanning electron microscope (SEM), figure 3.A.4 shows the SEM images of PTh thin films for three different thickness.
The vapor chopped thin films show smooth surface morphology as compared to those of nonchopped thin films, the nonchopped thin films shows nonuniform deposition with scattered grains where as the vapor chopped thin films show uniform deposition with less roughness and less defects. The vapor chopped thin films show reduced grain size than those of nonchopped thin films.

The thickness study shows that the roughness of the thin film is found to be reduced with respect to increase in the thickness of the film in both nonchopped and vapor chopped thin films. The increase in the thickness of the film causes decrease in the grain size, defects and the roughness of the film. Fig.3.A.5 shows the TEM images in (50 nm scale bar) of the nonchopped and vapor chopped polythiophene of thickness 250 nm. The matrix consist of isotropic, nanometer sized spherical grains.

The region in the TEM shown by “circle” indicates the particles of the polythiophene are closer in vapor chopped films while they are distributed in nonchopped thin films. The grain size observed in vapor chopped thin film (~ 25-30 nm) is less than the grain size in nonchopped thin films (~45-50 nm).

The horizontal cross sectional study only provides the information about surface morphology of top most surface of the thin film.

Instead of horizontal view vertical cross sectional scanning electron micrographs may provide internal structure of the thin film. Even though horizontal SEM showed smoothed structure of thin film, the film may or may not be uniform internally.

It may contain columnar structure. The vertical cross sectional micrographs gives the information about layer wise deposition, void formation, crack formation defect growth, columnar growth within the thin film deposition.

Fig. 3.A.6 shows the vertical cross section of vapor chopped and nonchopped PTh thin films of thickness 250 nm. It showed the vapor chopped thin
films have uniform growth with minimum voids whereas nonchopped thin films showed clear columnar growth with larger cracks and voids formation. In this study cross sectional micrographs of 250 nm thickness was more informative than that of the smaller thicknesses; hence SEM of 250 nm is only given here.

3. A.4 Optical properties

3. A.4.1 Optical absorbance and transmission

As mentioned in chapter II, the optical properties were measured by using UV-Visible spectrophotometer. The graph of wavelength (nm) Vs absorption was plotted for vapor chopped and nonchopped PTh thin films for three different thicknesses as shown in figure 3.A.7, from figure it can be clearly observed that the absorbance of vapor chopped PTh thin films is less than those of nonchopped thin films the absorption peak around 320 nm in nonchopped PTh thin films and is slightly shifted in vapor chopped thin films, this shifting of the absorption peak may be due to the cross-linking of short chain polymer-oligomers[10].

The optical absorption was also affected by film thickness the absorbance increased with increase in film thickness; similar effect was observed in the vapor chopped thin films also.

Figure 3.A.8 shows the graph of transmission (%) Vs wavelength (nm) of nonchopped and vapor chopped PTh thin films. The transmission of vapor chopped thin films is more than that of nonchopped thin films, the transmission of thin films was found to decrease with increase in the thickness of the film. The PTh thin films of thickness 250 nm shows lower transmission where as the thin films of thickness 150 nm show higher transmission.
Chapter III: Experimental results of polythiophene (PTh) thin films

Fig. 3.A.4 SEM images of vapor chopped and nonchopped PTh thin films.
Fig. 3.A.5 TEM images of vapor chopped and nonchopped PTh thin films.

Fig. 3.A.6 Vertical cross-sections images of vapor chopped and nonchopped PTh thin films.
Fig. 3.A.7 Optical absorbance of vapor chopped and nonchopped PTh thin films.

Fig. 3.A.8 Optical transmission of vapor chopped and nonchopped PTh thin films.
3. A.4.2 Optical band gap

There are two types of band gaps, one is semiconductor band gap and other is optical band gap. The semiconductor band gap is the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band. The energy required for an electron to move from the valence band to the conduction band, whereas in optical band gap photons (packet of energy in the form of light waves) are assisting the electrons to move from valence band to conduction band. The optical energy band gap of polythiophene thin films was estimated from optical absorption measurement. The optical absorption spectrum was recorded in the wavelength range of 300 nm to 900 nm at room temperature. The equation the band gap was calculated using the following equation:

\[
\alpha = \frac{\alpha_0 (h\nu-E_g)^n}{h\nu}
\]

Where,

- \(E_g\) - separation between bottom of the conduction band and top of the valence band.
- \(h\nu\) - photon energy.
- \(N\) - constant.

The value of ‘n’ depends on the probability of transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. The band gap can be determined by the extrapolation of best fit line between \((\alpha h\nu)^2\) and \(h\nu\) to intercept the \(h\nu\) axis, as shown in figure 3.A.9. The values of optical band gap of vapor chopped and nonchopped PTh thin films are tabulated in table 3.A.1. The band gap values of the vapor chopped PTh thin films are less than that of nonchopped ones.
Experimental results of polythiophene (PTh) thin films

Fig. 3.A.9 \((\alpha h \nu)^2\) against \(h \nu\) for nonchopped (NC) and vapor chopped (VC) PTh thin films.

The increase in the thickness of the nonchopped thin films causes increase in the band gap, the band gap of the nonchopped thin film of thickness (200 nm) is more than that of thickness (250 nm). In vapor chopped PTh thin films the band gap increases with increase in the thickness of the film.

Table 3.A.1 Optical band gap values of vapor chopped (VC) and nonchopped (NC) PTh thin films for different thickness.

<table>
<thead>
<tr>
<th>Thickness of the film</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>150 nm</td>
<td>2.78±0.03</td>
</tr>
<tr>
<td>200 nm</td>
<td>3.08±0.03</td>
</tr>
<tr>
<td>250 nm</td>
<td>3.0 ±0.03</td>
</tr>
</tbody>
</table>
3. A.4.3 Refractive Index

In this work vapor chopped and nonchopped polythiophene thin films were used for the study of optical waveguiding properties. The refractive index of polythiophene thin films was studied for 150 nm, 200 nm and 250 nm thicknesses. The Abele’s method [11] was used for the measurement of Brewster angle and the refractive index (n) is calculated from following formula:

\[ \theta_B = \arctan \left( \frac{n_f}{n_A} \right) \]

Where,

- \( n_f \) - is the refractive index of the films.
- \( n_A \) - is the refractive index of the medium (air)

The tangent value of the angle of incidence or reflection gives the value of the refractive index of the films.

The analytical method also has been used for the calculation of refractive index \( n \) using the following formula [12].

\[
n = \left[ \frac{n_s^2 T_f + n_s \left(1 + \sqrt{R_f}\right)^2}{T_f + n_s \left(1 - \sqrt{R_f}\right)^2} \right]^{1/2}
\]

Where,

- \( n \) = refractive index of the film
- \( n_s \) = refractive index of the substrate
- \( T_f \) = transmission of the film
- \( R_f \) = reflectance of the film

The values of refractive indices of nonchopped and vapor chopped PTh thin films are tabulated in table 3.A.2
Table 3.A.2 Refractive Indices of vapor chopped and nonchopped PTh thin films for different thicknesses.

<table>
<thead>
<tr>
<th>Sr.N o.</th>
<th>Thickness of the Film (nm)</th>
<th>R.I by Abele’s method</th>
<th>R. I by analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NC</td>
<td>VC</td>
</tr>
<tr>
<td>01</td>
<td>150</td>
<td>1.7±0.03</td>
<td>1.67±0.03</td>
</tr>
<tr>
<td>02</td>
<td>200</td>
<td>1.65±0.04</td>
<td>1.61±0.02</td>
</tr>
<tr>
<td>03</td>
<td>250</td>
<td>1.8±0.03</td>
<td>1.73±0.02</td>
</tr>
</tbody>
</table>

The presented values of refractive index for each thickness is an average R. I. value of five identical samples, from the table it can be seen that an increase in refractive index was observed in both nonchopped as well as vapor chopped thin films, the R.I. of nonchopped thin films in the range of 1.64-1.8 and those of vapor chopped thin films is in the range of 1.62-1.73. The vapor chopped PTh thin films shows the lower values of R. I. than those of nonchopped thin films. The Abele’s method and the analytical technique differ by a small quantity from 0.9 to 0.4.

3. A.4.4 Optical waveguiding properties

The optical waveguiding properties of the PTh thin films was studied by prism coupling method, which gives the intensity of the outcome light ray. From the following formula the optical transmission loss of the film the optical transmission loss of the film calculated [13].

\[ A = 10 \log \left( \frac{\text{Input intensity}}{\text{Output intensity}} \right) \] dB/cm

Where

A- Optical transmission loss

The optical signal transmission loss was measured for three different thicknesses of vapor chopped and nonchopped PTh thin film waveguide is shown in figure 3.A.10. It can be seen that, the optical transmission loss increases with increase in thin film thickness. The films of higher thickness 250 nm showed higher transmission loss.
Fig. 3.A.10 Graph of optical transmission loss Vs thickness of the film.

The nonchopped thin film having thickness 150 nm shows the transmission loss of 4.37 dB/cm, which is increased with increase in the thickness i.e. 4.94 dB/cm for 250 nm and 5.23 dB/cm for 250 nm (figure 3.A.10). In case of vapor chopped thin films the observed signal transmission loss is less than those of nonchopped ones. The optical transmission loss values of nonchopped (NC) and vapor chopped (VC) PTh thin films are tabulated in table 3.A.3.

Table 3.A.3 Optical transmission loss of nonchopped and vapor chopped PTh thin films.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Thickness of film (nm)</th>
<th>Optical Transmission Loss (dB/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>01</td>
<td>150</td>
<td>4.37 ± 0.02</td>
</tr>
<tr>
<td>02</td>
<td>200</td>
<td>4.94 ± 0.02</td>
</tr>
<tr>
<td>03</td>
<td>250</td>
<td>5.23 ± 0.02</td>
</tr>
</tbody>
</table>
3. A.5 Mechanical properties

3. A.5.1 Adhesion

The interaction between thin film and the substrate is in itself usually of little interest to those fabricating thin film devices, but the quality of this interaction is a vital factor in the determination of the durability of the thin film. The extent to which it can do this depends upon bonding between the substrate and the film. Adhesion of thin film is related to the bonding between film-substrate interface contact points and crystalline of thin film. There are various factors which can affect the adhesion of the film, like concentration of contact points is directly proportional to the adhesion of thin film and these contact point concentration depends on the surface morphology of thin film; hence adhesion varies with surface morphology of thin film.

The adhesion of the nonchopped PTh thin films increases from $26.3 \times 10^3$ N/m$^2$ to $50.6 \times 10^3$ N/m$^2$, with increase in the film thickness from (150 nm to 250 nm). Also in the vapor chopped thin films adhesion increases from $34.2 \times 10^3$ N/m$^2$ to $59.1 \times 10^3$ N/m$^2$ with respect to increase in the film thickness. The nonchopped thin films show relatively less values of adhesion than those of vapor chopped ones as shown in figure 3.A.11.

![Adhesion graph](image)

Fig. 3.A.11 Adhesion of nonchopped and vapor chopped PTh thin films.
3. A.5.2 Stress

The presence of defects, dislocations, voids, or impurities in the thin film during deposition are responsible for the stress formation in the thin film. The existence of such stress has considerable importance in the use of thin films in microcircuit and optoelectronics device fabrication technology. The stresses occurs due to defects, microstructural variation, material phase transformation, void formation during deposition or lattice mismatch between thin film-substrate interfaces [14, 15]. Several failure mechanisms due to formation of cracks or voids in thin film associated with the stress have drawn attention in integrated optoelectronic circuit industry. [16].

In this work total stress was measured by interferometric method [13]. This method works on the principle of Newton’s ring as explained in chapter II. The stress was calculated by measuring the variation in diameter of Newton’s ring before and after deposition using following formula

\[
S = \frac{Yh^2(K_x - K_y)}{6t(1-\nu)}
\]

Where,

\[Y = \text{Young’s modulus},\]
\[\nu = \text{Poisson’s ration},\]
\[t = \text{film thickness},\]
\[h = 0.022 \text{ cm (substrate thickness)},\]
\[K_x, K_y = \text{Slope difference of plot nλ/2 Vs radius Newton’s ring of before and after deposition}.\]

Table 3.A.4 Intrinsic stress of nonchopped and vapor chopped PTh thin films.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Thickness of the film (nm)</th>
<th>Intrinsic stress×10^8 N/m^2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>01</td>
<td>150</td>
<td>1.73±0.4</td>
</tr>
<tr>
<td>02</td>
<td>200</td>
<td>0.84±0.3</td>
</tr>
<tr>
<td>03</td>
<td>250</td>
<td>0.55±0.3</td>
</tr>
</tbody>
</table>
Table 3.A.4 shows the intrinsic stress values of nonchopped and vapor chopped PTh thin films, the intrinsic stress of nonchopped thin films varies from $1.73 \times 10^8 \text{ N/m}^2$ to $0.55 \times 10^8 \text{ N/m}^2$ and those of vapor chopped thin films varies from $1.33 \times 10^8 \text{ N/m}^2$ to $0.46 \times 10^8 \text{ N/m}^2$. The intrinsic stress of the PTh thin films decreases with increase in the film thickness in both nonchopped and vapor chopped thin films.

### 3. A.6 Air exposure study

The properties of the material is subjected to change due to surrounding ambient, this tendency to change the material property due to the surrounding ambient is called ageing of that material. The effect of air aging is an important parameter, which can explain the reliability and performance of any device depends upon stability of the properties of the material.

Ambient air aging study of the material is nothing but comparison between fresh thin films and those thin films exposed to air. The PTh thin films were studied for air aging effect, the fresh films of PTh were studied for various properties and the same properties were studied by exposing these film to ambient air for 10, 20 and 30 days.

#### 3. A.6.1 FTIR spectroscopy

Figure 3.A.12 shows the FTIR spectra of fresh PTh thin films and ambient air exposed (aged) PTh thin films of thickness (~250 nm). The effect of ambient air aging on the nonchopped thin films shows broad peak at 3404 cm$^{-1}$ representing the O-H vibrating mode, there is an increase in the intensity of peaks at C-H symmetric mode at 2925 cm$^{-1}$ and C-H symmetric mode of vibration at 2861 cm$^{-1}$.

The peak at 1634 cm$^{-1}$ is shifted to 1673 cm$^{-1}$ with a shoulder peak at 1748 cm$^{-1}$ presenting C=O vibration modes, the bands at 1662 cm$^{-1}$ in vapor chopped thin film is slightly shifted to lower value, C–S stretching was observed around 809 cm$^{-1}$ in NC and 822 cm$^{-1}$ in VC thin films are also shifted in both vapor...
chopped and nonchopped thin films, with an extra intense band at 786 cm\(^{-1}\) presenting C-H wagging modes, vapor chopped thin films showed less shifting in the band than those of nonchopped ones due to air aging.

3. A.6.2 Surface morphology

The FESEM images of the fresh and aged PTh thin films (thickness \(\sim 250\) nm) are as shown in the figure 3.A.13, it can be observed that the fresh vapor chopped PTh thin film shows more smooth and uniform surface morphology as compared to fresh nonchopped thin films. After 30 days formation of cracks was observed due to ambient air aging in the PTh thin films (shown by red circles), however the formation of the cracks (defects) in the nonchopped thin films is larger than those of vapor chopped thin films (i.e. more number of cracks were observed in nonchopped thin films. Similar results were observed for the thickness 200 nm and 150 nm.

Although the FTIR spectra did not show any significant change during air exposure, the surface morphology was seriously altered in both the vapor chopped and nonchopped PTh thin films.

Fig. 3.A.12 FTIR spectra of PTh thin films a) fresh and b) aged thin films.
3. A.6.3 Optical Properties

3. A.6.3.1 Optical transmission

Figure 3.A.14 shows the optical transmission graphs of fresh and ambient air exposed vapor chopped and nonchopped PTh thin films, the data was recorded for the freshly deposited thin films and exposed to ambient air and the optical transmission is recorded for different exposure period for 10 days, 20 days and 30 days.

Fig. 3.A.13 FESEM images of (a and b) fresh PTh thin films, (c and d) aged thin films (the red circles shown denotes the crack formation).
It was seen that the transmission varied significantly with the ambient exposure time. Fresh vapor chopped and nonchopped thin films showed higher transmission as compared to air exposed films. The optical transmission of the vapor chopped thin films decreases from 90% to 80% due to air exposure and those in nonchopped thin films it decreases from 80% to 60%. The saturation in the reduction of optical transmission was observed after 20 days. The optical transmission reduction in vapor chopped films was comparatively lower than the nonchopped PTh thin films.

![Graph](image)

**Fig. 3.A.14** Optical transmission of fresh and air exposed (aged) PTh thin films.

### 3. A.6.3.2 Optical band gap

The optical band gap of nonchopped and vapor chopped thin films for different air exposure duration is shown in figure 3.A.15, the optical band gap of nonchopped PTh thin films varies from (3. 0 to 2.77 eV) due to air exposure and those of vapor chopped thin films varies from (2.92 to 2.81 eV). The values of optical band gap of PTh thin films are tabulated in table 3.A.5.
Fig. 3.A.14 Optical band gap of fresh and air exposed (aged) PTh thin films.

Table 3.A.5 Optical band of fresh and air exposed PTh thin films for different durations.

<table>
<thead>
<tr>
<th>Exposure period (Day)</th>
<th>Optical Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>Fresh</td>
<td>3.0±0.03</td>
</tr>
<tr>
<td>10</td>
<td>2.83±0.03</td>
</tr>
<tr>
<td>20</td>
<td>2.71±0.03</td>
</tr>
<tr>
<td>30</td>
<td>2.77±0.03</td>
</tr>
</tbody>
</table>

It can be observed the optical band gap of PTh thin films decreased due to ambient air aging. However the vapor chopped PTh thin films show comparatively lower reduction in the band gap than the nonchopped ones.
3. A.6.3.3 Refractive index

The refractive index values of nonchopped and vapor chopped PTh thin films calculated using analytical formula for different air exposure is tabulated in table 3.A.6, the refractive index was found to increase with increase in the air exposure period. The effect of ambient air aging on vapor chopped PTh thin films is comparatively lower than those of nonchopped ones.

Table 3.A.6 Refractive index (n) of fresh and aged PTh thin films.

<table>
<thead>
<tr>
<th>Exposure period (Day)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>Fresh</td>
<td>1.8±0.02</td>
</tr>
<tr>
<td>10</td>
<td>1.87±0.02</td>
</tr>
<tr>
<td>20</td>
<td>1.93±0.02</td>
</tr>
<tr>
<td>30</td>
<td>2.0±0.02</td>
</tr>
</tbody>
</table>

3. A.6.3.4 Optical transmission loss (OTL)

The optical signal transmission loss after air exposure of vapor chopped and nonchopped PTh thin film waveguide of thickness 250 nm is as shown in the figure 3.A.16.

The values of optical transmission loss for fresh and air exposed PTh thin films varies from 5.23 dB/cm to 13.06 dB/cm and the optical transmission loss of vapor chopped thin films varies from 4.88 dB/cm to 8.56 dB/cm. The optical transmission loss of PTh thin films increased with increase in the air exposure duration.
3. A. 6. 4 Mechanical properties

3. A. 6. 4. 1 Adhesion

The adhesion of fresh and ambient air exposed nonchopped and vapor chopped PTh thin films for thickness are shown in the figure 3.A.17, the adhesion vapor chopped and nonchopped thin films decreased with respect to increase in the exposure period. The vapor chopped thin films (59.1×10^3 N/m^2 to 53.01× 10^3 N/m^2) shows less effect of ambient air as compared to nonchopped thin films (50.96× 10^3 N/m^2 to 34.03× 10^3 N/m^2).
Fig. 3.A.17 Adhesion of fresh and air exposed PTh thin films.

3. A.6.4.2 Intrinsic stress

Table 3.A.7 shows the intrinsic stress of fresh and ambient air exposed nonchopped and vapor chopped PTh thin films. The intrinsic stress of the nonchopped and vapor chopped PTh thin film increased with increase in the exposure period. The nonchopped thin films ($0.46 \times 10^8$ N/m$^2$ to $0.55 \times 10^8$ N/m$^2$) shows more increase in the stress due to air exposure than those of vapor chopped ($0.4 \times 10^8$ N/m$^2$ to $0.46 \times 10^8$ N/m$^2$).

Table 3.A.7 Intrinsic stress of fresh and ambient air exposed PTh thin films.

<table>
<thead>
<tr>
<th>Exposure period (Day)</th>
<th>Intrinsic stress $\times 10^8$ N/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>Fresh</td>
<td>0.46</td>
</tr>
<tr>
<td>10</td>
<td>0.47</td>
</tr>
<tr>
<td>20</td>
<td>0.49</td>
</tr>
<tr>
<td>30</td>
<td>0.55</td>
</tr>
</tbody>
</table>
3. A.7 Summary and Some Important Results

The summary of some important results observed from the investigation carried out are as follows:

1. The FTIR peaks of the vapor chopped thin films are shifted to lower values and some of them split into two peaks as compared to nonchopped thin films.
2. Vapor chopped PTh thin films showed smoother morphology than nonchopped films.
3. Surface smoothness deteriorates with increase in thickness of the film.
4. Vapor chopped PTh thin films showed lower surface roughness than nonchopped thin films.
5. Vertical cross section SEM study of vapor chopped and nonchopped PTh thin films showed that, vapor chopped thin films were grown with reduced columnar structure and contained lesser voids formation in deposited thin film than the nonchopped PTh thin films.
6. Optical transmission decreases with thin film thickness enhancement.
7. Vapor chopped PTh thin films showed higher transmission than nonchopped films.
8. Optical transmission increases with increase in thin film thickness.
9. Vapor chopped thin films showed lesser optical absorbance than nonchopped PTh thin films.
10. Optical band gap increases with increases in thin film thickness and decreases due to vapor chopping.
11. Refractive index increases with increase in thin film thickness whereas it decreases due to vapor chopping.
12. Optical transmission loss increases with increase in thin film thickness.
13. Vapor chopped thin films showed lesser optical transmission loss than nonchopped films.
14. Adhesion of PTh thin films increases with increase in thickness of thin film.
15. Vapor chopped thin films showed higher adhesion than nonchopped films.
16. Intrinsic stress increased with thin film thickness and it decreases due to vapor chopping.

17. Surface morphology was seriously affected in both the vapor chopped and nonchopped PTh thin films. Because of air exposure for 10 days and more Void/defect formation was observed in nonchopped thin films.

18. Optical transmission and band gap decreases due to exposure effect. Vapor chopped thin films showed lesser effect than nonchopped films.

19. Adhesion is decreased whereas intrinsic stress increased due to exposure effect whereas vapor chopped PTh thin films showed lesser effect.

20. PTh thin films properties were changed rapidly in after 10 days exposure duration and these properties were moved towards the saturation with respect to exposure duration.

21. Optical transmission loss increased due to air exposure, vapor chopped thin films showed lesser reduction than nonchopped films.
SECTION 3. B: Chemical Bath deposited Polythiophene (PTh) thin films.

3. B.1 Thickness measurement and growth mechanism

The thickness of the chemical bath deposited polythiophene thin films was measured by surface profiler; the graph of film thickness against concentration of FeCl₃ is shown in figure 3.B.1, which shows that the thickness of the PTh thin film increased with increase in FeCl₃ concentration from 150 nm to 350 nm. Such a phenomenon can be explained by considering the two competing processes that take place in the deposition bath: one process includes the heterogeneous precipitation and homogeneous precipitation of PTh, which leads to the film growth and the other one involves the desorption and/or dissolution of the preformed PTh film that results into change in film thickness.

![Graph of film thickness Vs oxidant (FeCl₃) concentration.](image)

In the initial stage of film deposition, the source materials are sufficient and the solution has a high degree of supersaturation, the process of homogenous precipitation (ion-by-ion nucleation and growth mechanism) or aggregation of colloidal particles (cluster by cluster nucleation and growth mechanism) in the solution plays more important role than the dissolution
process, which leads to an increase in PTh film thickness, with the oxidation concentration being increased. If the oxidation concentration increased more than 0.5 M, then the rate of polymerization reaction increases, and the film peels out from the surface and no deposition takes place.

3. B.2 FTIR spectroscopy

Figure 3.B.2 shows the FTIR spectra of chemical bath deposited polythiophene thin films deposited with various concentrations of FeCl₃ (0.1M, 0.2 M, 0.3 M, 0.4 M and 0.5 M).

The FTIR spectra of chemically deposited polythiophene thin films as shown in fig.2. The absorption peak corresponds to 3408 cm⁻¹ in all the PTh thin films is the humidity due to KBr [3]. The peak at 2921 cm⁻¹ and 2845cm⁻¹ corresponds to C-H symmetric and C-H asymmetric stretching vibrations respectively. The bands at 1628 cm⁻¹ and 1384 cm⁻¹ represents the C=C symmetric and C=C asymmetric vibrating modes in the thiophene ring [2]. The band at 1134cm⁻¹ represents C-H in plane bending [3]. The weaker feature in the range 1030 to 1018cm⁻¹ corresponds to (C-C stretching + C-H wagging components) [2]. As the concentration of the oxidant increases the peak corresponding to 1134 cm⁻¹ becomes sharper representing the C-H bending vibrations, the band at 836 cm⁻¹ which represents C-S stretching vibrations [3], shifts to 869 cm⁻¹ as the oxidant concentration increases. The band at 666 cm⁻¹ representing C-S-C ring deformation [3] becomes sharper and appears with a shoulder peak due to increase in oxidant concentration. While the band at 781 cm⁻¹ corresponds to C-Hα out of plane bending in mono substituted thiophene rings [17], become sharper due to increase in oxidant concentration. This peak was not observed in the vacuum evaporated PTh thin films. The increase in concentration of FeCl₃ increases the rate of polymerization process [18] due to which there may be formation of short chain oligomers or back bone polymers, this may be the reason for presence of bending vibrations in FTIR.
Chapter III: Experimental results of polythiophene (PTh) thin films

3. B.3 XPS studies

Figure 3.B.3 (a), 3.B.4 (a) and 3.B.5(c) show the survey scans of chemically bath deposited PTh thin films for oxidant concentration 0.1 M, 0.3 M and 0.5 M respectively.

- The figures illustrate the presence of distinct bands at binding energies corresponding to the S2p, S2s, C1s, and O1s.
- Figure 3.B.3 (a) shows S2p at 164 eV, S2s at 227 eV, C1s at 284 eV and O1s at 532 eV.
- The evolution of C1s is shown in figure 3.B.3 (b), 3.B.4 (b) and 3.B.5 (b) the standard carbon signal is at 284.3 eV, 284.12 eV and 284.2 eV associated with α and β carbon atoms in the polymeric chains [7], which is at 284.5 eV for vacuum evaporated PTH thin films.
Fig. 3.B.3 XPS of chemical bath deposited PTh thin films for oxidant concentration 0.1 M.
Fig. 3.B.4 XPS of chemical bath deposited PTh thin films for oxidant concentration 0.3 M.
Fig. 3.B.5 XPS of chemical bath deposited PTh thin films for oxidant concentration 0.5 M.

- The peaks at 286.1 eV and 286.9 eV in 0.1 M FeCl₃, 285.7 eV and 286.3 eV in 0.3 M FeCl₃ 285.75 eV in FeCl₃ 0.5 M presents C-S bonds [6].
- The evolution of S2p spectra is shown in 3.B.3 (c), 3.B.4(c) and 3.B. 5 (c) respectively.
For the oxidant concentration 0.1 M, the energy difference between S2p$_{3/2}$ 163.5 eV (FWHM 0.62 eV) and S2p$_{1/2}$ 164.62 eV (FWHM 0.75 eV) is 1.12 eV is nearly close to accepted value 1.17 eV [9].

For oxidant concentration 0.3 M, the energy difference between S2p$_{3/2}$ 163.37 eV (FWHM 0.5 eV) and S2p$_{1/2}$ 164.33 eV (FWHM ~ 0.87 eV) is 1.2 eV.

For the oxidant concentrations 0.5 M, the energy difference between S2p$_{3/2}$ 163.23 eV (FWHM 0.5 eV) and S2p$_{1/2}$ 164.38 eV (FWHM 0.5 eV) is 1.13 eV.

The energy difference between S2p$_{3/2}$ and S2p$_{1/2}$ of chemical bath deposited PTh thin films is nearly similar to vacuum evaporated PTh thin films.

3. B.4 Surface morphology

Figure 3.B.6 FESEM images of chemical bath deposited PTh thin films, for different oxidant concentrations.

It can be seen clearly from figure that the oxidant concentration strongly affects the surface morphology of PTh thin film. Initially when the concentration of oxidant is equal to monomer concentration i.e. 1:1 Ratio the surface morphology shows starting of agglomeration of polymer grains flakes like, when the ratio of monomer and oxidant is 1:2 then there are presence of more lone pair free electrons of FeCl$_3$ to attack on the weak bonds of monomer due to which the polymerization process becomes rapid results in the formation of polymer chain starts with the formation of rounded grains. As soon as the oxidant concentration is increased to 0.3 M then the polymerization was observed with interlinked chain pattern including spherical grains connecting each other. If the monomer concentration increases beyond this i.e. 0.4 M the polymerization process becomes rapid reaction time reduces and it gives interconnecting chain like structure with reduced grain size, if the monomer concentration increases to 0.5 M a well grown polymer chain consisting of spherical grains is observed.
Chapter III: Experimental results of polythiophene (PTh) thin films

Fig. 3.B.6 FESEM images of PTh thin films with various oxidant concentrations
If the concentration of oxidant is increased beyond 0.5 M then the polymerization process takes place so fast and the precipitate forms very quickly and no deposition takes place on the glass. The obtained surface morphology is totally different from those of vacuum evaporated thin films (Figure 3.A.4).

The surface morphology was found to be affected strongly by the oxidant concentration; it was observed that as the oxidant concentration increases, the grain size of the PTh thin films starts to decrease. Higher concentration of oxidant gives more complicated surface morphology with reduced porosity.

In order to get the information regarding the size, shape and orientation of crystallites, transmission electron microscopic image was studied. The figure 3.B.7 shows transmission electron micrographs of PTh thin film for oxidant concentration 0.5 M, shows that the growth has taken place in terms of spherical grains of diameter (> 100 nm) interconnecting each other with random orientation and formation of chain pattern along with amorphous matrix.

![TEM images of PTh thin film for oxidant concentration 0.5 M.](image)

**Fig. 3.B.7 TEM images of PTh thin film for oxidant concentration 0.5 M.**

### 3. B.5 Optical properties

#### 3. B.5.1 Optical transmission

The optical transmission of the PTh thin films is as shown in figure 3.B.8.
Fig. 3.B.8 Optical transmission of PTh thin films for various oxidant concentrations.

It gives $\lambda_{\text{max}} = 498$ nm representing $\pi-\pi^*$ electronics transitions in thiophene ring which is slightly higher than those of previously obtained results in case of polythiophene derivatives by Daik et. al. [19]. The absorbance peak of the PTh thin film is shifted to higher wavelength region as compared to those of vacuum evaporated thin films. PTh thin films show higher absorbance in the lower wavelength range. In the higher wavelength range the films shows higher transmission. The PTh thin films show an increase in optical absorption and a decrease in transmission due to increase in the thickness (i.e. concentration of dopant). This is possibly due to the increase in grain size [19].

The increase in the oxidant concentration leads to increase in the thickness of the film, which results increase in the absorbance and simultaneous decrease in the transmission higher absorbance was for the highest concentration of the oxidant.
3. B.5.2 Optical band gap

Figure 3.B.9 shows the optical band gap of chemical bath deposited PTh thin films for different oxidant (FeCl₃) concentrations. The values of optical band gap tabulated in Table 3.B.1, the band gap found increased with respect to increase in the oxidant concentration (from 1.8 eV to 2.05 eV). The values of optical band gap of chemical bath deposited PTh thin films are comparatively lower than those of vacuum evaporated PTh thin films.

**Table 3.B.1** Optical band gap of PTh thin films for various FeCl₃ conc.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>FeCl₃ concentration (M)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>1.8 ±0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.95 ±0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>2.0 ±0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>2.03 ±0.03</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2.05 ±0.03</td>
</tr>
</tbody>
</table>
3. B.5.3 Refractive Index

The analytical method has been used for the calculation of refractive index (n) using the following formula [12].

\[
    n = \left[ \frac{n_s^2 T_f + n_s \left(1 + \sqrt{R_f}\right)^2}{T_f + n_s \left(1 - \sqrt{R_f}\right)^2} \right]^{1/2}
\]

Where,

- \(n\) = refractive index of the film
- \(n_s\) = refractive index of the substrate
- \(T_f\) = transmission of the film
- \(R_f\) = reflectance of the film

The values of refractive indices of chemical bath deposited PTh thin films are tabulated in table 3.B.2.

**Table 3.B.2 Refractive indices of PTh thin films for various oxidant concentrations.**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>FeCl₃ concentration (M)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>1.79±0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.96±0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>1.99±0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>2.0±0.03</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2.1±0.03</td>
</tr>
</tbody>
</table>

The refractive index of the chemically deposited PTh thin films increased with increase in the oxidant concentration, the increase in the oxidant concentration is responsible for increase in the film thickness this may be the reason for the increase of the refractive index.
The chemical bath deposited thin films show higher values of refractive indices than those of vacuum evaporated PTh thin films.

### 3. B.5.4 Optical waveguiding properties

The optical waveguiding properties of the PTh thin films was studied by prism coupling method, which calculates optical transmission loss of the film [13]. The optical signal transmission loss was measured for five different PTh thin film waveguide, prepared with five different oxidation concentration are tabulated in table 3.B.3. The reported values are average of five values of the same film. It can be seen that, the optical transmission loss increases with increase the oxidant concentration from 5.8 dB/cm to 6.64 dB/cm). The films deposited with higher oxidant concentration shows higher optical transmission loss. The table values revels that the obtained values of optical transmission loss of chemical bath deposited thin films are higher than those of vacuum evaporated PTh thin films.

**Table 3.B.3 Optical transmission loss of PTh thin films prepared with different oxidant concentrations.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Oxidant Concentration (M)</th>
<th>Optical Transmission Loss (dB/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.1</td>
<td>5.8 ± 0.02</td>
</tr>
<tr>
<td>02</td>
<td>0.2</td>
<td>6.23 ± 0.02</td>
</tr>
<tr>
<td>03</td>
<td>0.3</td>
<td>6.4 ± 0.03</td>
</tr>
<tr>
<td>04</td>
<td>0.4</td>
<td>6.51 ± 0.03</td>
</tr>
<tr>
<td>05</td>
<td>0.5</td>
<td>6.64 ± 0.03</td>
</tr>
</tbody>
</table>

### 3. B.6 Adhesion

The adhesion of chemical bath deposited PTh thin films with the substrate is measured by direct Pull Off method.

Figure 3.B.10 shows the graph of adhesion Vs FeCl$_3$ concentration in mole and it is seen that the adhesion is increased with increase in the oxidant concentration from $34.8 \times 10^3$ N/m$^2$ to $41.5 \times 10^3$ N/m$^2$. The PTh thin films prepared with lowest concentration of FeCl$_3$ shows lowest adhesion, the increase in the film thickness
may be responsible for this rise in the adhesion. The adhesion of chemical bath deposited PTh thin films is higher than those of vacuum evaporated PTh thin film.

![Adhesion PTh](image)

**Fig. 3.B.10 Adhesion of PTh thin films prepared with different oxidant concentrations.**

3. B.7 Air aging studies

To study the change in the properties due to surrounding ambient the PTh thin films were studied for air aging effect, the fresh films of PTh were studied for various properties and the same properties were studied by exposing these film to ambient air for 10, 20 and 30 days.

3. B.7.1 Optical transmission

The optical transmission of PTh thin films prepared with oxidant concentration of (0.1 M, 0.3 M and 0.5 M) are as shown in figure 3.B.11, it is seen that the optical transmission decreases with respect to ambient air exposure.
Chapter III: Experimental results of polythiophene (PTh) thin films

The optical transmission decreases from 29% to 27% (for 0.1 M FeCl₃), 28.0% to 27% (for 0.3 M FeCl₃) and 25% to 24% (for 0.5 M FeCl₃) during first 10 days the rapid decrease was observed between 10 and 20 days i.e 21.8% for (for 0.1 M FeCl₃), 21.05% (for 0.3 M FeCl₃) and 19.87% (for 0.5 M FeCl₃). After 20 days the saturation was observed in the decrease of optical transmission. Similar results were observed in case of 0.2 M and 0.4 M FeCl₃.

3. B.7.2 Optical Band gap

The optical band gap of fresh and ambient air exposed PTh thin films are tabulated in table 3.B.4, the decrease in the band gap was observed due to ambient air aging. The optical band gap varies from 1.8 to 1.73 eV for 0.1 M of FeCl₃, 1.95 to 1.86 eV for 0.2 M of FeCl₃, 2.0 to 1.89 eV for 0.3 M of FeCl₃, 2.03 to 1.97 eV for 0.4 M of FeCl₃, and 2.05 to 1.99 eV for 0.5 M of FeCl₃.

3. B.7.3 Refractive index

The values of refractive indices of fresh and ambient air exposed PTh thin films are given in table 4.4, it is seen that the refractive index increased due to ambient aging from 1.79 to 1.93 for 0.1 M of FeCl₃, 1.96 to 2.2 for 0.2 M of FeCl₃, 1.99 to 2.23 for 0.3 M of FeCl₃, 2.0 to 2.29 for 0.4 M of FeCl₃, and 2.1 to 2.29 for 0.5 M of FeCl₃. The refractive index decreases within first 10 days due to ambient air while the decrement becomes slower during 20 and 30 days.
Fig 3.B.11 Optical transmission of fresh and air exposed PTh thin films prepared with 0.1 M, 0.3 and 0.5 M of FeCl$_3$.

3. B.7.4 Optical waveguiding properties

The optical signal transmission loss values are shown in table 3.B.5, from table it is observed that the optical transmission loss decreases with respect to increase in the ambient air aging, the optical transmission loss varies from 5.8 dB/cm to 6.12 dB/cm
for PTh thin films deposited with 0.1 M of FeCl₃, 6.23 dB/cm to 6.28 dB/cm for PTh thin films deposited with 0.2 M of FeCl₃, 6.4 dB/cm to 6.46 dB/cm for PTh thin films deposited with 0.3 M of FeCl₃, 6.51 dB/cm to 6.57 dB/cm for PTh thin films deposited with 0.4 M of FeCl₃ and 6.64 dB/cm to 6.72 dB/cm for PTh thin films deposited with 0.5 M of FeCl₃. The effect of aging was observed intensely during first 10 days for all films.

The important feature of the planar optical waveguide is the possibility of light being guided in the film layer of the structure. In planar optical waveguide light travel on the basis of Total Internal Reflections (TIR) at the film/cover and film/substrate interface, shown in figure 3.B.12, which shows the guiding of light ray through chemical bath deposited polythiophene thin films, for this measurement five identical samples were used.

Total Internal Reflections (TIR) takes place when following conditions are satisfied.

The refractive index of the core medium (n₂) should be higher than the surrounded cladding medium (n₁, n₃).

The angle of incident on the boundary of core cladding interface should be higher than the critical angle (θ Critical). At critical angle the angle of refraction is equal to 90° and the ray travels parallel to interface along the direction of the propagation.
Fig 3.B.12. PTh thin film Optical waveguide.

Figure 3.B.12 shows the photograph of light guiding through chemical bath deposited PTh thin film. The maximum change in the optical transmission loss was observed in between 10 and 20 days, after 20 days the saturation was observed for all oxidant concentration after 20 days. The effect of ambient air aging in chemical bath deposited thin films is more than that of vacuum evaporated PTh thin films.
Table 3.B.4 Optical band gap and refractive index (n) of fresh and ambient air exposed PTh thin films for various FeCl$_3$ concentrations.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Exposure period (no. of days)</th>
<th>Optical band gap (eV), FeCl$_3$ concentration (M)</th>
<th>Refractive Index, FeCl$_3$ concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>01</td>
<td>Fresh</td>
<td>1.8</td>
<td>1.95</td>
</tr>
<tr>
<td>02</td>
<td>10 days</td>
<td>1.77</td>
<td>1.9</td>
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<tr>
<td>03</td>
<td>20 days</td>
<td>1.73</td>
<td>1.87</td>
</tr>
<tr>
<td>04</td>
<td>30 days</td>
<td>1.73</td>
<td>1.86</td>
</tr>
</tbody>
</table>
### Table 3.B.5 Optical transmission loss of fresh and air exposed PTh thin films for different oxidant concentrations.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Oxidant Concentration (M)</th>
<th>Exposure period (No of days)</th>
<th>Optical Transmission Loss (dB/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.1</td>
<td>Fresh</td>
<td>5.8</td>
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<tr>
<td></td>
<td></td>
<td>10 days</td>
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<td>20 days</td>
<td>6.12</td>
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<tr>
<td></td>
<td></td>
<td>30 days</td>
<td>6.12</td>
</tr>
<tr>
<td>02</td>
<td>0.2</td>
<td>Fresh</td>
<td>6.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 days</td>
<td>6.27</td>
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</tr>
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<td>Fresh</td>
<td>6.51</td>
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<td></td>
<td></td>
<td>30 days</td>
<td>6.72</td>
</tr>
</tbody>
</table>

### 3. B.7.5 Adhesion

To study the effect of ambient air aging on the adhesion the PTh thin films deposited with various oxidant concentrations exposed to ambient air for 30 day and the adhesion was measured after every 10 days, table 4.6 shows the values of
adhesion for PTh thin films, the reported value for PTh thin film is an average value of five values measured from the identical sample. From table it is seen that the adhesion decreased with respect to increase in the ambient air exposure period.

**Table 3.B.6 Adhesion of Fresh and air exposed PTh thin films.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Oxidant Concentration (M)</th>
<th>Exposure period (No of days)</th>
<th>Adhesion ×10³ N/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.1</td>
<td>Fresh</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 days</td>
<td>29.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 days</td>
<td>27.83</td>
</tr>
<tr>
<td></td>
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<td>30 days</td>
<td>26.8</td>
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<td>02</td>
<td>0.2</td>
<td>Fresh</td>
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<td>30 days</td>
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<td>10 days</td>
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<td>34.23</td>
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<tr>
<td></td>
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<td>30 days</td>
<td>33.91</td>
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3. B.8 Summary and Important Results

The summary of some important results observed from the investigation carried out as follows:

- The oxidant concentration plays an important role in the polymerization reaction.
- The increase in the oxidant concentration enhances thickness of the film.
- The shifting in bands was observed in FTIR due to increase in the oxidant concentration.
- Surface morphology was strongly affected by oxidant concentration showing different types of morphologies with different oxidant concentration.
- The optical absorbance found increased with simultaneous decrease in the optical transmission due to increase in the oxidant concentration.
- The optical band gap and refractive index increased with increase in the oxidant concentration.
- Optical transmission loss increased with increased in the oxidant concentration.
- The adhesion of PTh thin films increased with oxidant concentration.
- Ambient air aging affects the optical transmission of the thin films the optical transmission found decreased with increase in the air exposure time
- The optical band gap was decreased with increase in the air exposure time.
- The refractive index and optical transmission loss increased with increase in the air exposure.
- The adhesion increased with increase in the air exposure period.
References


