

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of conducting plastic by CVD of pyrrole.

Conducting plastic films were prepared by coating PVA/FeCl₃ solutions onto various plastic film substrates such as PVC, PP and LDPE, then polymerizing the pyrrole onto plastic film substrates by CVD method. The reaction conditions were studied based on FeCl₃ initiator concentration, pyrrole monomer, reaction temperature, reaction time, iodine doping time, and iodine doping temperature.

4.1.1 The effect of FeCl₃ concentration.

The polymerization of pyrrole was carried out with various concentrations of FeCl₃ and pyrrole solution by keeping the reaction time and reaction temperature constant. The CVD of pyrrole results in the formation of insoluble black powders. Initially, the substrate was coated by ferric chloride solution and subjected to measure the electrical conductivity, the value of the electrical conductivity of resulting film is equal to zero, the electrical conductivity can be observed when starting polymerization of pyrrole onto plastic film substrates. It can be concluded that the intrinsic ferric chloride is not a conductive materials. Table 4.1 and Figure 4.1 show the dependence of electrical conductivity on the concentration of ferric chloride solution with polymerizing the pyrrole. The electrical conductivity of the conducting plastic film is increased when increasing the concentration of FeCl₃ and reaches a maximum value at 25%wt of FeCl₃. This implies the incorporation of doping moieties into the polymer, this features is a typical of chemical polymerization of pyrrole and it is well known that the specific nature of the dopant and method of polymer synthesis influence the maximum uptake of the dopant species.

Table 4.1 Effect of FeCl_3 on electrical conductivity of conducting plastic film while other parameters were kept constant as follows:

Pyrrole monomer concentration : 25% in distilled water

Reaction temperature : $-15\text{ }^\circ\text{C}$

Reaction time : 10 hours

Plastic films : PVC

: PP

: LDPE

Reaction condition : in reduced pressure

Plastic	σ (S/cm)					
	0% FeCl_3	5% FeCl_3	10% FeCl_3	15% FeCl_3	20% FeCl_3	25% FeCl_3
PVC	0	2.929×10^{-2}	5.545×10^{-2}	1.306×10^{-1}	1.418×10^{-1}	1.451×10^{-1}
PP	0	2.912×10^{-2}	5.475×10^{-2}	1.355×10^{-1}	1.389×10^{-1}	1.493×10^{-1}
LDPE	0	2.992×10^{-2}	5.615×10^{-2}	1.330×10^{-1}	1.316×10^{-1}	1.428×10^{-1}

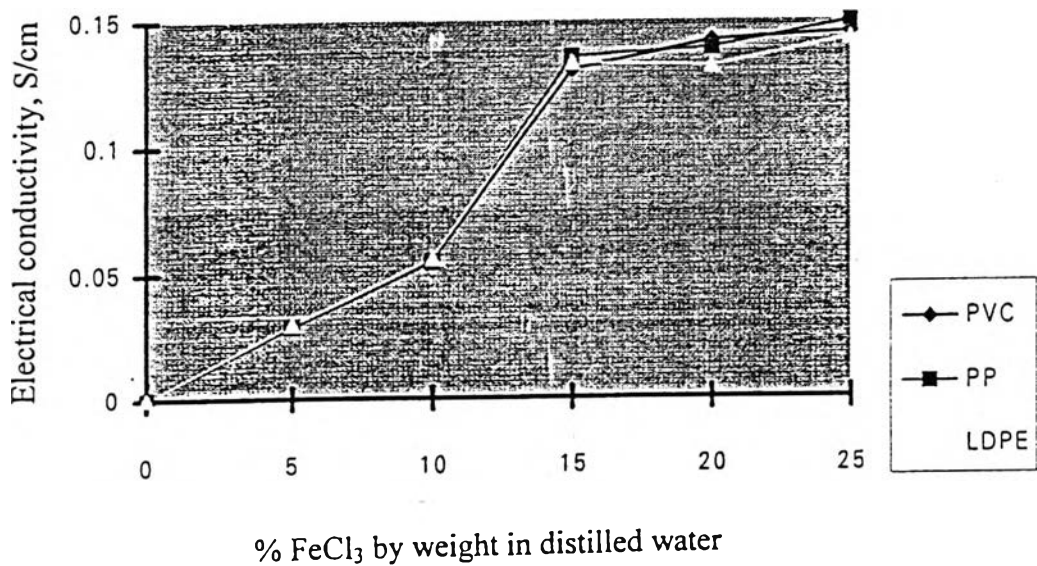


Figure 4.1 Effect of FeCl_3 initiator concentration on electrical conductivity of conducting plastic film.

4.1.2 Effect of pyrrole monomer concentration.

The effect of the concentration or vapor pressure of pyrrole (pyrrole mixed with water) on the electrical conductivity of the prepared plastic films were investigated by varying the concentration of pyrrole monomer from 0, 5, 10, 15, 20 to 25% in distilled water. Its electrical conductivity related to the concentration of pyrrole monomer, was shown in Table 4.2 and Figure 4.2. The electrical conductivity of the prepared conducting plastic films increases with increasing the concentration of pyrrole monomer, and it reaches a maximum value about 0.145 S/cm at a pyrrole concentration of 25%wt. It was clear that as the vapor pressure of pyrrole monomer decreased, the polymerization took longer time to complete, and PPY was little obtained. It was found that the electrical conductivity of the conducting plastic films prepared from 25%v/v of pyrrole monomer gave the maximum value.

Table 4.2 Effect of pyrrole monomer concentration on electrical conductivity of conducting plastic film while other parameters were kept constant as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Reaction temperature	: -15 °C
Reaction time	: 10 hours
Plastic films	: PVC
	: PP
	: LDPE
Reaction condition	: in reduced pressure

Plastic	σ (S/cm)					
	0%PYR	5%PYR	10%PYR	15%PYR	20%PYR	25%PYR
PVC	0	3.852×10^{-2}	7.570×10^{-2}	1.259×10^{-1}	1.388×10^{-1}	1.451×10^{-1}
PP	0	3.872×10^{-2}	7.967×10^{-2}	1.284×10^{-1}	1.431×10^{-1}	1.493×10^{-1}
LDPE	0	3.848×10^{-2}	7.709×10^{-2}	1.205×10^{-1}	1.340×10^{-1}	1.428×10^{-1}

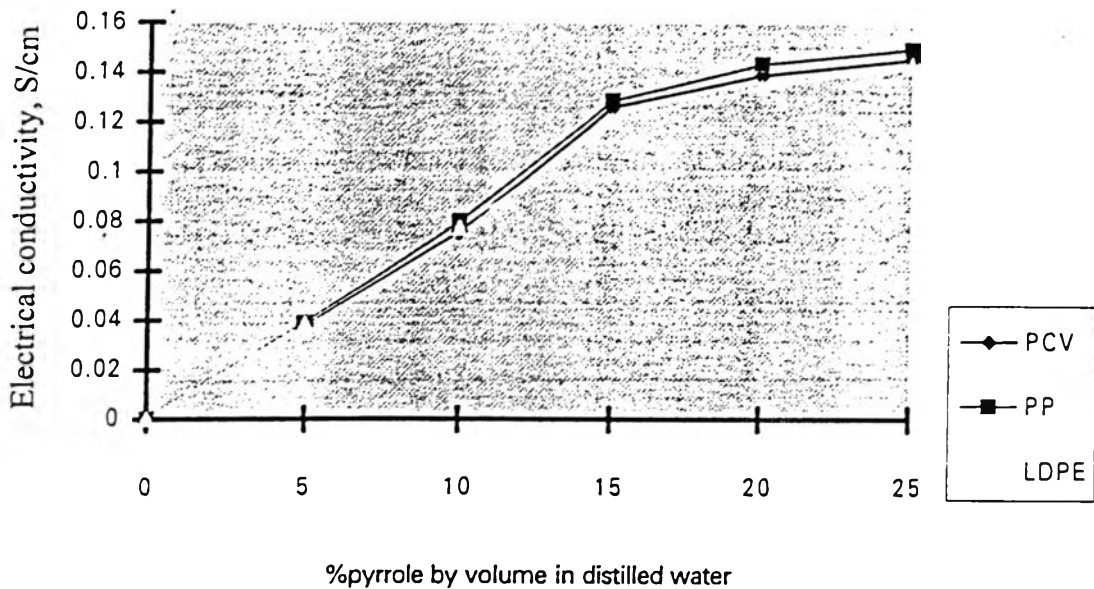


Figure 4.2 Effect of pyrrole monomer concentration on electrical conductivity of conducting plastic film.

4.1.3 Effect of reaction temperature.

The reaction temperature imposes a strong effect on the electrical conductivity because the reaction temperature affects the vapor pressure of pyrrole monomer and surface morphology of polymer matrix and substrates which more effect to electrical conductivity. The effect of reaction temperature on electrical conductivity was shown in Table 4.3 and Figure 4.3. In the high temperature condition, the low electrical conductivity of the resulting conducting film was obtained. It could be the 3 factors as follows: (1) The decomposition of FeCl_3 increased at higher temperature, which reduced the catalyst molecule, so that less PPY was produced. (2) The diffusion rate of the pyrrole was very fast, then the diffusion of pyrrole vapor to the FeCl_3 was reduced at high temperature and the polymerization of pyrrole was also reduced and (3) The surface of the prepared conducting films were denatured at high temperature, which destroyed the surface

morphology that for the reducing electrical conductivity at high temperature. Finally, preparation of conducting plastic films from many types of plastic films were obtained PVC/PPY, PP/PPY and LDPE/PPY, respectively. Obviously, the electrical conductivities of PP/PPY and LDPE/PPY slightly decreased 42 and 40%, respectively, with increasing reaction temperature from room temperature ($\sim 30^\circ\text{C}$) to high temperature (70°C). On the other hand, the electrical conductivity of PVC/PPY film was lower than PP/PPY and LDPE/PPY about 48% with increasing reaction temperature from room temperature to high temperature. Therefore the PVC film has the poorest thermal stability which compared to PP and LDPE films at high temperature.

Table 4.3 Effect of reaction temperature on electrical conductivity of conducting plastic film while other parameters were kept constant as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Pyrrrole monomer concentration	: 25% in distilled H ₂ O
Reaction time	: 10 hours
Plastic films	: PVC
	: PP
	: LDPE
Reaction condition	: in reduced pressure

Plastic	σ (S/cm)					
	-15°C	0°C	10°C	30°C	50°C	70°C
PVC	1.451×10^{-1}	1.435×10^{-1}	1.390×10^{-1}	7.192×10^{-2}	5.129×10^{-2}	3.735×10^{-2}
PP	1.493×10^{-1}	1.417×10^{-1}	1.292×10^{-1}	6.819×10^{-2}	4.939×10^{-2}	3.927×10^{-2}
LDPE	1.428×10^{-1}	1.438×10^{-1}	1.271×10^{-1}	7.165×10^{-2}	5.334×10^{-2}	4.276×10^{-2}

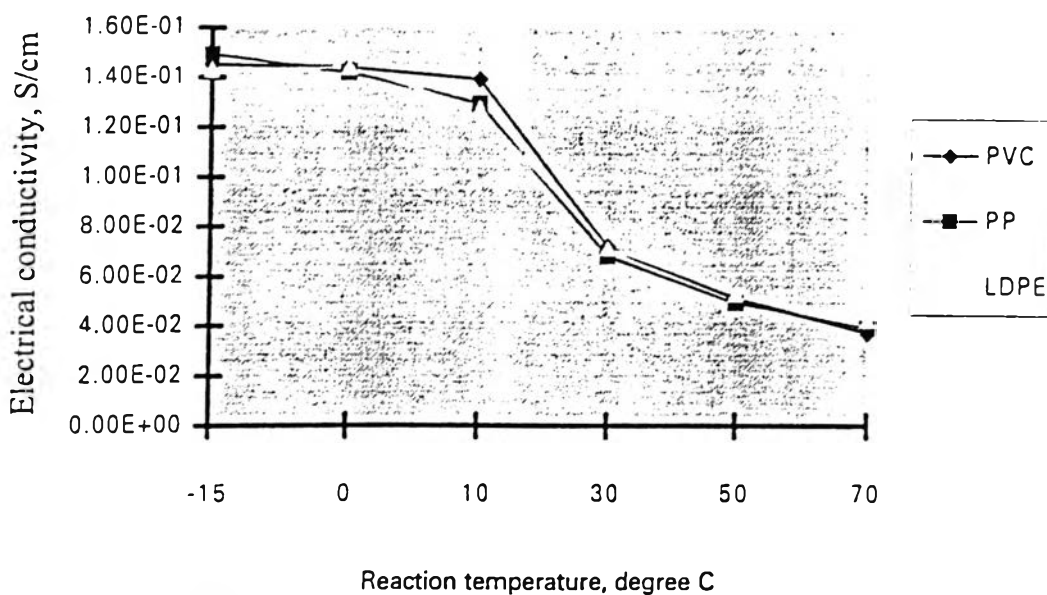


Figure 4.3 Effect of reaction temperature on electrical conductivity of conducting plastic film.

4.1.4 Effect of reaction time.

The electrical conductivity increases with increasing the reaction time, and it reaches a maximum value about 0.160 S/cm at the reaction time as 20 hours. When the reaction time was 10 hours, the electrical conductivity is constant. This is expected due to the vapor pressure of pyrrole was saturated at this time, the final electrical conductivity of the prepared conducting film was not dependent on the reaction time above 10 hours.

Table 4.4 Effect of reaction time on electrical conductivity on plastic film substrates while other parameters were kept constant as follows:

FeCl₃ initiator concentration : 25% in distilled H₂O

Pyrrole monomer concentration : 25% in distilled H₂O

Reaction temperature : -15°C

Plastic films : PVC

: PP

: LDPE

Reaction condition : in reduced pressure

Plastic	σ (S/cm)					
	0 hrs.	5 hrs.	10 hrs.	15 hrs.	20 hrs.	25 hrs.
PVC	0	5.746×10^{-2}	1.451×10^{-1}	1.584×10^{-1}	1.589×10^{-1}	1.552×10^{-1}
PP	0	3.758×10^{-2}	1.493×10^{-1}	1.586×10^{-1}	1.568×10^{-1}	1.575×10^{-1}
LDPE	0	4.020×10^{-2}	1.428×10^{-1}	1.555×10^{-1}	1.611×10^{-1}	1.561×10^{-1}

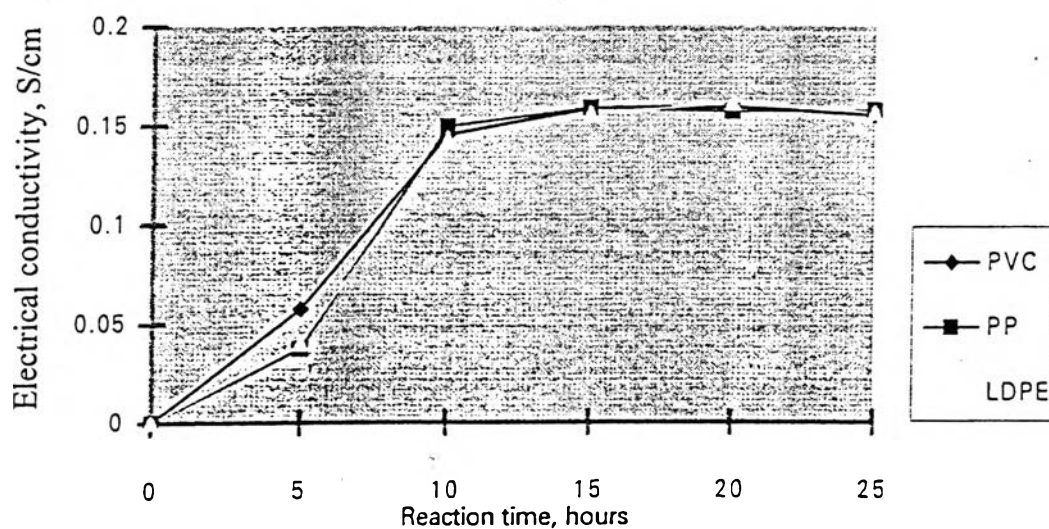


Figure 4.4 Effect of reaction time on electrical conductivity of conducting plastic film.

4.1.5 Effect of iodine doping time.

Iodine vapor has strong effect on the electrical conductivity. The effect of iodine doping time on electrical conductivity was shown in Table 4.5 and Figure 4.5. The electrical conductivity of the resulting conducting plastic film increases with increasing the doping time, and it reaches a maximum value about 19.05 S/cm at a doping time of 60 minutes. The possible reason of higher electrical conductivity of the conducting film was due to iodine. Iodine has been observed to produce significant changes in electrical conductivity of polymers, it is believed that charge transfer complexes between iodine ions and monomer units are formed.

Table 4.5 Effect of iodine doping time on electrical conductivity of PP/PPY film with parameters as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Pyrrole monomer concentration	: 25% in distilled H ₂ O
Reaction temperature	: -15°C
Reaction time	: 20 hrs.
Plastic film	: PP
Reaction condition	: in reduced pressure
Exposure condition	: 30°C in reduced pressure

Doping time, min	σ , S/cm
0	1.568x10 ⁻¹
30	16.81
60	19.05
90	18.80
120	18.79

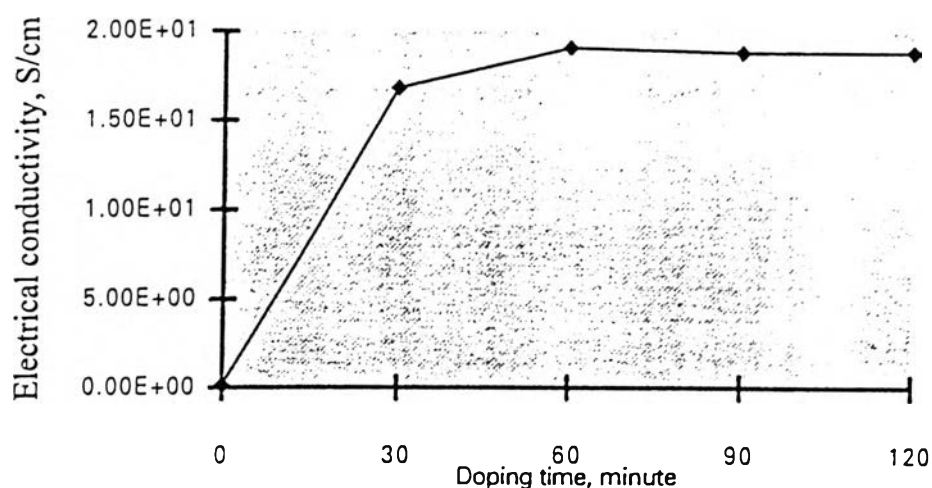


Figure 4.5 Effect of iodine doping time on electrical conductivity of PP/PPY film.

4.1.6 Effect of iodine doping temperature.

The effect of iodine doping temperature on electrical conductivity as shown in Table 4.6 and Figure 4.6. The doping temperature imposes a strong effect on the electrical conductivity, because the doping temperature affects the iodine vapor pressure and surface morphology of prepared conducting films. The electrical conductivity of the doped film strongly depends on the doping temperature, as shown in Table 4.6 and Figure 4.6. The maximum electrical conductivity of the doped film at low temperature (-15°C) under reduced pressure on 60 minutes of doping time is 26.45 S/cm, which is the highest that compared with the prepared conducting film doped at 30 and 70°C , especially the minimum electrical conductivity of the doped film at 70°C is very low as 3.75 S/cm. These results indicate that the diffusion of dopant in polymer is low at high temperature.

The iodine doping also affects its electrical conductivity. For example, the undoped film has an electrical conductivity of 0.16 S/cm, which is two orders of magnitude lower than that of the conducting plastic film doped with iodine vapor. It implies incorporation of doping moieties into the polymer. This feature is a typical of chemical polymerization of pyrrole and it is well known that the specific

nature of the dopant and method of polymer synthesis influence the maximum uptake of the dopant species.

Table 4.6 Effect of iodine doping temperature on electrical conductivity of PP/PPY film with parameters as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Pyrrrole monomer concentration	: 25% in distilled H ₂ O
Reaction temperature	: -15°C
Reaction time	: 20 hrs.
Plastic film	: PP
Reaction condition	: in reduced pressure
Exposure condition	: 60 minutes in reduced pressure

Doping temperature, °C	σ , S/cm
-15	26.4550
30	19.0476
70	3.7495

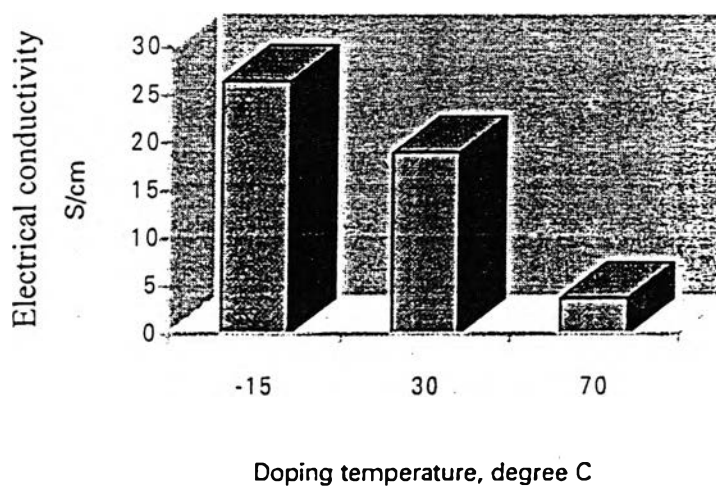


Figure 4.6 Effect of iodine doping temperature of PP/PPY film.

4.2 Characterization of prepared conducting plastic film by CVD of pyrrole.

The prepared conducting plastic films were characterized by elemental analysis and measurement of electrical conductivity, infrared spectrum, UV-visible spectrum, optical microscopy, mechanical properties, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). All equipments were reported in Section 3.2.

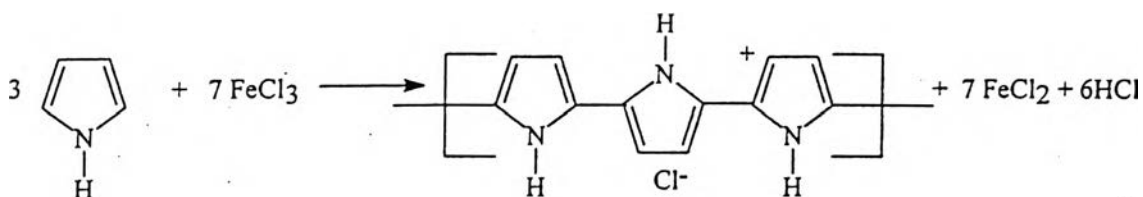
Table 4.7 shows mole fraction of Fe, Cl, N, C, H and O, and oxidizing polymerization (by CVD method) of pyrrole via conditions were kept as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Pyrrole monomer concentration	: 25% in distilled H ₂ O
Reaction temperature	: 30°C
Reaction time	: 10 hrs.
PVA	: 1 g.
Reaction condition	: in reduced pressure

Table 4.7 Elemental analysis of polypyrrole (in mole fraction of elemental)

C (mole fraction)	N (mole fraction)	H (mole fraction)	Cl(mole fraction)	Fe(mole fraction)	O(mole fraction)
4.00	1.00	3.25	0.33	0.003	0.001
3.99	1.01	3.26	0.31	0.003	0.001
4.01	0.99	3.24	0.32	0.003	0.001
4.00	1.01	3.25	0.33	0.002	0.001
4.00	0.98	3.24	0.32	0.003	0.0007
4.00	0.998	3.25	0.322	0.003	0.00094

Armes (1987) [26] reported the optimum conditions for the polymerization of pyrrole monomer in aqueous solution using FeCl_3 as the initiating/doping species. The approximate stoichiometric reaction is thought to proceed as shown below. There is one Cl^- ion associated with every three pyrrole moieties in the polymer chains. Therefore, from the reference and data in Table 4.7, the reaction was as:



4.2.1 Characterization and effect of FeCl_3 initiator concentration.

The effect of FeCl_3 initiator concentration was determined by UV-visible spectrometer. UV-visible absorption spectrum is shown in Figure 4.7, it shows an absorption band at 197 nm and 520 nm. Brame [27] and David [28] reported UV-visible spectra for these composite films, this absorption band should be considered as the presence of residual acetate groups in PVA molecule chain and conjugated double bond from some dehydroxy of OH group in PVA chain. Figures 4.8-4.25 show UV-visible spectra of polypyrrole-PVA composite films which coated on various plastic film substrates (PVC PP and LDPE). The absorption bands shift to 220 nm and 318 nm which suggest the formation of free carrier and $\pi-\pi^*$ transition formed in the plastic substrates. Absorption intensity wavelength at 220 nm and 318 nm are shown in Figures 4.26-4.28. The absorption intensity increases with increasing concentration of FeCl_3 due to the metal atom which was introduced into polymer matrix may be leading to a new residual.

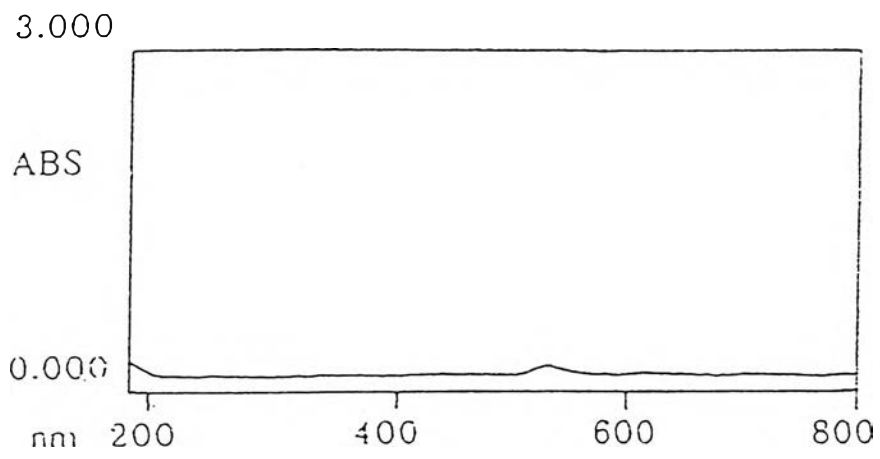


Figure 4.7 UV-vis. absorption spectrum of PVA film.

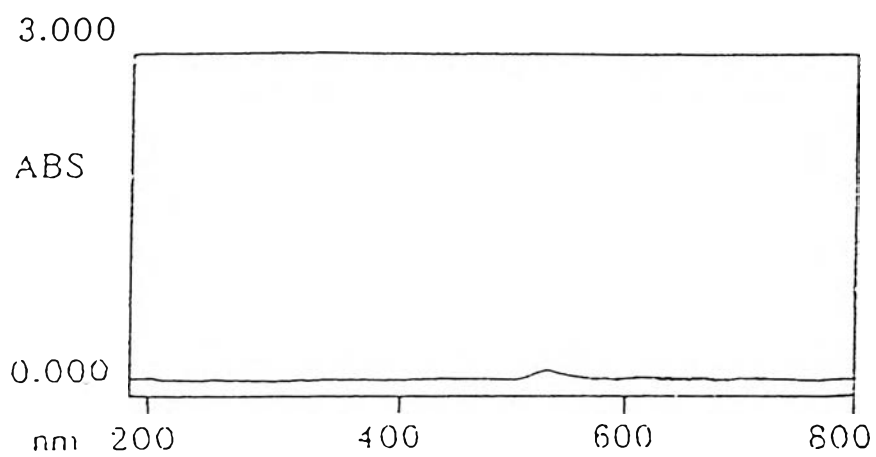


Figure 4.8 UV-vis. absorption spectrum of PVC film.

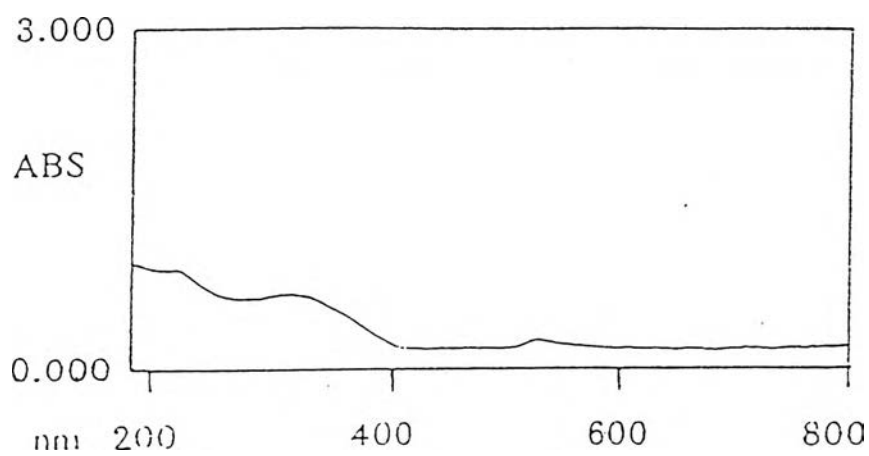


Figure 4.9 UV-vis. absorption spectrum of PVC/PVA/5%FeCl₃ film.

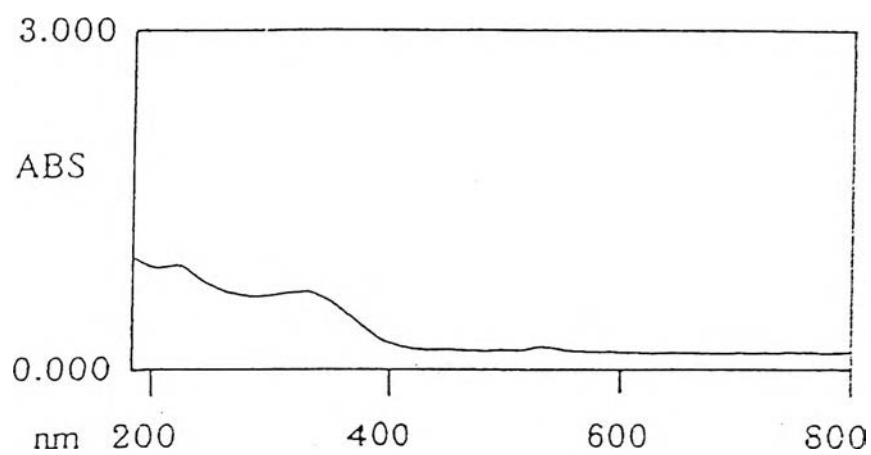


Figure 4.10 UV-vis. absorption spectrum of PVC/PVA/10%FeCl₃ film.

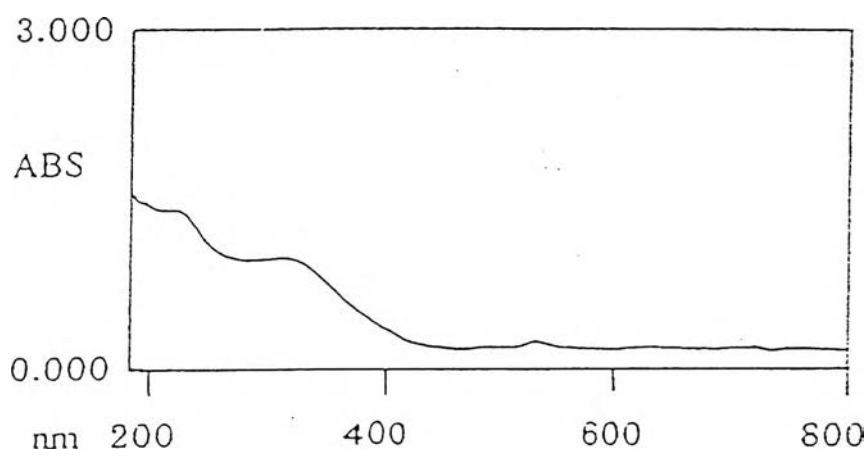


Figure 4.11 UV-vis. absorption spectrum of PVC/PVA/15%FeCl₃ film.

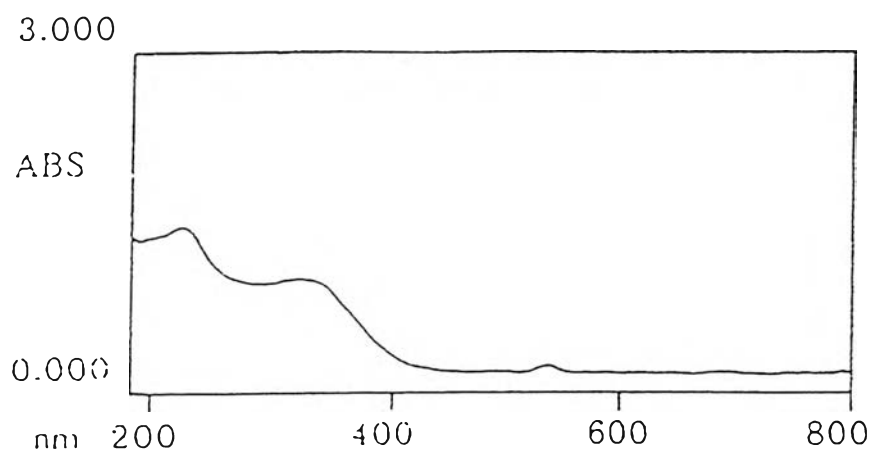


Figure 4.12 UV-vis. absorption spectrum of PVC/PVA/20%FeCl₃ film.

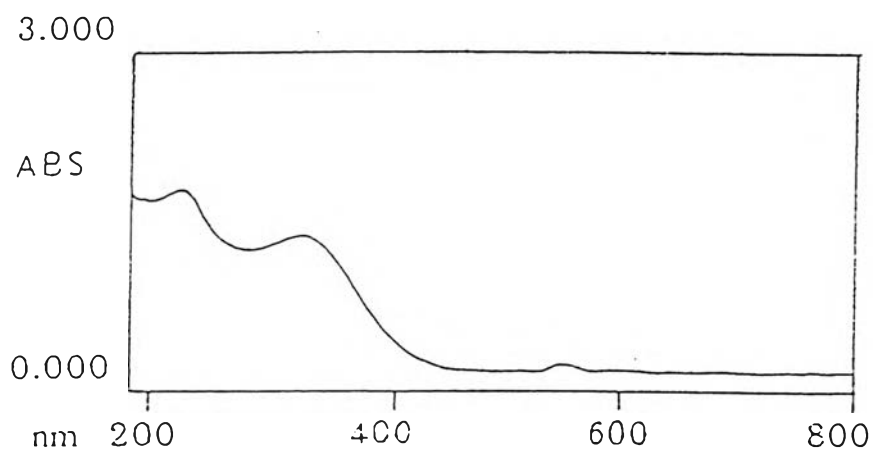


Figure 4.13 UV-vis. absorption spectrum of PVC/PVA/25%FeCl₃ film.

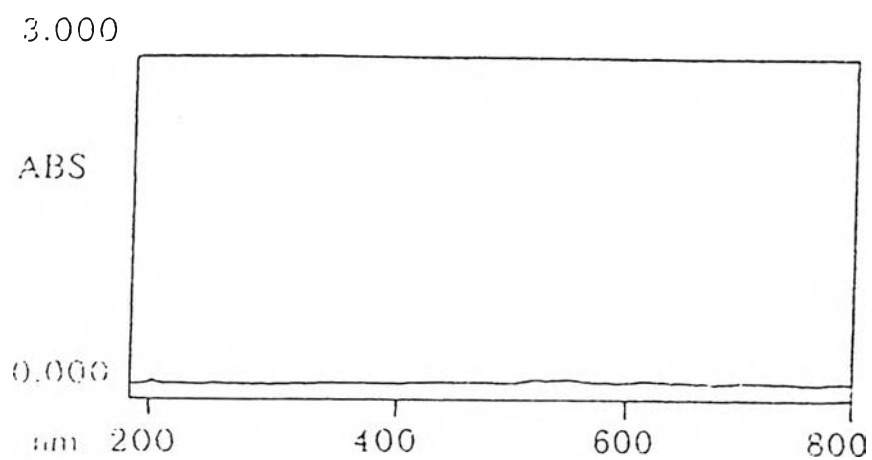


Figure 4.14 UV-vis. absorption spectrum of PP film.

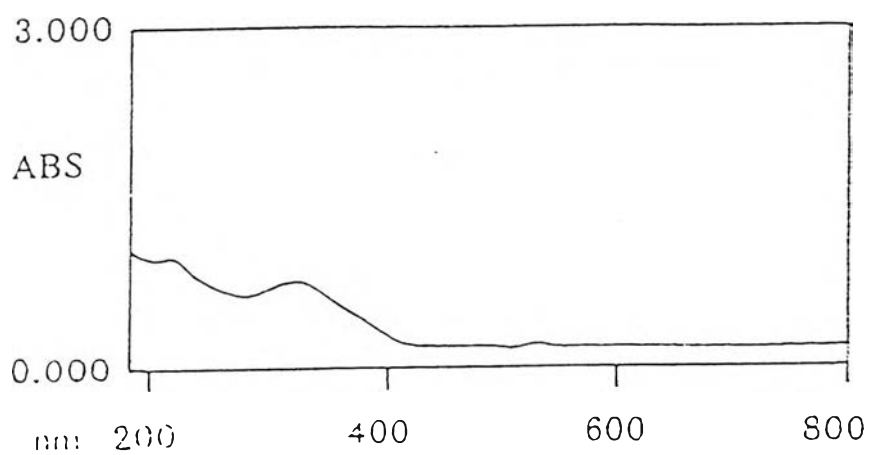


Figure 4.15 UV-vis. absorption spectrum of PP/PVA/5%FeCl₃ film.

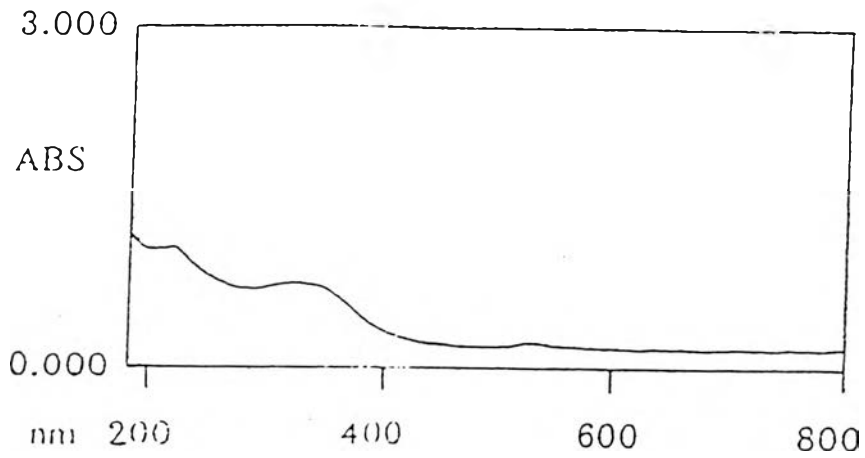


Figure 4.16 UV-vis. absorption spectrum of PP/PVA/10%FeCl₃ film.

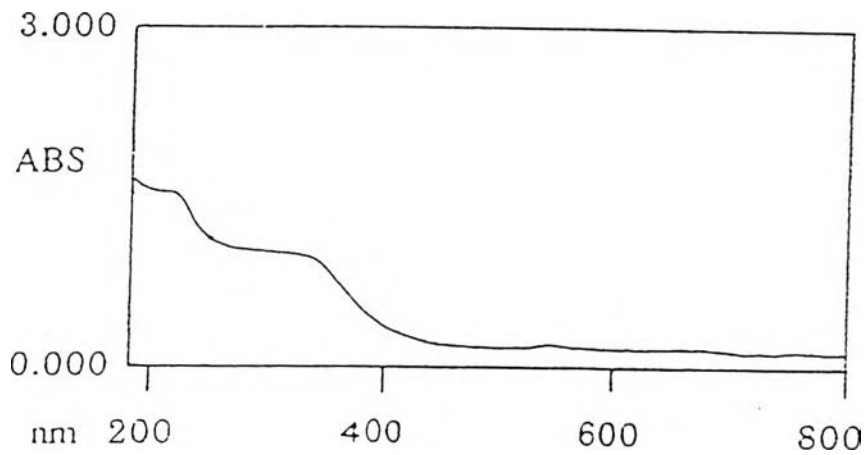


Figure 4.17 UV-vis. absorption spectrum of PP/PVA/15%FeCl₃ film.

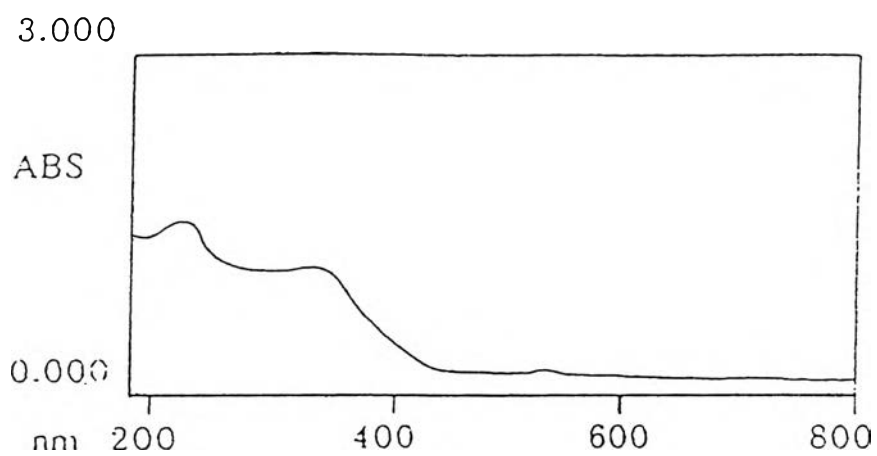


Figure 4.18 UV-vis. absorption spectrum of PP/PVA/20%FeCl₃ film.

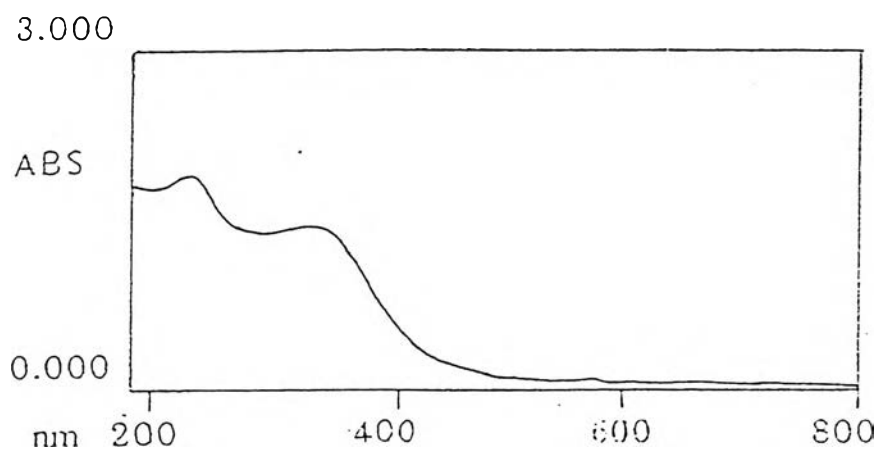


Figure 4.19 UV-vis. absorption spectrum of PP/PVA/25%FeCl₃ film.

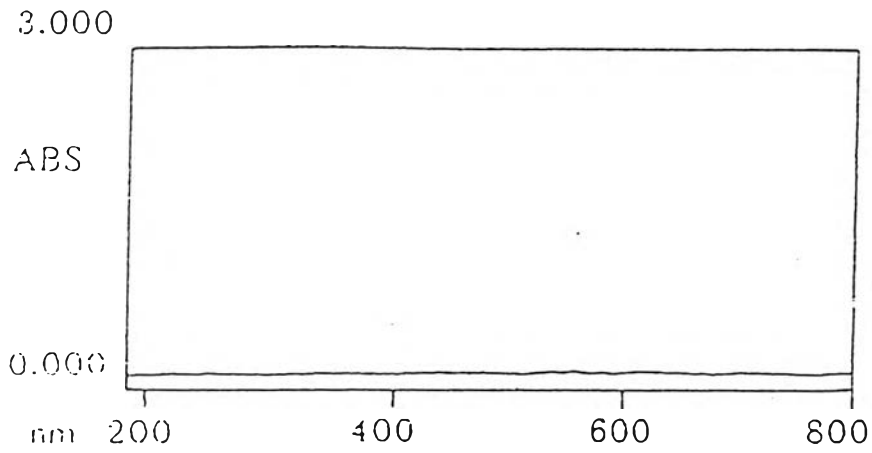


Figure 4.20 UV-vis. absorption spectrum of LDPE film.

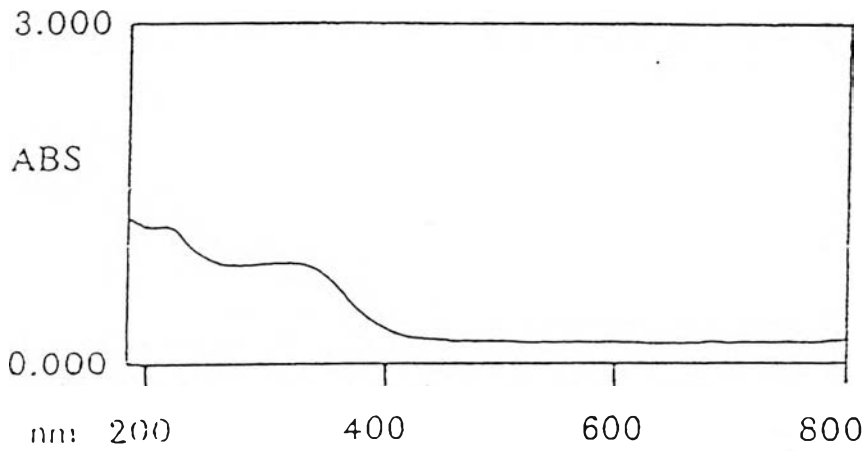


Figure 4.21 UV-vis. absorption spectrum of LDPE/PVA/5%FeCl₃ film.

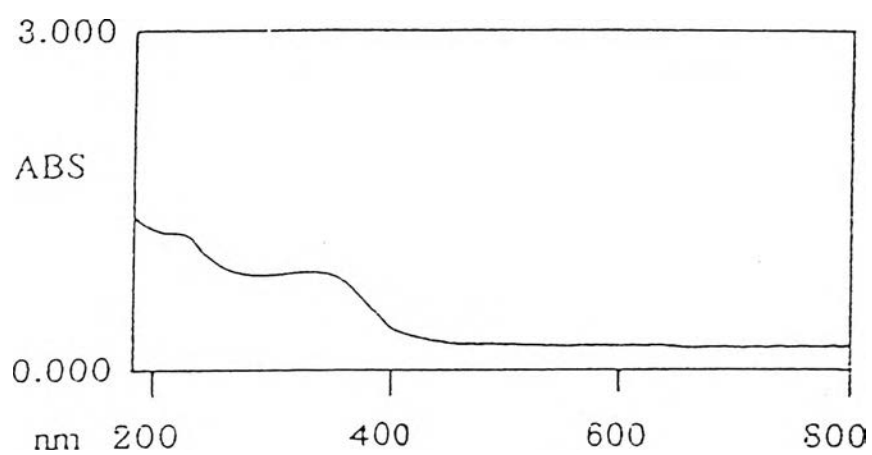


Figure 4.22 UV-vis. absorption spectrum of LDPE/PVA/10%FeCl₃ film.

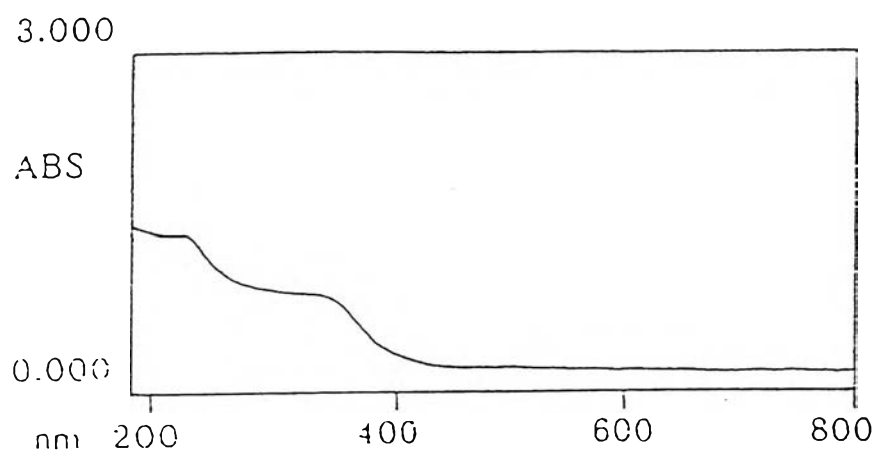


Figure 4.23 UV-vis. absorption spectrum of LDPE/PVA/15%FeCl₃ film.

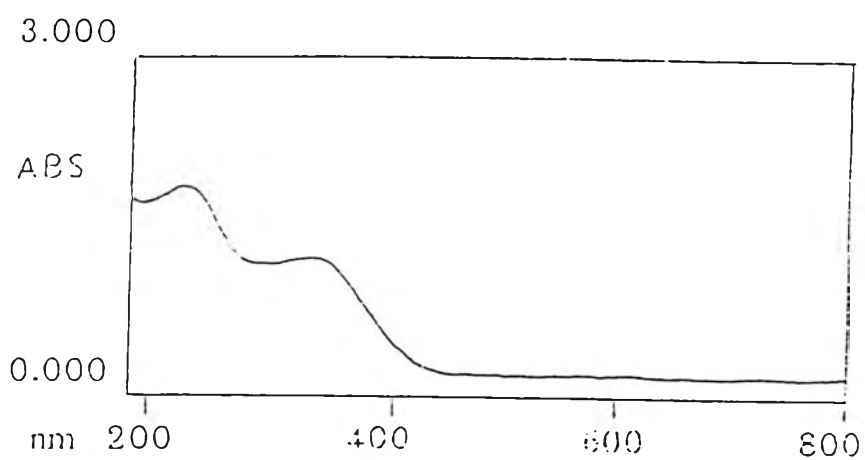


Figure 4.24 UV-vis. absorption spectrum of LDPE/PVA/20%FeCl₃ film.

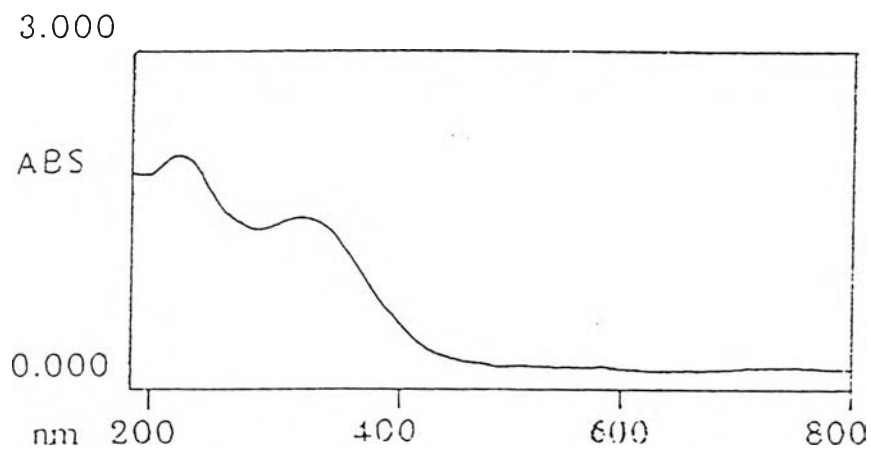


Figure 4.25 UV-vis. absorption spectrum of LDPE/PVA/25%FeCl₃ film.

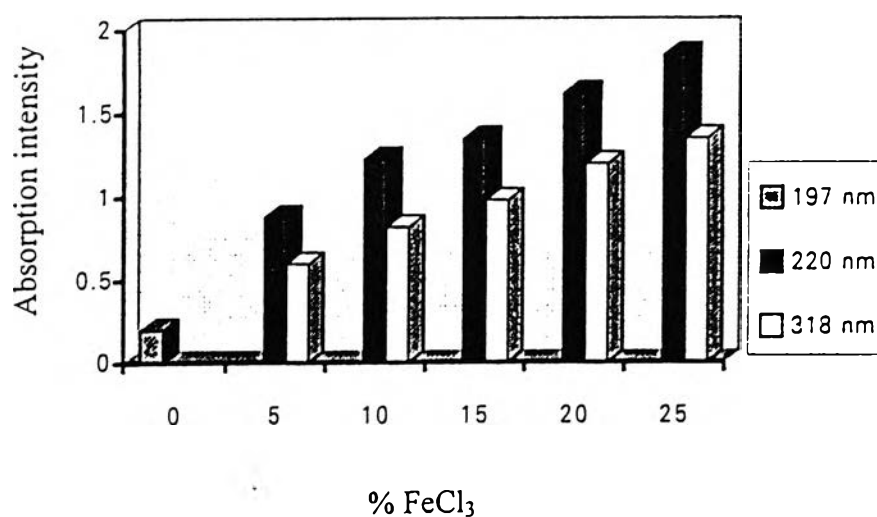


Figure 4.26 Absorption intensity at 220 nm and 318 nm of PVC/PVA/FeCl₃ depending on FeCl₃ initiator concentration.

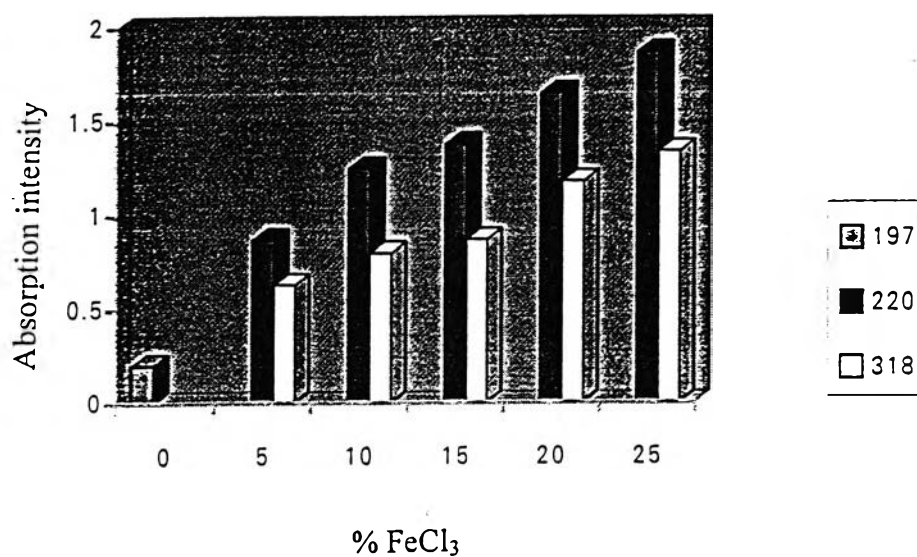


Figure 4.27 Absorption intensity at 220 nm and 318 nm of PP/PVA/FeCl₃ depending on FeCl₃ initiator concentration.

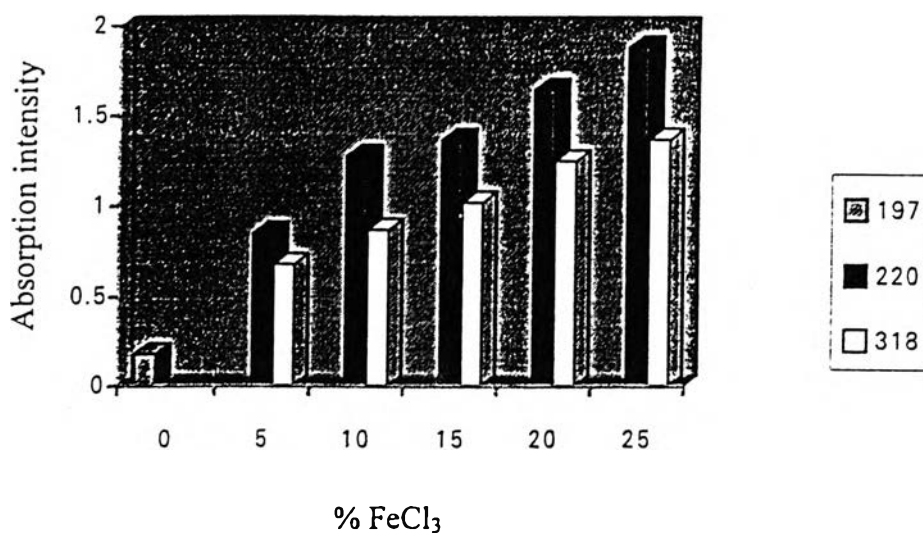


Figure 4.28 Absorption intensity at 220 nm and 318 nm of LDPE/PVA/FeCl₃ depending on FeCl₃ initiator concentration.

4.2.2 Characterization and effect of pyrrole monomer concentration.

Table 4.2 and Figure 4.2 show the electrical conductivity increases with increasing pyrrole monomer concentration. It can be confirmed by FT-IR. The FT-IR spectra of prepared conducting plastic films were shown in Figures B-8-B-12 for PVC/PPY films, Figure B-13 for PP/PPY and Figure B-14 for LDPE/PPY films. All reaction condition were kept as follows:

FeCl ₃ initiator concentration	: 25% in distilled H ₂ O
Reaction temperature	: -15°C
Reaction time	: 10 hrs.
Plastic film	: PVC
	: PP
	: LDPE
Reaction condition	: in reduced pressure.

In Figures B-8-B-12 show FT-IR spectra of PVC/PPY conducting plastic films and Table 4.8 presents the relevant and characteristic IR absorptions of prepared conducting plastic films in this work. In the 3480-3600 cm^{-1} region indicates the N-H stretching band of PPY gradually tends to shift to higher frequencies and intensity with increasing pyrrole concentration. This implies a gradual reduction in the extent of H-bonding. Tentatively, with increasing FeCl_3 concentration, more and more pyrrolic N atoms will enter into the charge-transfer interaction with Fe^{3+} ions. This will tend to reduce the chance of H-bonding interaction of these N atoms with the pyrrolic H atoms of another PPY chain. Further, the possibility of the manifestation of polaron-bipolaron structures, as commonly envisaged for conducting PPY produced during oxidative polymerization, will further disfavor the above H-bonding process. In the 1800-500 cm^{-1} regions, the appearance of IR absorption at 1660-1600 cm^{-1} corresponds to C=C and C=N stretching band, which would be expected to a conjugated structure postulated for the polarons and bipolarons. At 3325 cm^{-1} indicates the O-H stretching of PVA, that the broad and intensive band are indicated in this region. From Figure B-13 are similar to Figures B-8-B-12 which are previously implied. FT-IR spectra of original plastic films are shown in Figures B-1-B-7 in Appendix B.

4.2.3 Characterization and effect of reaction temperature.

The effect of reaction temperature on electrical conductivity of prepared conducting plastic films were investigated by optical microscopy (surface morphology) which used at 100 times magnification. The electrical conductivity decreases with increasing reaction temperature that are shown in Table 4.3 and Figure 4.3. Optical microscopy photographs of the samples prepared with different reaction temperature are shown in Figure C at 100 times magnification. In general, the PPY prepared with FeCl_3 at different reaction temperature appears to be characterized by a smooth and continuous surface. However, with increasing

reaction temperature, the resultant conducting plastic film seems rough and uncontinuous. Therefore, the prepared conducting plastic films were prepared at high reaction temperature which are not suitable for using. The PVC/PPY film has the lowest electrical conductivity at higher temperature compared with PP/PPY and LDPE/PPY film, it can be concluded that the PVC/PPY is not suitable for high temperature.

4.2.4 Characterization and effect of reaction time.

The effect of reaction time on electrical conductivity are shown in Table 4.4 and Figure 4.4. The electrical conductivity are increased with increasing reaction time. It can be investigated by FT-IR spectrophotometer. The FT-IR spectra of the effect of reaction time on electrical conductivity are shown in Figures B-15-B-20. The important characteristic assignment peaks are shown in Table 4.8. The band about 3580 cm^{-1} and the region from $1600\text{--}400\text{ cm}^{-1}$ indicates the N-H stretching and pyrrole ring vibrations of PPY, the broad and intensive bands are indicated when increasing reaction time, the remaining bands are characteristic of plastic film substrates. In Figures B-15-B-18 show characteristic assignment bands of PVC and includes ones at 2980 cm^{-1} and 2950 cm^{-1} indicating the -C-H stretching peak, at 730 cm^{-1} indicates the -CH₂ rocking and at 630 cm^{-1} indicates the -C-Cl stretching, Figure B-19 indicate characteristic assignment peaks for PP at 2990 cm^{-1} , 2950 cm^{-1} which indicate the -C-H stretching, at 1450 cm^{-1} indicates the -C-H bending of -CH₃ and at 720 cm^{-1} indicates the -CH₂ rocking, Figures B-20 show characteristic assignment peaks for LDPE at 3000 cm^{-1} , 2960 cm^{-1} which indicate the -C-H stretching and at 740 cm^{-1} indicates the -CH₂ rocking. Important characteristic assignment peaks at 1650 cm^{-1} and 1600 cm^{-1} which assigned to the -C=C and -C=N stretching of PPY, these mean that the conjugated structure occurred in PPY.

Table 4.8 The important characteristic assignment peaks for the FT-IR spectrum of the prepared conducting polymer [29-33].

Wave number (cm ⁻¹)	Assignment
3620	N-H stretching of PPY
3580	
3530	
3350	O-H stretching of hydrogen bonding in
3320	PVA
3300	
3250	
3000	C-H stretching of PVA PVC PP and
2980	LDPE
2950	
2920	
2853	
1780	C=C and C=N stretching of PPY ring
1710	
1650	
1600	
1495	C-H in-plane bending of PPY ring
1340	
1300	
1220	Doping-induced mode of PPY structure
1200	
1460	C-H bending of -CH ₃ group in PP
1410	
730	C-H rocking of aliphatic polymer chain
720	
635	C-Cl stretching vibration of PVC

4.2.5 Characterization and effect of iodine doping time.

The PP/PPY films were exposed in iodine vapor at various times and characterized by FT-IR spectrophotometer as shown in Figures B-21-B-24. The characteristic assignment bands are shown in Table 4.8. The absorption bands at 3620 cm^{-1} and 3600 cm^{-1} indicate the -N-H stretching of PPY, at 3280 cm^{-1} , 3250 cm^{-1} indicate -O-H stretching of hydroxy groups in PVA. Obviously, the C=C and C=N stretching of PPY are sharp and intensive bands at 1650 cm^{-1} and 1600 cm^{-1} , as would be expected, because the conjugated structure can be much produced that the polaron and bipolarons structure were occurred by adding I-dopant, which may be inserted to incorporate on polymer chain. The electron density was changed by I-ions and Cl-ions from FeCl_3 initiator oxidizing agent, these can be confirmed by FT-IR spectra in Figures B-21-B-22. However, the absorption bands in the same region are not increased with increasing doping time because the prepared conducting films were saturately doped.

4.2.6 Characterization and effect of iodine doping temperature.

The doping temperature imposes a strong effect on electrical conductivity of prepared conducting films as following in Section 4.1.6. Figures B-22, B-25 and B-26 are FT-IR spectra of PP/PPY which doped with iodine at -15 , 30 and 70°C , respectively. The effects of iodine doping temperature were implied in Section 4.1.6, these are not clear, and the result in Figure B-22 and Figures B-25-B-26 are also similar. The morphologies of the prepared conducting films at various doping temperatures are demonstrated in Figure C in Appendix C. Interestingly, the surface of the resulting film at the highest doping temperature ($\sim 70^\circ\text{C}$) has very some rough and broken parts. Therefore, the electrical conductivity are rapidly decreased by increasing iodine doping temperature.

4.3 Mechanical and Thermal properties of prepared conducting plastic film.

4.3.1 Mechanical properties of the prepared conducting plastic film.

Physical properties of the conducting plastic films were investigated by Universal testing material Machine: Lloyd 500. Average value of technical data from testing are shown in Appendix D. The tensile strength of PVA/FeCl₃ composite films on various FeCl₃ initiator concentrations are shown in Table 4.9 and in Figure 4.29. It can be seen that tensile strength are decreased with increasing FeCl₃ concentration. On the other hand, % elongation at break are increased with increasing FeCl₃ initiator concentration as shown in Table 4.10 and Figure 4.30. It may be explained, when FeCl₃ initiator concentration was increased, its affect PVA structure. The metal atoms incorporate in PVA that may decrease interaction force between polymer chains. Additionally, the composite film absorbs more water from air.

The tensile strength and % elongation at break were increased with polymerizing of pyrrole by CVD on original film substrates. The tensile strength and %elongation at break of PP/PPY and LDPE/PPY film are less decreased than the tensile strength and %elongation at break of PVC/PPY film with increasing reaction temperature as shown in Figures 4.31-4.32. The effects of iodine vapor on mechanical properties of prepared conducting plastic films were investigated, as shown Figures 4.33-4.36. The tensile strength and %elongation at break of PVC/PPY film doped at high temperature (~70°C) which has the poorest value, it can expected that the PVC film has poorer thermal stability than PP and LDPE film that also leads to the prepared PVC/PPY film which has less mechanical properties than PP/PPY and LDPE/PPY films. The poorest mechanical properties of PP/PPY is obtained at the longest doping time, it may be explained that the PP/PPY film has the highest gas permeability coefficient because the conducting plastic films should

be permeated or inserted by doping species that interaction force between polymer chain can be reduced, and also decreasing mechanical properties.

Table 4.9 Average tensile strength of PVA/FeCl₃ film on FeCl₃ initiator concentration.

%FeCl ₃	Tensile strength (N/mm ²)
0	25.56
5	25.49
10	25.21
15	25.01
20	24.63
25	24.10

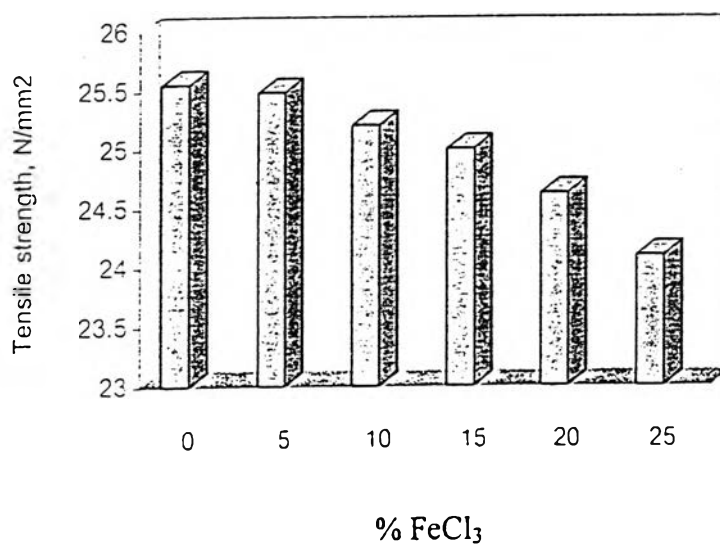


Figure 4.29 Plotting of tensile strength and FeCl₃ concentration on PVA/FeCl₃ composite film.

Table 4.10 Average %elongation at break of PVA/FeCl₃ film on FeCl₃ initiator concentration.

%FeCl ₃	%Elongation at break
0	420.3
5	286.6
10	299.3
15	322.7
20	351.4
25	372.5

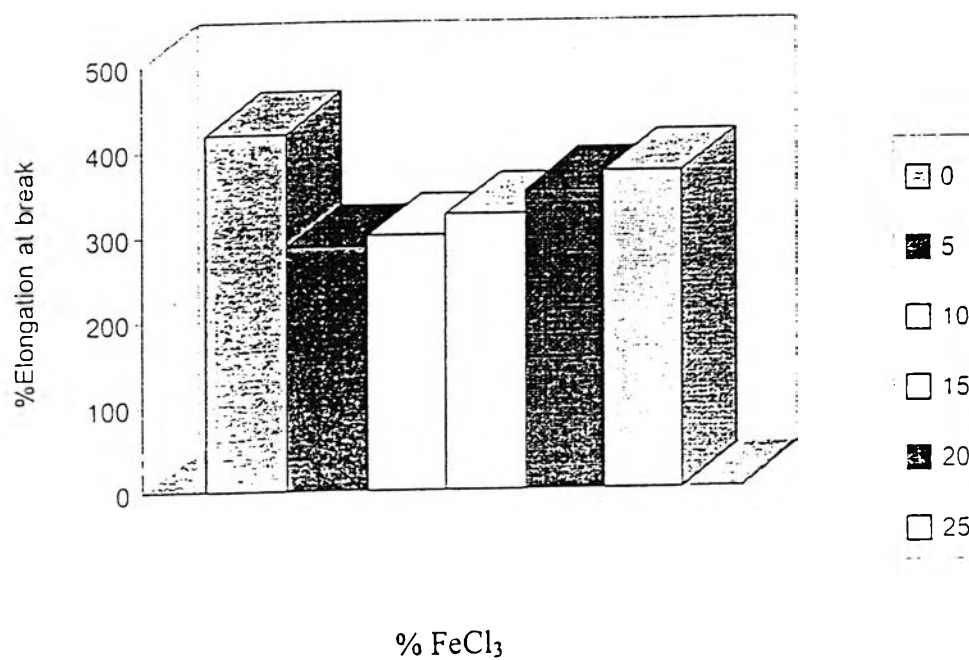


Figure 4.30 Plotting of %elongation at break and FeCl₃ concentration on PVA/FeCl₃ composite film.

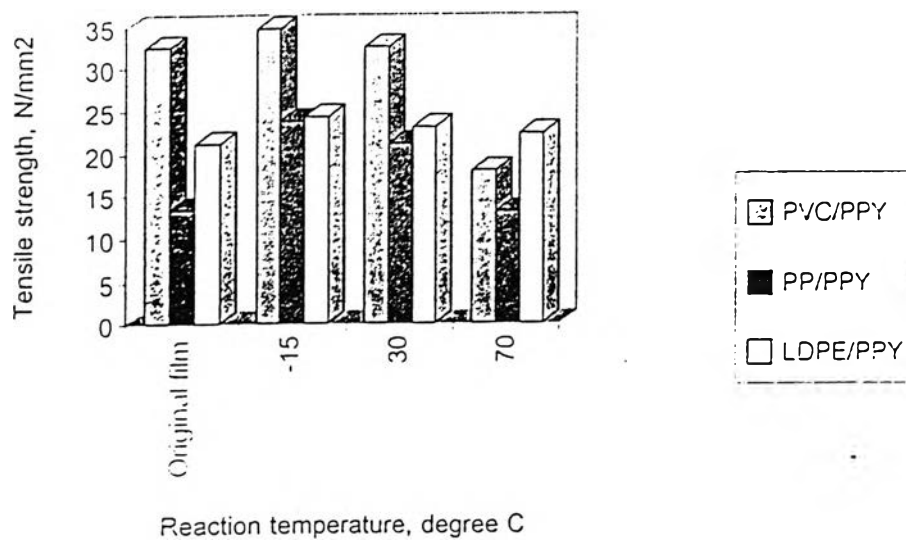


Figure 4.31 Plotting of tensile strength and reaction temperature on plastic types.

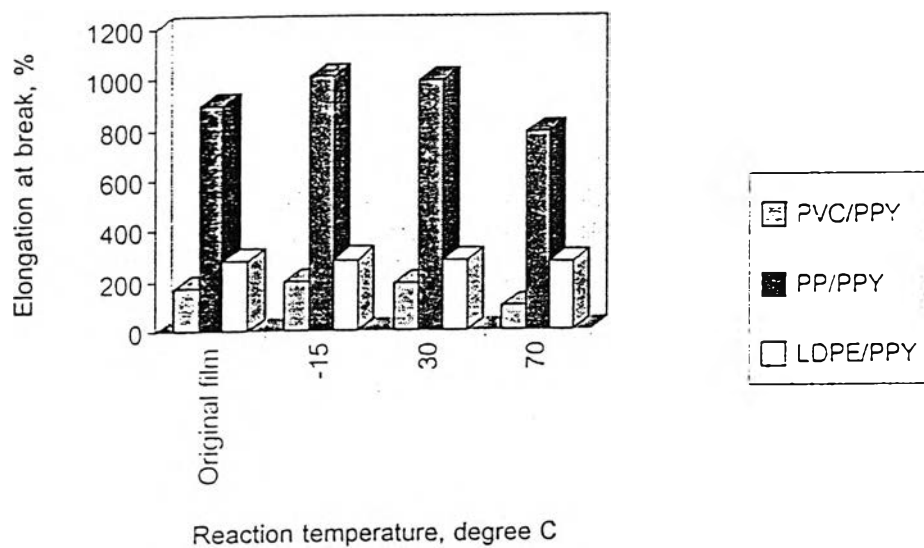


Figure 4.32 Plotting of %elongation at break and reaction temperature on plastic types.

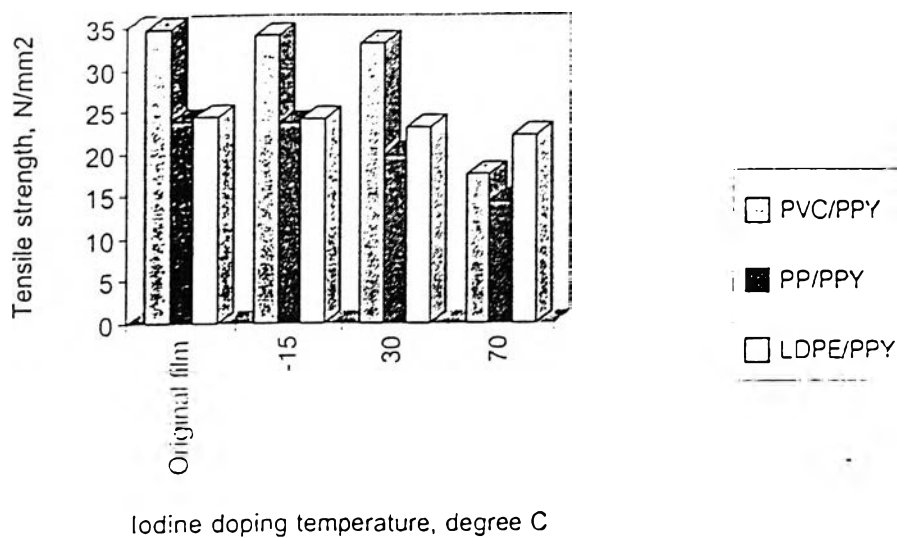


Figure 4.33 Plotting of tensile strength and iodine doping temperature on plastic types.

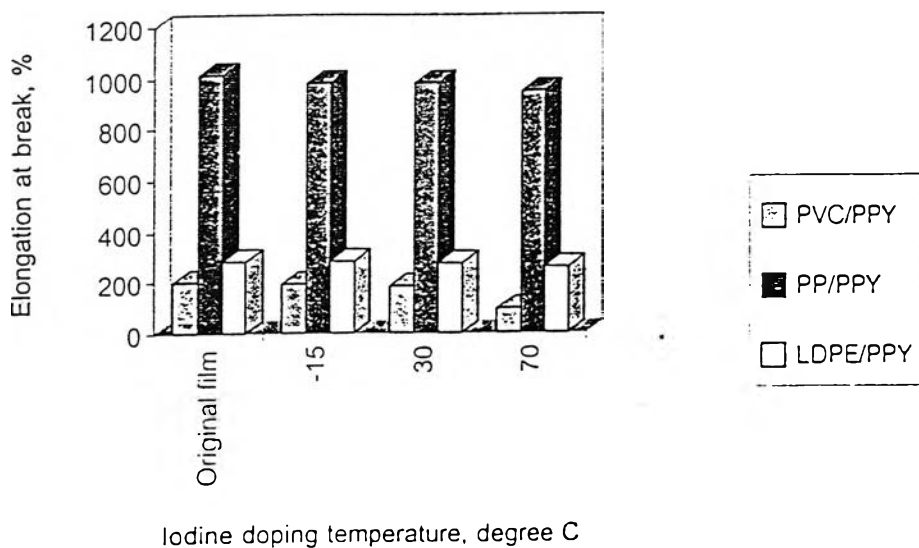


Figure 4.34 Plotting of %elongation at break and iodine doping temperature on plastic types.

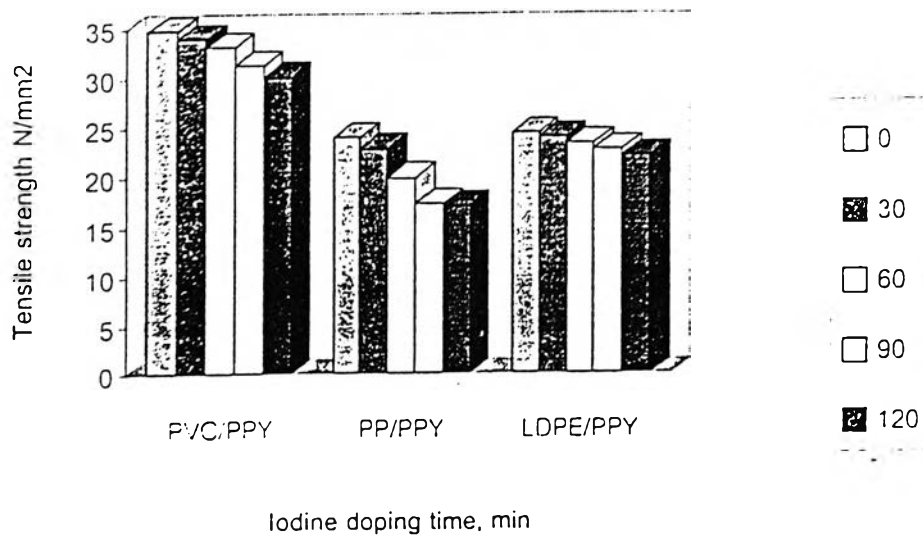


Figure 4.35 Plotting of tensile strength and iodine doping time on plastic types.

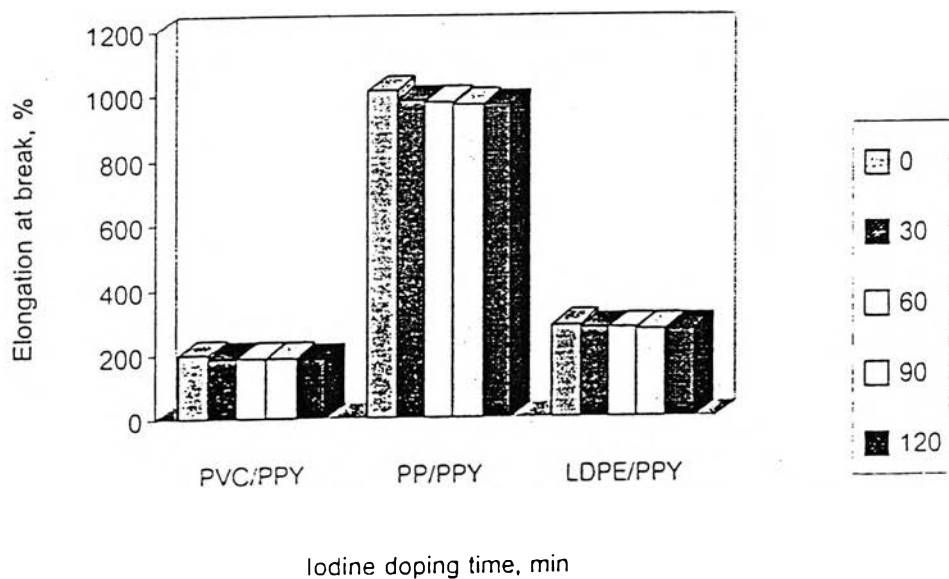


Figure 4.36 Plotting of %elongation at break and iodine doping time on plastic types.

4.3.2 Thermal properties of prepared conducting plastic films.

The thermal properties of prepared conducting plastic films were examined by DSC (thermal transition) and TGA (thermal decomposition). Using the DSC technique, T_g and T_m values were recorded according to the midpoint method for a heating of $10^\circ\text{C}/\text{min}$. The T_g , T_m , and T_d of original and the prepared conducting plastic films are revealed in Table 4.11.

Table 4.11 The thermal transition and decomposition temperatures of original and prepared conducting films.

Plastic film	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)
LDPE	114-115	-90	340-440
PP	176	-27	320-400
PVC	184	80	200-300
PVA	120	28	220-300
PPY	-	160	200-380

Figures E-1-E-4 in Appendix E show DSC thermograms of original plastic films that T_m , T_g , and T_d are revealed in Table 4.11. Figure E-5, it was found that PVA film has reduced T_g , T_m , and T_d . However, T_g and T_d are increased with increasing FeCl_3 initiator concentration, but no T_m as shown in Figure E-6, it clearly exhibited the effect of PPY film on thermal transition and thermal decomposition of PVA/ FeCl_3 composites film. With increasing amount of FeCl_3 in the polymerization recipe, a greater number of PPY chains will be formed. Consequently, interchain interaction probability will be enhanced. This may materialize through possible H-bonding between the N heteroatoms of PPY chain and the pyrrolic H atoms of another such chain. To imply that, more and more

thermal energy should be required to break a H-bonding. Figures E-7-E-9 show DSC thermograms of PVC/PPY films on various reaction temperatures, it was found that the T_g and T_m of PVC/PPY films prepared at -15°C and 30°C similar to original PVC film. DSC thermograms of PP/PPY film on various reaction temperatures are shown in Figures E-10-E-12, it can be seen that they are similar to PP films in Figures E-10-E-11. However, T_g , T_m , and T_d are decreased at high reaction temperature ($\sim 70^\circ\text{C}$). It can be explained as same as evidence in PVC/PPY film. Figures E-13-E-15 show DSC thermograms of LDPE/PPY films on various reaction temperatures, whereas T_d of LDPE/PPY film at high reaction temperature is less than T_d of LDPE film, but T_g and T_m are similar to LDPE film. It can imply that LDPE film has a good thermal stability, which was confirmed by TGA.

Effect of iodine vapor on thermal properties are shown in Figures E-16-E-19. The T_m , T_g , and T_d are little decreased with doping iodine, but more decreased with increasing iodine doping temperature. It was found that, the doping temperature imposes more strong effect on thermal properties than doping time. Finally, from the DSC thermograms, it clearly show that thermal transition values of prepared conducting plastic films are similar to the original films. It was proposed that the prepared conducting films are not homopolymers or copolymers, but polypyrrole is coated on plastic film only.

The decomposition temperature (T_d) of prepared conducting plastic films were determined by TGA. Table 4.12 gives the range of T_d for the original and the prepared conducting plastic films.

Table 4.12 The range of decomposition temperature of the original and prepared conducting plastic films.

Plastic film	T_d (°C)
PVC	200-300
PP	300-420
LDPE	350-450
PVC/PPY at -15°C	200-320
PVC/PPY at 30°C	220-350
PVC/PPY at 70°C	180-300
PP/PPY at -15°C	320-410
PP/PPY at 30°C	330-430
PP/PPY at 70°C	280-400
LDPE/PPY at -15°C	365-460
LDPE/PPY at 30°C	370-460
LDPE/PPY at 70°C	310-440
PP/PPY doping at 30 mins.	330-430
PP/PPY doping at 120 mins.	300-420
PP/PPY doping at -15°C	300-430
PP/PPY doping at 70°C	270-420

From Table 4.12, it clearly exhibited that T_d are increased with polymerizing at -15 and 30°C, and decreased at high reaction temperature (~70°C). Figures E-20-E-31 show the TGA thermograms of the original and prepared conducting plastic films, it was found that T_d of PVC/PPY, PP/PPY, and LDPE/PPY films are increased when polymerizing at -15°C and 30°C, but their T_d 's are decreased compared with original films. It may also explain that the PVC film has the lowest thermal stability, thus leading to reduced T_d at high temperature.

Effects of iodine vapor on T_d of prepared conducting plastic films are shown in Figures E-28-E-31, it can be seen that the iodine doping temperature has stronger effect on T_d than iodine doping time, these are shown in Table 4.12 and Figures E-28-E-31.