CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary study of polypyrrole coating composite

The polypyrrole composites were prepared via oxidative polymerization on the surface of selected host. In this study, pyrrole was polymerized in the presence of PS and $FeCl_3$ at 0 °C. The resulting polymer composite was then washed exhaustedly with methanol to ensure that there is no Fe(III) trapping in the composite. The presence of PPy is confirmed by Fourier transform infrared spectroscopy. The IR spectra of the polymer composite in this research were obtained by Attenuated Total Reflectance (ATR FT-IR) technique. This technique allows the measurement of the IR spectrum of the sample surface. Figure 4.1 shows the ATR FT-IR spectrum of PS/PPy composite prepared by using 0.5 pyrrole: PS weight ratio. The IR spectrum shows strong absorption bands of aromatic C=C stretching at 1550 cm^{-1}, doping induced mode at 1320 and 1180 cm^{-1} which are characteristics of polypyrrole. And it also shows weak absorption bands of aromatic C=C stretching at 1490 cm^{-1}, CH_2 in plane bending at 1450 cm^{-1}, and C=CH aromatic out of plane bending at 700 cm^{-1} which are characteristic of PS. The characteristic of PS host polymer corresponds to the PS absorption peaks reported by Lascelles [39].

Theoretically, the PS host should be coated completely by PPy during the polymerization process and no IR absorption bands of PS should be observed. Some PS absorption peaks, however, appeared as shown in Figure 4.1. This may be due to several reasons. One reason is an inadequate coating of PPy over the surface of PS due to the ineffectiveness of the polymerization. The other may be due to the physical damage of the polymer composite during the sample preparation. Fortunately the absorption bands of PS are quite low, it is therefore possible to ignore the uncoated part of PS.

Attempts were made to study the ATR FT-IR of PVC/PPy composite. However, it was not achieved since the feature of PVC particle is not appropriate. The strong absorption peaks could not be found. The roughly surface and the large size of PVC/PPy particle are the causes of very weak absorption bands in IR spectra. It can be explained that the bigger size of PVC particle is not suitable for casting on the ATR prism. Too much space between PVC/PPy sample and prism surface leads to the little contact of PVC/PPy particles with prism.

Nevertheless, to investigate the incorporation of PPy on PVC, the regular KBr-disc technique was used to study the PVC/PPy samples. Figure 4.2 shows the spectrum of 0.5 weight ratio of PVC/PPy composite, which was prepared at 0 °C. The spectrum shows weak absorption bands due to PVC of C-Cl stretching at 620 cm^{-1}, CH_2 in plane bending at 1430 cm^{-1}, and CH out of plane bending at 1250 cm^{-1}. Since the IR measurement involves the whole sample not just only the surface, the intensities of absorption at each position are therefore the same. This demonstrates that pyrrole was indeed polymerized to PPy on the surface of PVC.

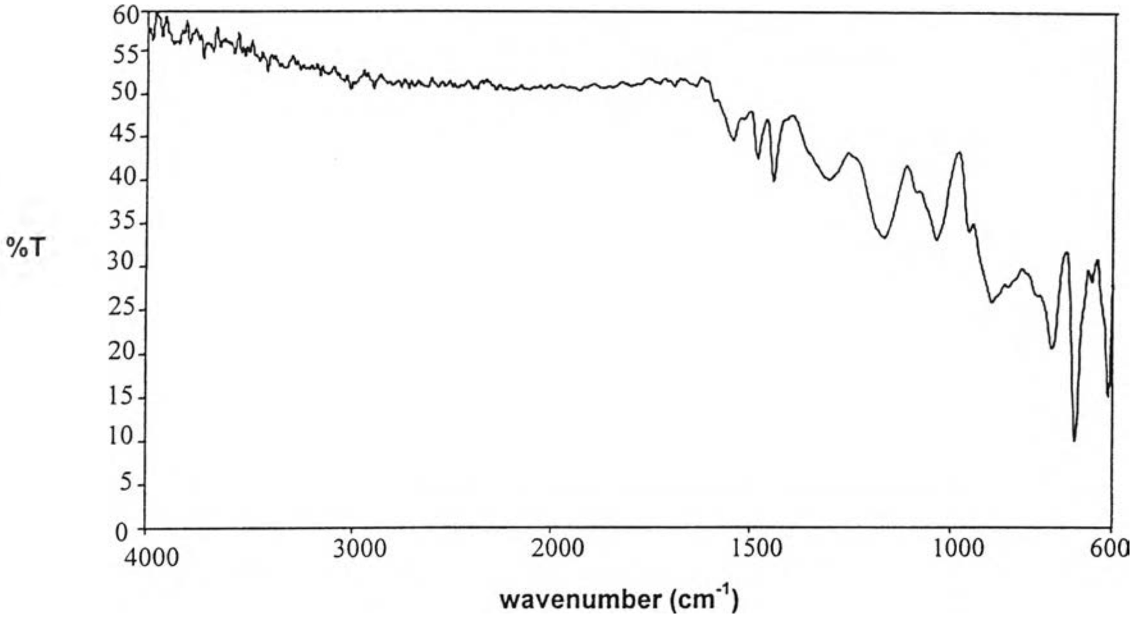

Figure 4.1 ATR FT-IR spectrum of PS/PPy composite

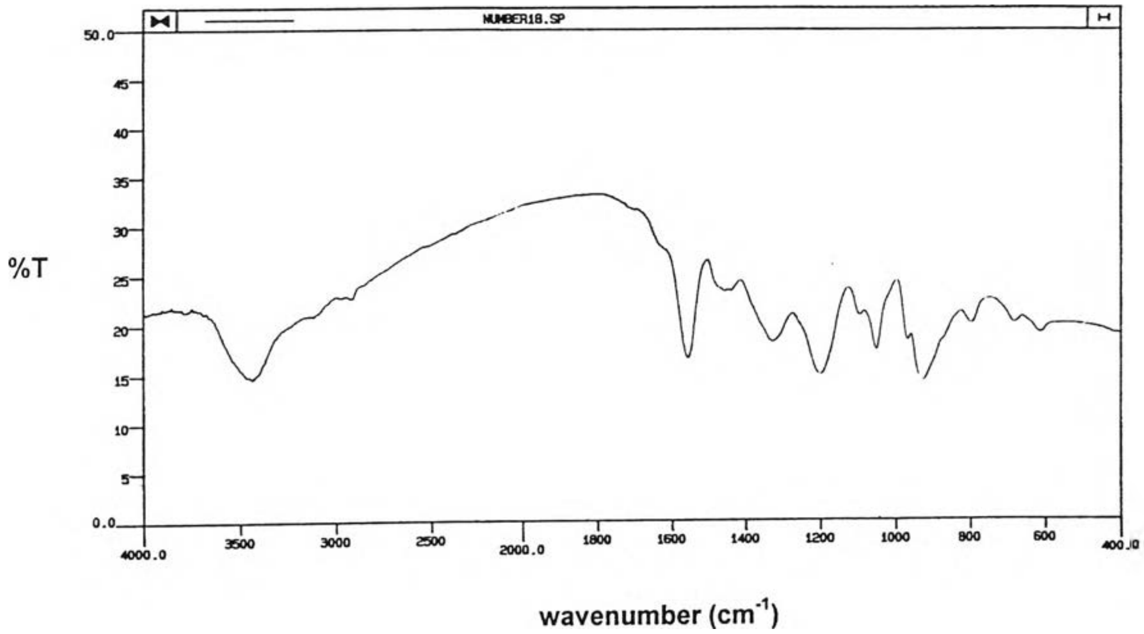

Figure 4.2 FT-IR spectrum of PVC/PPy composite

4.2 Effect of host polymer on polypyrole coating composite

Various hosts such as PS, PVC, PE, and PP were employed in the synthesis of PPy composites. Even though these polymer composites were synthesized by the same manner, their physical and chemical properties are different. This section will describe the effects of host polymers on the polymer composite in details.

4.2.1 Polystyrene/Polypyrrole composite

Polystyrene used in this research was prepared by emulsion polymerization technique [44]. This technique provided finely divided polystyrene which was redispersed in methanol in order to obtain homogeneous smooth particles. Polystyrene prepared from this process allowed PPy to be coated thoroughly on the surface of the particles. Figure 4.3 shows the scanning electron micrograph of PS/PPy composite. Each sphere represents each particle of polystyrene. It is appeared that the PPy distributes homogeneously over all the surface of PS particle.

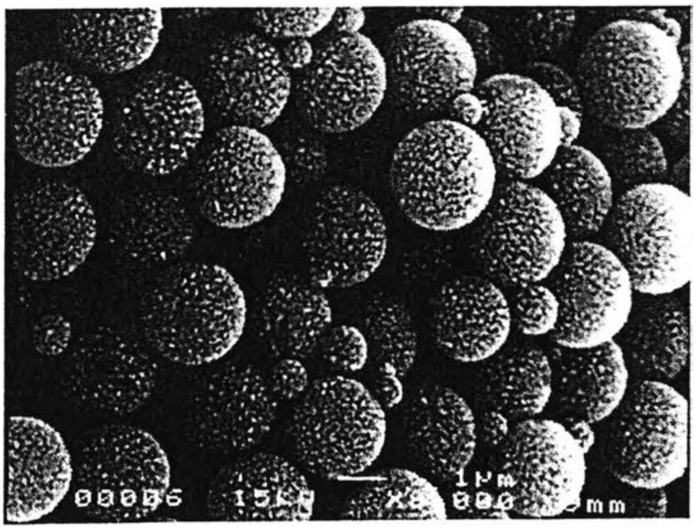

Figure 4.3 Scanning electron micrograph of PS/PPy composite

Lascelles and Armes [39] reported that poly(N-vinyl pyrrolidone) was used as a stabilizer in order to bind PPy onto the surface of PS. Our observation indicates that PPy can be coated on PS surface even without stabilizers.

Our experimental results demonstrate that the conductivity of the synthesized PS/PPy composite is quite high in the range of 1-10 Scm^{-1} while other researchers reported that their value is less than 1 Scm^{-1} [39]. This may be due to the high concentration of $FeCl_3$ used during the polymerization of pyrrole. It was shown that PPy coated on the surface of PS almost instantly.

This experiment demonstrates that PS/PPy composite with high conductivity can be obtained from the chemically oxidative method even without stabilizer by using our condition. The effects of various experimental conditions on physical properties such as electrical conductivity, morphology, and stability will be further investigated and described in details.

4.2.2 Poly(vinyl chloride)/Polypyrrole composite

PVC/PPy composite was prepared in the same manner as in Section 4.2.1, however, PVC was obtained from the industry and used as received. The appearance of PVC particle is not as fine as in the case of synthesized PS. However, the procedure to synthesis PVC requires sophisticated set-up we therefore decide to use the commercial one.

Figure 4.4 shows the scanning electron micrograph of PVC and PVC/PPy composite. It is noted that the surface of PVC is not smooth and particles are not homogeneous as expected. The scanning electron micrograph of the

PVC/PPy composite also demonstrates the inhomogeneity of the coating of PPy on the surface of PVC. This is due to the difficulty of PPy to penetrate into the ditch area of the PVC surface. However, we could obtain the black powder of PVC/PPy composite. Figure 4.4(a) shows the morphology of PVC particle. It can be seen that PVC particles are not uniform and their sizes are bigger than PS, which caused the incomplete coating of PPy on PVC particle. In Figure 4.4(b), the small particles of PPy distribute on the rock-liked surface of PVC particle. Even though PPy can not be coated on the surface of PVC as well as PS, the conductivity of the PVC/PPy composite is about the same as PS/PPy composite.

According to Meng and Chi [34], they used PVC particle as host polymer. Those works showed that the composite particle was analogous to this study. However, they found that PPy content on PVC particle was much lower than the original ratios of pyrrole to the PVC powder. It is responsible for the incomplete conversion of the pyrrole monomer into PPy in the oxidative polymerization and the loss of PPy that deposited on the reactor wall. These factors might be present also in this research.

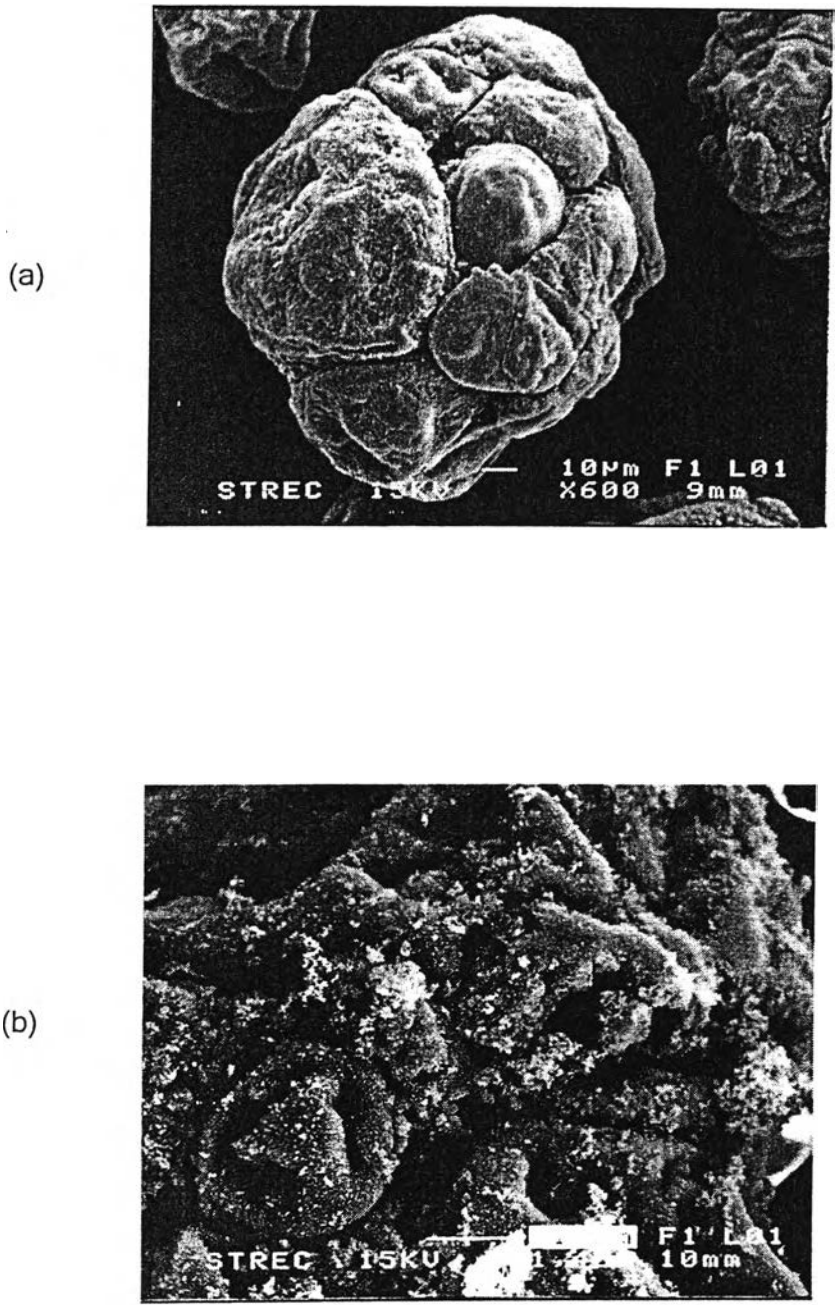

Figure 4.4 Scanning electron micrographs of

(a) PVC particle

(b) PVC/PPy composite surface

4.2.3. Other insulating polymer/Polypyrrole composite

Polyethylene (PE) and polypropylene (PP) were also chosen to be host polymer for the synthesizing of PPy composite since they can be obtained from the industry in Thailand. The polymerization method is the same as described before. The particle sizes of PE and PP are bigger than PS and PVC. We could expect an incomplete coating of PPy over the surface of PE and PP similar to the case of PVC. Unfortunately, PE and PP cannot form composite polymer upon the employed experimental conditions. PE and PP floated on the surface of the reaction medium. This may be due to the much lower density of PE and PP than the reaction medium. Since PE and PP floated in the reaction medium, it is difficult for the PPy to penetrate onto the surface of PE and PP.

However, there is a research which PP/PPy composite was succesfully produced. Omastova studied the synthesis of PP/PPy polymer composite in the mixture of water and methanol using less oxidant concentration [37]. They reported that they could obtain PP/PPy composite particle with the conductivity about 10^{-2} Scm^{-1}.

When the concentration of $FeCl_3$ in methanol is quite low, it is possible to synthesize PE/PPy and PP/PPy composites but the conductivities of the resulting polymer composites are also very low. Therefore, it is not suitable to use PE and PP as host polymers in the synthesis of high conductivity PPy polymer composites.

4.3 Effect of poly(vinyl pyrrolidone) on dispersion polypyrrole

Polypyrrole was also prepared by the chemical oxidative polymerization of pyrrole in the dispersion media. The dispersing agent was added in the reaction to enhance the dispersion of polypyrrole particle. In this research, poly(vinyl pyrrolidone)(PVP) had been used as the dispersing agent, which is also called stabilizer. Other components are similar to the components of PPy-coated polymerization method. The PVP powder were dissolved in the oxidant solution ($FeCl_3$/methanol) before initialize the polymerization process to form the stabilizing feature. This polymeric stabilizer act by way of adsorption on the PPy particles formed during the polymerization [21]. After the polymerization succeed the sediment of PPy dispersion was obtained. PPy powder were washed exhaustedly by water and methanol then filtered, the black precipitates were dried and stored in the desiccator.

The morphology of the dispersion PPy is shown in Figure 4.5. It can be seen that although PPy powder were agglomerated there is also the dispersion character throughout the PPy sample. The agglomeration of PPy particle is present in most of the PPy synthesis.

The result from SEM shows that PPy powder did not exist as individual particle. This result is different from Armes and co-worker. They explained that the ratio of stabilizer to monomer is needed to form the spherical particle. Furthermore, the order of reagent addition is also necessary to form spherical particles.

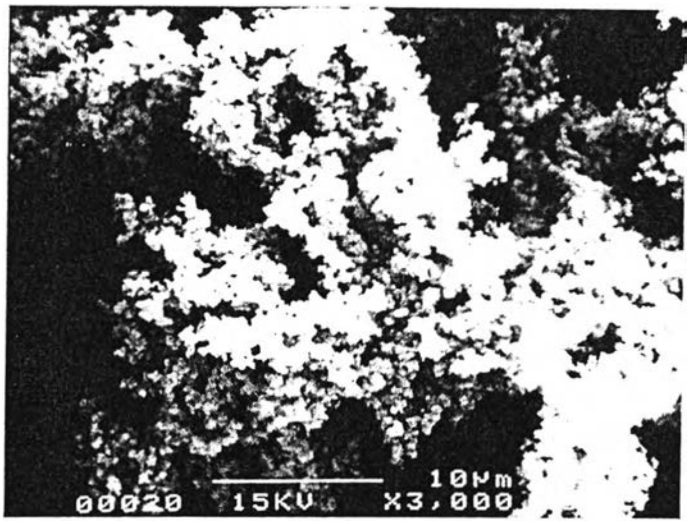

Figure 4.5 Scanning electron micrograph of dispersion PPy, using PVP stabilizer

The main problem of this procedure is the unable synthesis of spherical PPy particles. This may be due to the high concentration of the $FeCl_3$ oxidant solution, which results in the difficulty of dissolving the stabilizer. The solubility of PVP was diminished when PVP concentration is increased. However, if the oxidant concentration was reduced, the high conductivity could not be obtained.

4.4 Determination of various effects on Polystyrene/Polypyrrole composite

In order to prepare high electrical conductivity of PS/PPy composite, various polymerization conditions were studied to obtain the optimum conditions. The concentration of $FeCl_3$/methanol solution is 2.5 M. 2 g of polystyrene powder were used in the polymerization. Other parameters are varied as follows:

4.4.1 Effect of pyrrole

The effect of pyrrole is determined in order to find the threshold level in the edge of electrical conductivity. This means that how the employed pyrrole is suitable for the high electrical conductivity given. Table 4.1 shows the electrical conductivity of composites with various pyrrole: PS weight ratios. The reaction temperature was controlled constantly at 0 °C for 1 hour polymerization time.

Tables 4.1 Conductivity of PS/PPy composite depends on the pyrrole: PS ratio

Sample code	Pyrrole: PS ratio	Conductivity(Scm^{-1})
PS01	0.1	1.53
PS02	0.2	2.72
PS03	0.5	7.57
PS04	0.8	8.10
PS05	1.0	9.98

According to Table 4.1, the conductivity of PS/PPy composite depends on the amount of pyrrole. The conductivity of PS/PPy composite increases as pyrrole ratio increases. The conductivity of PS01 is about 1.53 Scm^{-1}, which is an acceptable conductivity in the composite form.

Nevertheless, the slope of the graph plotted between conductivity and pyrrole: PS ratio is shown in Figure 4.6. It clearly exhibits that the conductivity does not increase rapidly after 0.5 pyrrole: PS ratio and it seems to be level off.

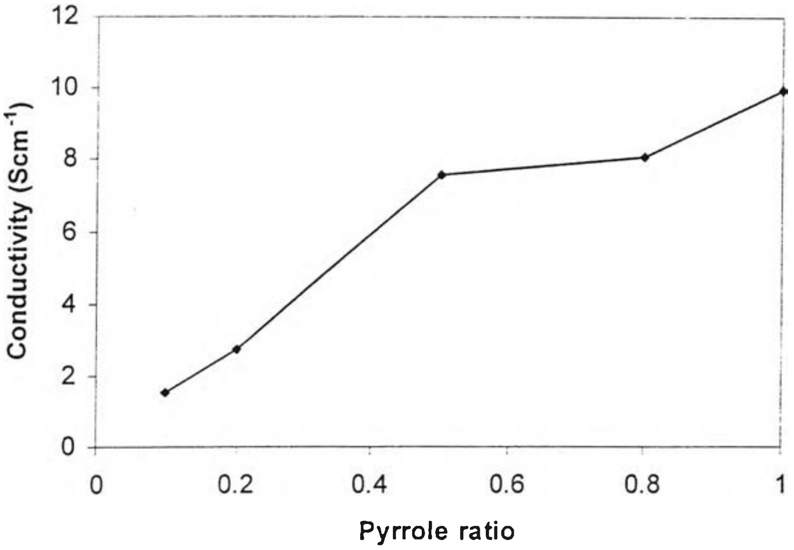

Figure 4.6 The conductivity of PS/PPy composite versus pyrrole: PS ratio

Analogous results were obtained by Lascelles [39] and Omastova [37]. They suggested that the conductivity of the polymer composite stayed constant after the concentration of pyrrole through some threshold level. The 'core shell' morphology of these materials is responsible for this phenomenon. Charge transport can occur through the material without significant interference from the underlying electrically insulating polystyrene component.

The coating of PPy on the surface of PS particles is supported by SEM as shown in Figure 4.7. The SEM of PS/PPy composites, which were synthesized from 0.5 and 1 pyrrole: PS ratios, are shown in Figure 4.7(b) and (c), respectively. The SEMs demonstrate no difference on the surface of PS particles.

FT-IR spectra of PS/PPy composites with various pyrrole ratios are shown in Figure 4.8, according to the electrical conductivity evidence and Lascelles and Armes [39]. The characteristics of FT-IR spectra depend on the pyrrole volume. PS absorption bands at 700, 1450 and 1490 cm^{-1} are decreased continuously as the pyrrole increases while the absorption bands of PPy showing in every spectrum are exhibited at 1180, 1320, and 1550 cm^{-1}. This demonstrates that PPy can coat the surface of PS particle more completely when the added pyrrole is increased.

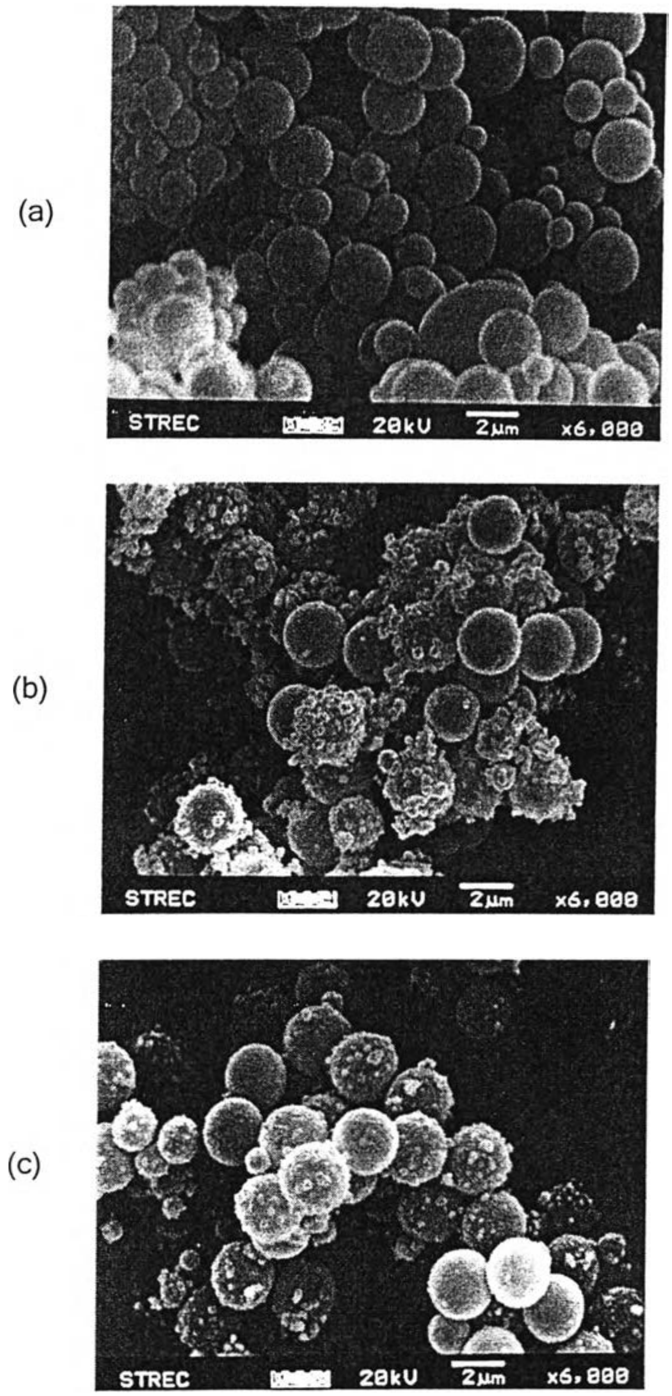

Figure 4.7 Scanning electron micrographs of

(a) polystyrene micro-particles

(b) PS/PPy composite treated with 0.5 pyrrole: PS ratio

(c) PS/PPy composite treated with 1 pyrrole: PS ratio

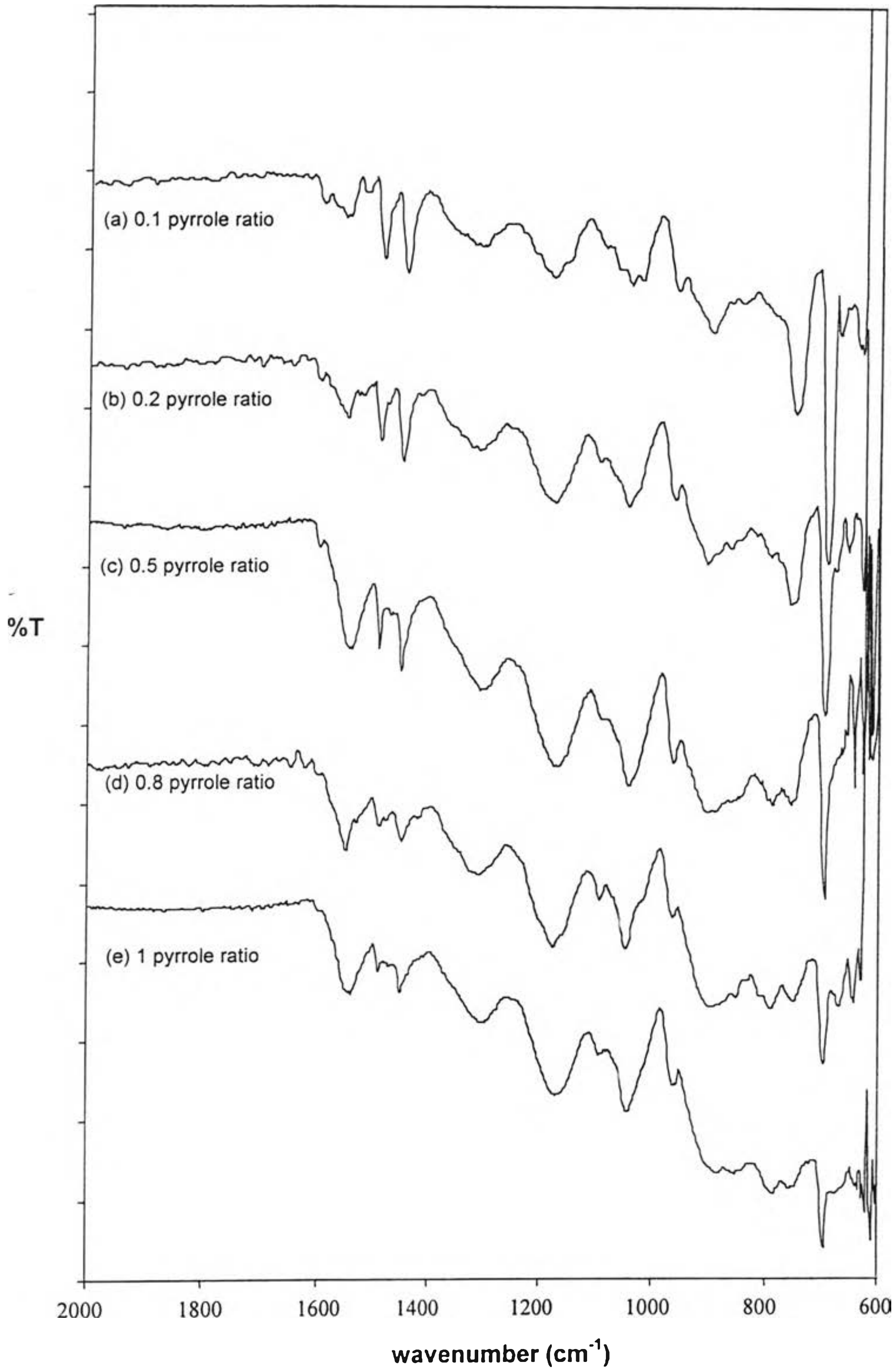

Figure 4.8 FT-IR spectra of PS/PPy composite as a function of pyrrole: PS ratio

(a) PS01 (b) PS02 (c) PS03 (d) PS04 (e) PS05

4.4.2 Effect of reaction time

The polymerization reaction was accomplished by various reaction times from 1 to 3 hours. The electrical conductivity of PS/PPy composites are shown in Table 4.2 while the other parameters were kept constant, i.e. 2.5 M $FeCl_3$ solution, 0 °C reaction temperature.

Table 4.2 Conductivity of PS/PPy composite depends on the reaction time

Sample code	Reaction time (hour)	Pyrrole: PS ratio	Conductivity(Scm^{-1})
PS02	1	0.2	2.72
PS03		0.5	7.57
PS04		0.8	8.10
PS06	2	0.2	2.53
PS07		0.5	5.34
PS08		0.8	3.20
PS12	3	0.2	2.31
PS13		0.5	2.81
PS14		0.8	2.26

Table 4.2 shows that the highest electrical conductivity is obtained at 1 hour , which is the lowest reaction time. In Tanawadee research [5], the maximum conductivity was obtained when low polymerization time was used. This is due to the effect of oxidation potential of the reaction solution. While polymerization time was increased, the oxidation potential was slowly decreased.

This phenomenon can be explained follows by the observation of Machida's report [22]. They suggested that the oxidation potential of the solution plays an important role in the polymerization process and the conductivity of the synthesized polypyrrole. In the equilibrium state the oxidation potential (E) is expressed by Nernst's equation as

$$E = E_0 + (RT/nF) \ln (A_{ox}/A_{red})$$

Where A_{ox} and A_{red} are the activities of the oxidant ($FeCl_3$) and reductant ($FeCl_2$), respectively. During this reaction, the $FeCl_3$ concentration decreases while the $FeCl_2$ concentration increases. Hence, the oxidation potential will decrease during the process as the reaction time increases. This feature led to low conductivity occurs because of the less oxidized polypyrrole.

The relationships between the electrical conductivity and the polymerization time at various pyrrole ratios are shown in Figure 4.9. It can be seen that the longer polymerization time is not suitable for polypyrrole preparation.

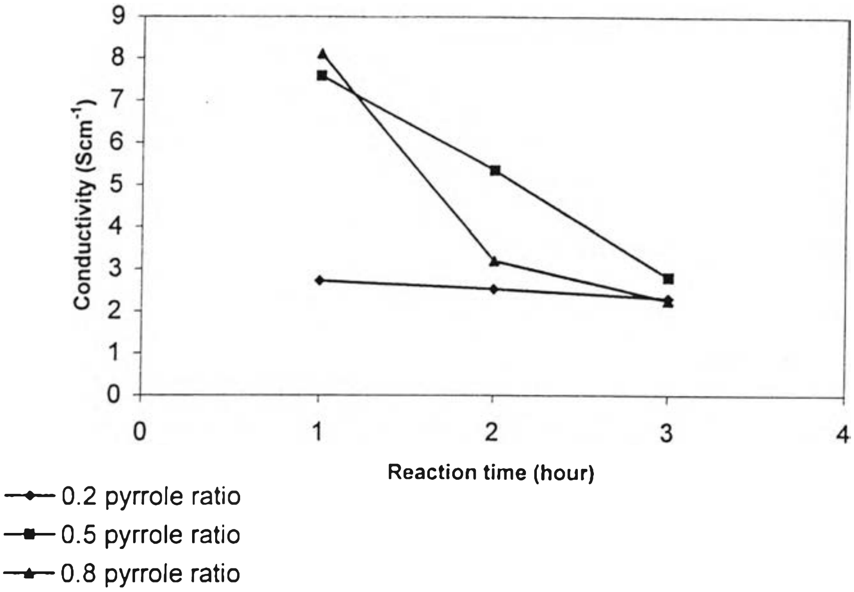

Figure 4.9 The conductivity of PS/PPy composite versus reaction time

4.4.3 Effect of solvent

Various types of solvents for polypyrrole synthesis were studied to achieve the optimum conductivity. The favorite one is methanol. From previous works [22,5], methanol is the best solvent for polypyrrole preparation since PPy could be synthesized with high conductivity, beyond 100 Scm^{-1}. Other solvent such as water can be used to polymerize polypyrrole, Meng and Chi [34] used water to prepare the $FeCl_3$ solution. The similar results were also obtained by Omastova [37], they used water as solvent in polymerization of PMMA/PPy composite. However, preparation of high concentrate oxidant solution by using only water to disperse the host polymer powder is very difficult. This research acclaimed that other solvent such as methanol was added to the reaction in the binary solvent form. To disperse the host polymer, decreasing solvent density is needed. Hence, in this research, the polymerization reactions were carried out in three kinds of solvents, i.e. water, 50% methanol/water, and methanol. Water, however, was not a suitable solvent for the preparation of PS/PPy composite since all PS powder in the reaction mixture was floated. Table 4.3 shows the dependence of the electrical conductivity on the various solvents.

Table 4.3 indicates that the highest conductivity is 8.73 Scm^{-1} for PS sample, which was polymerized in 50% methanol/water solvent at 0.5 pyrrole: PS ratio. It was also found that when 50% methanol/water was used as solvent, the higher conductivity PS/PPy composite as seen at 0.1, 0.2, and 0.5 pyrrole: PS ratios were obtained. This seems that 50% methanol/water solvent system is better than methanol for the preparation of PPy coating composite. However, the threshold level of conductivity in 50% methanol/water system is low while the conductivity of PS/PPy composite in methanol system might be reached a higher level.

Machida [22] studied the effect of solvents for the preparation of PPy. He suggests that the best solvent was methanol because of its low oxidation potential, which can make the high conductivity PPy. However, for this research, it was found that the yield of PPy product from 50% methanol/water solution was larger.

Tables 4.3 Conductivity of PS/PPy composite depends on the solvent

Sample code	Pyrrole: PS ratio	Solvent	Conductivity(Scm^{-1})
PS01	0.1	Methanol	1.53
PS02	0.2		2.75
PS03	0.5		7.57
PS16	0.1	50% Methanol/water	6.51
PS17	0.2		7.25
PS18	0.5		8.73

Hence, it can be acclaimed that the binary solvent (50% Methanol/water) is the best solvent for coating polymerization. Furthermore, it can be observed that when the polymer composite was prepared in methanol or 50% methanol/water, the conductivity of each composite reached the value of 8 Scm^{-1}, when the pyrrole ratio increases to 0.5. (Figure 4.10). The presence of percolation threshold of PPy in the composite is responsible for these observations.

The scanning electron micrograph of PS/PPy composite, which was prepared in 50% water/methanol, is shown in Figure 4.11. The morphology of PS/PPy particles exhibited that in the mixed water-methanol solvent polypyrrole can coat on the PS particle completely. Furthermore, the rough surface which is present in Figure 4.11 shows that PS particles were coated in the same fashion as composite prepared from methanol solvent (Figure 4.7 (b)). This demonstrates that the reaction is rapid in these solvent systems.

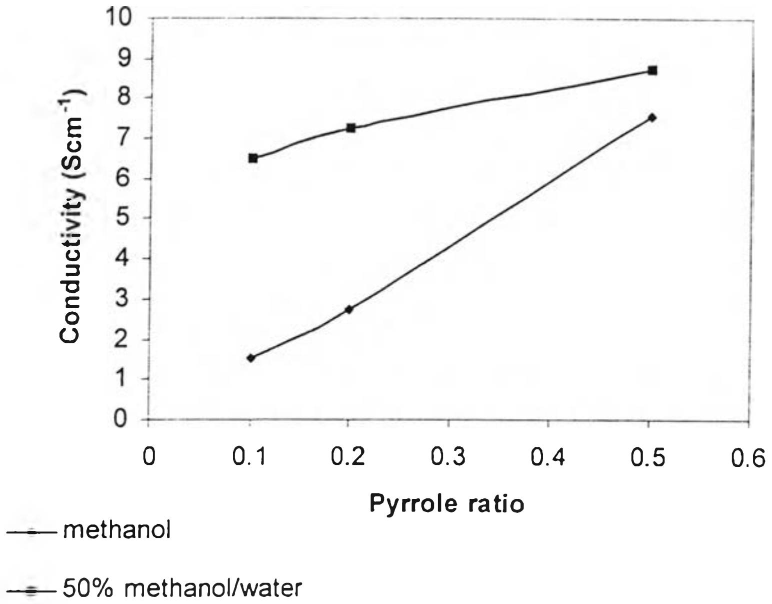

Figure 4.10 The conductivity of PS/PPy composite versus pyrrole ratio in various solvents

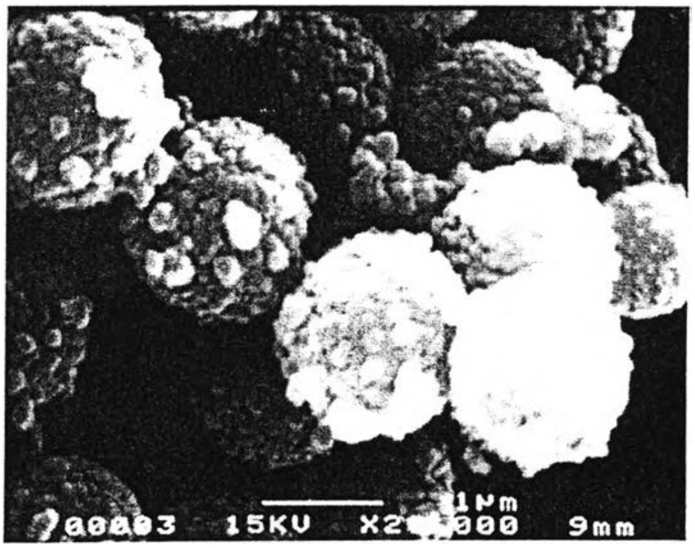

Figure 4.11 Scanning electron micrograph of PS/PPy composite using 50% water/ methanol as solvent

4.5 Conductive stability of Polystyrene/Polypyrrole composites

In order to study the conductive stability, the conductivities of PS/PPy composites with 0.1, 0.2, 0.5, 0.8, and 1 pyrrole: PS weight ratio assigned to PS01, PS02, PS03, PS04, and PS05, respectively, were measured by van de Pauw method at every 2 weeks until 10 weeks. The PS/PPy conductivities with various times are shown in Table 4.4. The other parameters were kept constant, i.e. 0 °C reaction temperature, 1 hour polymerization time, methanol solvent, and 2.5 M $FeCl_3$ solution.

Table 4.4 Conductivity of PS/PPy composite as storing time

Time (week)	Conductivity (Scm^{-1})				
	PS01	PS02	PS03	PS04	PS05
0	1.53	2.72	7.57	8.10	9.98
2	1.88	2.56	5.88	6.28	3.63
4	1.06	1.68	4.22	4.58	2.60
6	1.21	1.78	3.92	2.08	1.73
8	0.92	1.30	3.56	1.82	1.48
10	0.88	1.12	3.22	0.64	0.74

Table 4.4 indicates that the conductivity of PS/PPy samples were decreased rapidly at the initial time of 0-4 weeks and the rate of decreasing of conductivity was slowed down after 6 weeks. The electrical conductivities increase when the pyrrole ratios increase. The highest conductivity was obtained at 1 pyrrole ratio, PS05. However, this sample is not the best because the conductivity of PS03 is the most stable. It can be seen that at the conductivity of PS03 is the highest even after 10 weeks.

From Figure 4.12, it can be seen that the conductivities of all samples are decreased rapidly when the time was passed. This behavior was suggested by Tanawadee [5] that the possibility of anions on the surface of the polymer matrix were less than those hold below the surface due to the interference of moisture or temperature. The presence of conductivities after 10 weeks is due to the presence of trapped chloride ions within the sample disc. Analogous to pure PPy, the PS/PPy sample could have the same phenomena. The high conductivity of PS/PPy composite after 10 weeks is due to the trapped chloride ions in reservoir between closed-packed PS particle.

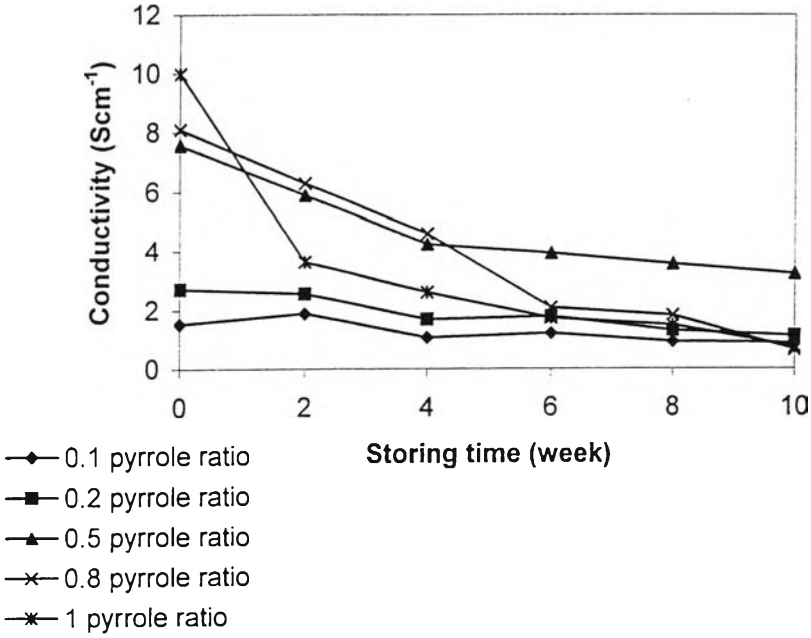

Figure 4.12 The conductive stability of PS/PPy composites versus storing time

4.6 Determination of various effects on Poly(vinyl chloride)/Polypyrrole composite

Similar to PS/PPy composite, the polymerization of PVC/PPy composite was accomplished in the $FeCl_3$ solution. Many parameters were studied to obtain the suitable conditions for synthesizing high conductivity composite. The details of the study are discussed as follows.

4.6.1 Effect of pyrrole

The amount of pyrrole was varied for the preparation of PVC/PPy composite in order to obtain the suitable condition. As previously discussed the random coating of PPy on PVC particles occurred on the nonspherical particles of PVC. Thus, the electrical conductivity of PVC/PPy composite was less than in the case of PS/PPy and could not be obtained at the low pyrrole ratio. Tables 4.5 shows the electrical conductivity of PVC/PPy composite at 1 hour polymerization time.

The electrical conductivities of PVC/PPy composite were not obtained at 0.1 and 0.2 pyrrole: PVC weight ratios because the coating of PPy on the PVC particles was not successful. The electrical data, current (I) and potential (V), which were necessarily used to calculate the conductivity of the composite were very small and unstable. This is due to the incomplete polymerization of PPy on PVC particle. It can be ascribed that since PVC particles are bigger than PS and not spherical, the amount of pyrrole and the reaction time must be high enough for the coating. It is shown that PPy cannot coat successfully on PVC particles, which have many ditches on the particles. Moreover, the ditches on PVC particles are the cause of a little contact between PPy layer in compressed sample disc.

Tables 4.5 Conductivity of PVC/PPy composite depends on pyrrole: PVC ratio

Sample code	Pyrrole: PVC ratio	Conductivity(Scm^{-1})
PVC01	0.1	-
PVC02	0.2	-
PVC03	0.5	5.33
PVC04	0.8	9.52
PVC05	1.0	10.02

Even though the coating is not homogeneous, the conductivity of PPy composite at high pyrrole loads, i.e. 0.5, 0.8, and 1 ratio can be obtained. The polymerization of pyrrole on PVC particles takes place at high pyrrole: PVC ratio rather than low ratio. At 1 pyrrole: PVC ratio, the conductivity is quite high at a value of 10 Scm^{-1}. This is the highest reported conductivity. However, the high amount of pyrrole may be not a good choice due to the difficulty of the polymerization in the concentrated reaction mixture. It could be found that in high oxidant concentration and high pyrrole level the reaction mixture was very viscous and it was difficult to stir the reaction mixture. Furthermore, the use of high pyrrole volume is not economical.

The conductivity of PVC/PPy composite with various pyrrole ratios is shown in Figure 4.13. It can be noted that the value of conductivity of the resulting composite levels off after 0.8 pyrrole ratio.

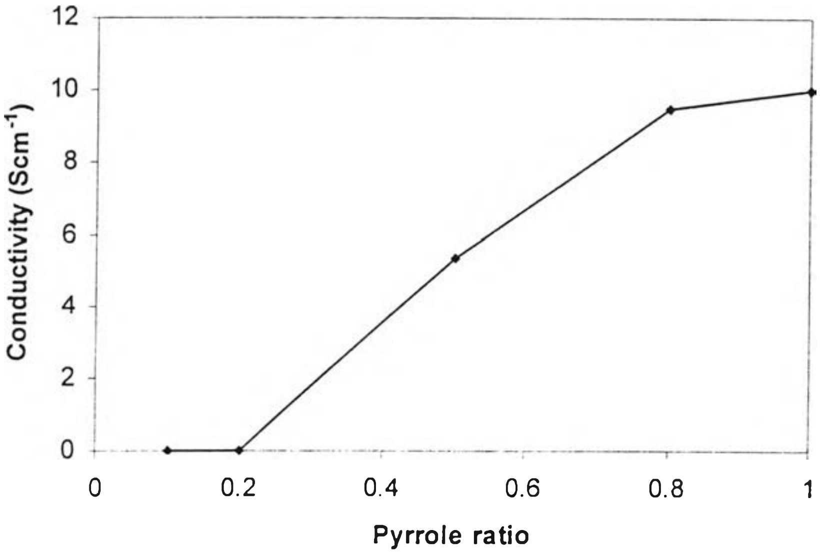

Figure 4.13 The conductivity of PVC/PPy composite versus pyrrole: PVC ratio

Figure 4.14 shows the morphology of PVC/PPy composite particle, which was prepared at 0 °C temperature for 1 hour polymerization time. The pyrrole was added to the reaction about 0.5 weight ratio. The SEM in Figure 4.14(a) shows that the feature of polypyrrole coated PVC particles is similar to the uncoated PVC, indicating that PPy cannot polymerize on the surface of successfully PVC particle. The PVC/PPy particle in Figure 4.14(a), which is magnified to 3500 times, is shown in Figure 4.14(b). There are small particles distributed on PVC particle, which illustrates the ditch of PVC particle. The ditch was the cause of incomplete contact of PPy on PVC surface. However, PVC/PPy composite can occur rapidly by using 0.8 pyrrole: PVC weight ratio. This is due to the large amount of pyrrole monomer and high concentration of $FeCl_3$.

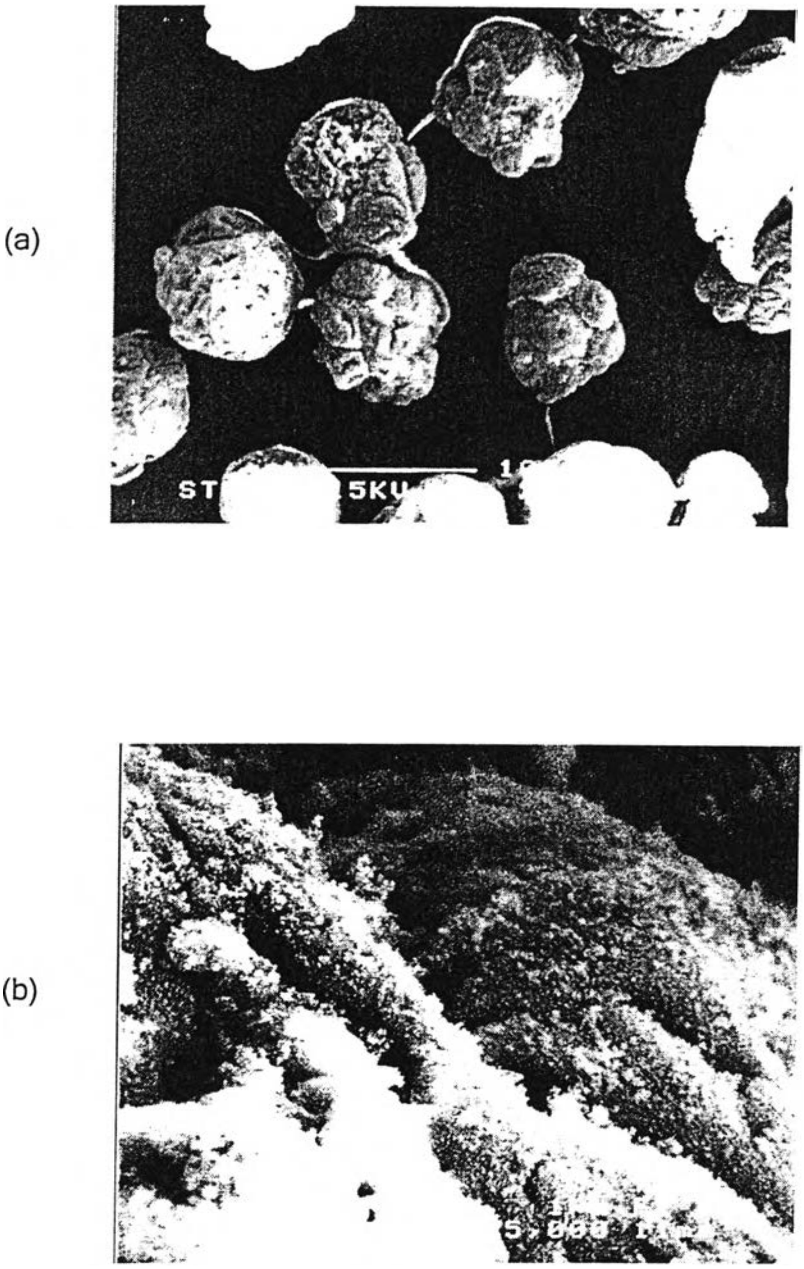

Figure 4.14 Scanning electron micrographs of

(a) PVC/PPy composite treated with 0.5 pyrrole: PVC ratio.

(b) PVC/PPy particle surface (treated with 0.5 pyrrole: PVC ratio)

In order to confirms the polymerization of PPy on PVC particles, FT-IR spectroscopy was used. In this study, it was found that the PPy could cover PVC particle at the higher pyrrole ratio. As seen in Figure 4.15(a-e), the IR spectra were recorded in the region of 400-1800 cm^{-1}.

The modification of sample spectra depending on pyrrole volume can be observed. Analogous to the PS/PPy composite spectra, the absorption bands of PPy and PVC are changed contrarily. The absorption bands at 1180, 1320, 1550 cm^{-1} due to PPy increase while the absorption bands at 620, 1250 and 1430 cm^{-1} due to PVC decrease when the pyrrole ratio increases. These results show that PPy is coated on PVC particle completely. In addition, the weak absorption bands of PVC indicates that the coating of PPy increased when increasing the pyrrole: PVC ratio.

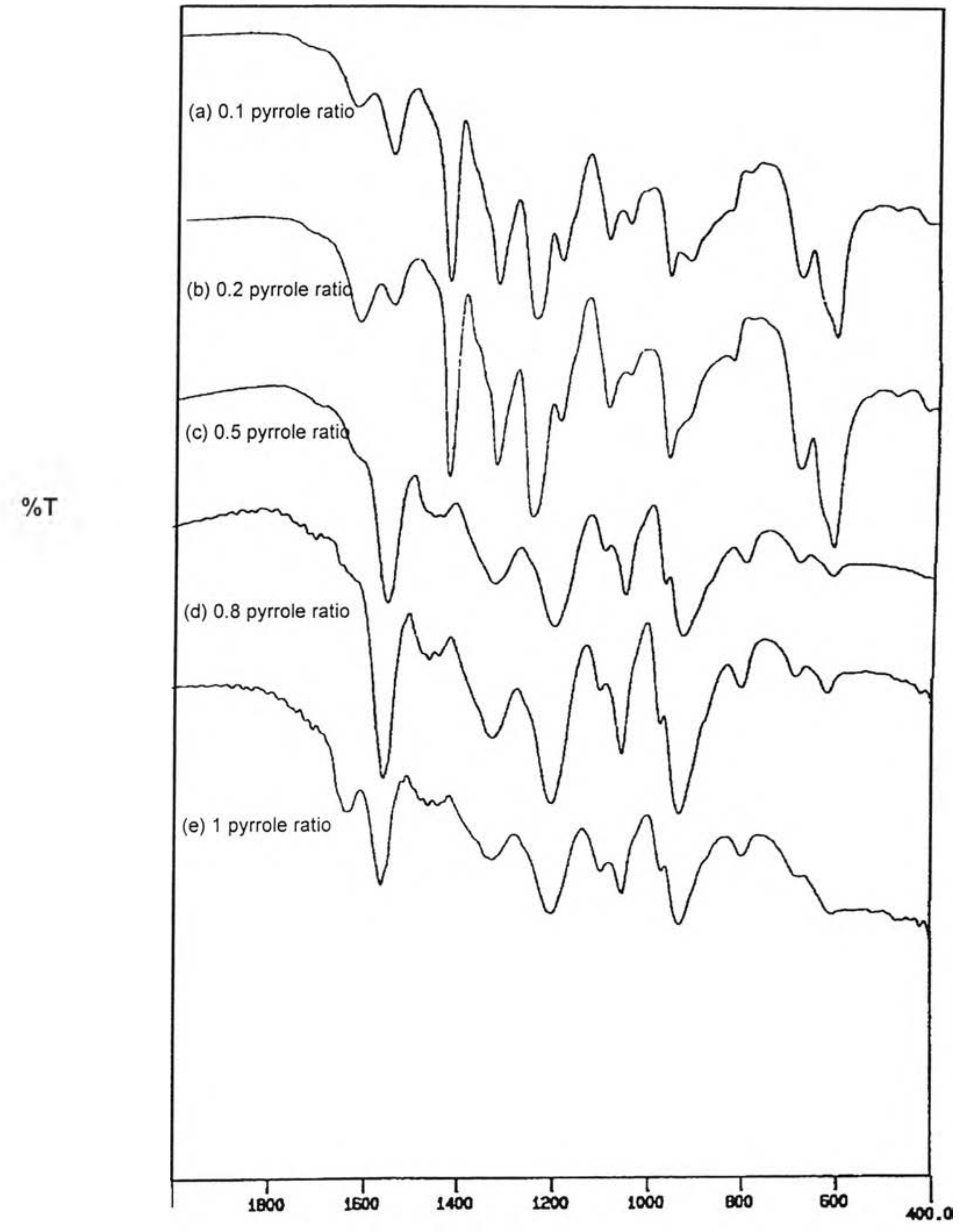

Figure 4.15 FT-IR spectra of PVC/PPy composites as a function of pyrrole: PVC ratio

(a) PVC01 (b) PVC02 (c) PVC03 (d) PVC04 (e) PVC05

4.6.2 Effect of reaction time

The polymerization was carried out by varying times from 1 to 3 hours. The electrical conductivities of PVC/PPy composites are shown in Table 4.6 while the other parameters were kept constant, i.e. 2.5 M $FeCl_3$ solution, 0 °C reaction temperature. This method is similar to PS/PPy composite preparation system.

Tables 4.6 Conductivity of PVC/PPy composite depends on the reaction time

Sample code	Reaction time (hour)	Pyrrole: PVC ratio	Conductivity(Scm^{-1})
PVC17	1	0.2	-
PVC18		0.5	5.33
PVC19		0.8	9.52
PVC22	2	0.2	2.24
PVC23		0.5	7.68
PVC24		0.8	7.41
PVC27	3	0.2	0.98
PVC28		0.5	1.97
PVC29		0.8	1.58

Again, the electrical conductivities of PVC/PPy composites also decreased when the polymerization time increased. These phenomena are analogous to the PS/PPy composite. Beside, it is interesting to note that the conductivity decreased when pyrrole ratio is higher than 0.5. The decreasing of conductivity was also observed when the polymerization was conducted after 2 hours. It can be ascribed that the higher level of pyrrole adding to the reaction and long polymerization time are not suitable for polymerization of PVC/PPy composite, especially, at 3 hours polymerization time. This led to the low electrical conductivity about 1 Scm^{-1}, which is undesirable in this research. Hence, the short time is the good choice for the preparation of the high conductivity composite. Figure 4.16 demonstrates that the conductivities increase when the polymerization time is 2 hours in the cases of 0.2 and 0.5 pyrrole ratio. However, when the pyrrole ratio is 0.8 the conductivity keeps decreasing with time. After 2 hours, the decreasing of conductivity in all cases was observed.

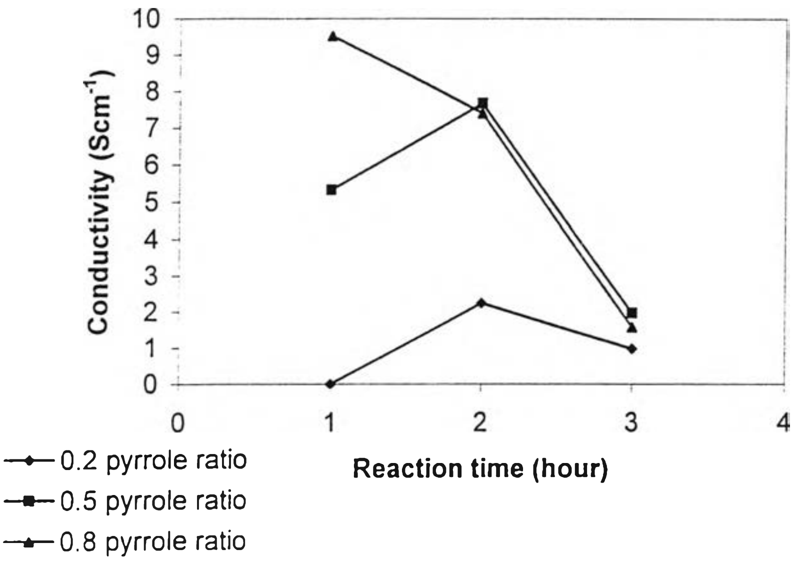

Figure 4.16 The conductivity of PVC/PPy composite versus reaction time

The electrical conductivities of PVC/PPy composites at any polymerization time are shown in Figure 4.16. It clearly exhibits that the highest conductivity is obtained when polymerization time is 1 hour at 0.8 pyrrole ratio. However, Figure 4.16 shows that the high conductivities are found at 2 hours polymerization time in the cases of 0.2 and 0.5 pyrrole ratio. In fact, the 1 hour is the suitable reaction time to produce the high conductivity composite because in the short reaction time the efficiency of oxidant to oxidize the reaction is still high.

However, in 1 hour system the coating of polypyrrole on host particles was not yet complete. Therefore the electrical conduction behavior on the particle surface was not occurred. The decreasing of the oxidation potential of oxidant solution at long polymerization time was described previously in Section 4.4.2. When the oxidation potential become low, the conductivity of produced composite is also decreases.

Contrast to our research, Armes et al. [27] reported that the low oxidant and monomer concentrations could slow the rate of reaction, thus promote of the polymerization of pyrrole surface rather than the polymerization of PPy in the solution. These researchers used mild conditions to conduct the polymerization in the long polymerization time (24 hours). In this research, we need high concentration of the oxidant and short reaction time to synthesize high conductivity PPy composite, which is the aim of our research. The conductivities of these composites were obtained. It can be seen that, mostly, PPy could coat on PVC surface in adequate amount for electrical transportation along the composite surface.

4.6.3 Effect of solvent

In this section, effect of various solvents on the polymerization was studied in details. Similar to the solvent effect study of PS/PPy polymerization, the composite conductivities were compared between methanol and 50% methanol/water solvent. The obtained conductivities are shown in Table 4.7.

Tables 4.7 Conductivity of PVC/PPy composite depends on the solvent

Sample code	Pyrrole: PVC ratio	Solvent	Conductivity(Scm^{-1})
PVC01	0.1	Methanol	-
PVC02	0.2		-
PVC03	0.5		5.33
PVC16	0.1	50% Methanol/water	0.50
PVC17	0.2		2.42
PVC18	0.5		3.56

The other parameters were kept constant, i.e. 2.5 M $FeCl_3$ solution, 0 °C reaction temperature, and 1 hour polymerization time. The data from the table show that the conductivities of PVC/PPy composite prepared in 50% methanol/water were obtained at 0.1, 0.2, and 0.5 pyrrole: PVC ratio while the conductivity was obtained only when the pyrrole ratio was 0.5 when the reaction was carried out in methanol. It is different from Machida et al.'s report [22]. They found that the oxidation potential of methanol is suitable for the preparation of the highest conductivity composite. It is reported the conductivity of polymer composite depends on the oxidation potential of the solvent system used. This can explain the high conductivity of 5.33 Scm^{-1} when the reaction was carried out in methanol and the low conductivity but better coating when the reaction was carried out in 50%methanol/water.

Figure 4.17 shows the relationships between conductivity and pyrrole: PVC ratio. The difference of conductivity when the reactions were carried out in methanol or 50% methanol/water system was also observed.

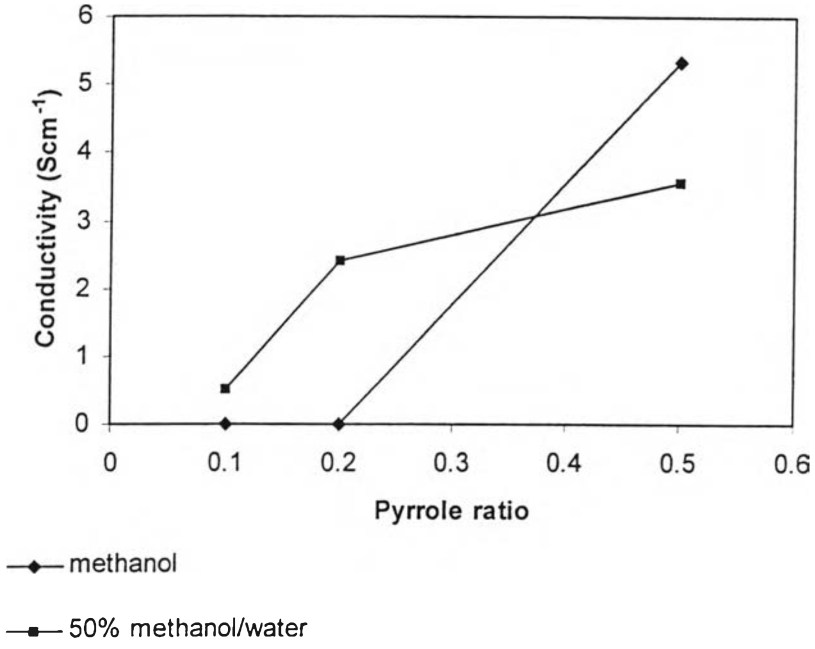

Figure 4.17 The conductivity of PVC/PPy composite versus pyrrole ratio in various solvents

The SEMs of PVC/PPy composites, which were prepared in different solvents, are shown in Figure 4.18. It is clearly demonstrated that the amount of PPy coated on PVC in methanol solvent is lower than in 50% methanol/water. It can be observed that the low and random coating of PPy on PVC particle can occur by using short polymerization period in methanol solvent (Figure 4.18(b)). On the other hand, the PPy was coated on PVC in the large amount when 50% methanol/water was used as solvent (Figure 4.18(c)). These data are agreed with the higher conductivity PVC/PPy composite in 50%methanol/water solvent.

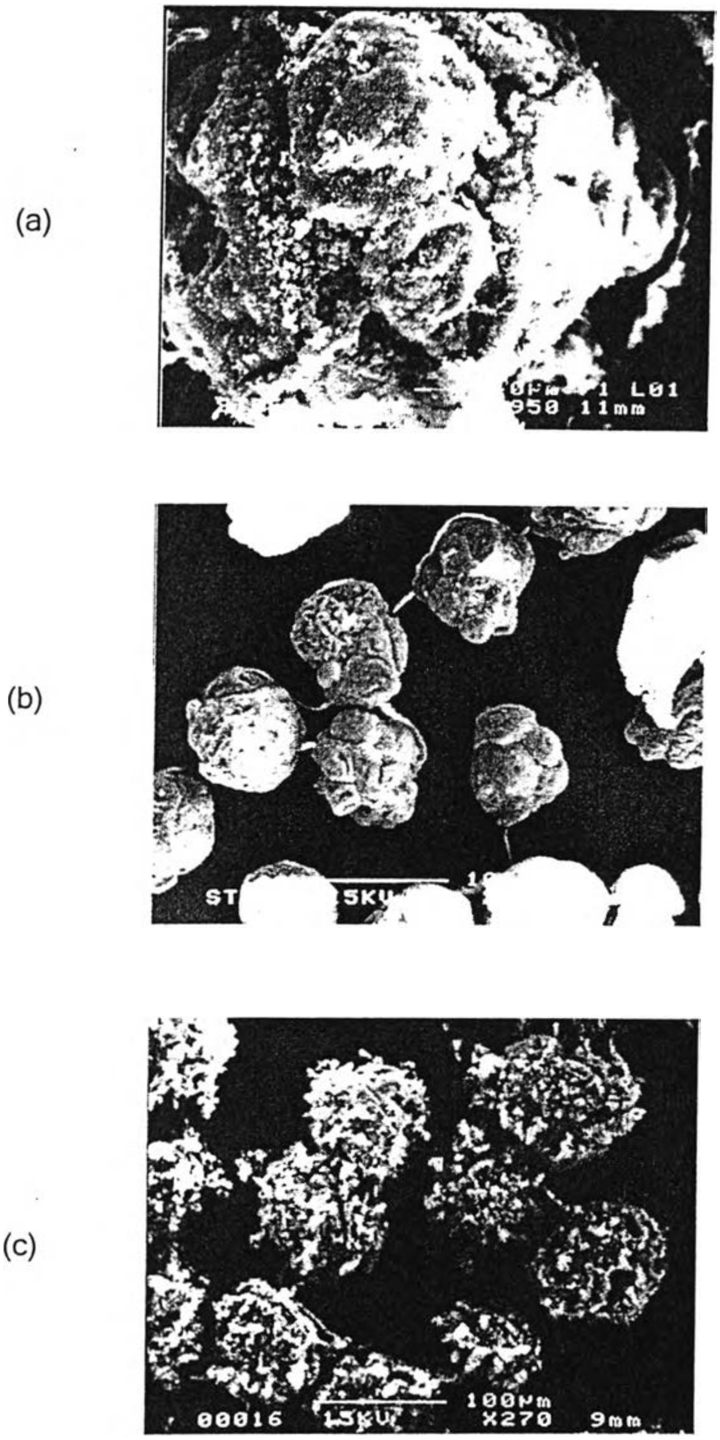

Figure 4.18 Scanning electron micrographs of PVC/PPy composites 0.1 pyrrole:

PVC ratio polymerized in

(a) methanol (x950) (b) methanol (x270)

(b) 50% methanol/water (x270)

4.7 Conductive stability of Poly(vinyl chloride)/Polypyrrole composite

The electrical conductivity of PVC/PPy composites assigned to code PVC03, PVC04, and PVC05 with 0.5, 0.8, and 1 pyrrole: PVC weight ratio were measured by van de Pauw method every 2 weeks until 10 weeks in order to studied the stability of conductivity. Table 4.8 shows the conductivity of PVC/PPy composites that were observed for 10 weeks. The other parameters were kept constant, i.e. 0 °C reaction temperature, methanol solvent, 1 hour polymerization time, and 2.5 M $FeCl_3$ solution.

Table 4.8 Conductivity of PVC/PPy composite as storing time

Time (week)	Conductivity (Scm^{-1})		
	PVC03	PVC04	PVC05
0	5.33	9.52	10.02
2	2.14	3.94	3.19
4	1.50	3.14	2.12
6	1.19	3.70	1.68
8	0.81	1.80	1.12
10	0.74	1.19	1.02

From this study, it was found that the conductivity of PVC03, PVC04, and PVC05 were rapidly decreased with the storing time. The final conductivities of these samples were rather low but they leveled off. It can be assumed that the moisture in the atmosphere can affect the conductivity of sample. The conductivities of PVC/PPy composites and PS/PPy composites are lowered to about the same value after 10 weeks.

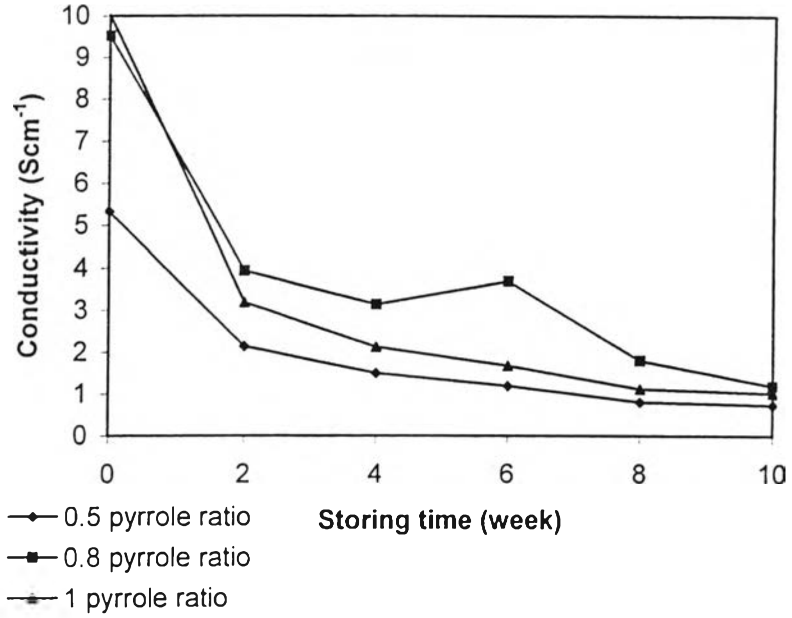

Figure 4.19 The conductive stability of PVC/PPy composites versus storing time

Figure 4.19 shows the decreasing of the conductivities of PVC/PPy composites. Initially, the conductivities decrease rapidly. It is possible that the anions around the surface of sample disc are removed easily. When the outer layer of sample matrix has low conductivity, the inner layer still has anions for charge transportation. The conductivities finally stay constant after storing for sometime. This detail was described previously in Section 4.3.4.

4.8 Determination of various effects on dispersion polypyrrole

The dispersity of PPy powder can be increased by adding poly(vinyl pyrrolidone) (PVP), which is the dispersing agent. So, this section discusses about the polymerization of PPy in the presence of dispersing agent. The preparation of PPy coating composite in this section is different from the previous section. The polymer product was obtained in the different feature. The effects of various conditions were studied as follow.

4.8.1 Effect of pyrrole

The effect of pyrrole amount is the main attention in this research. In this part, the pyrrole: PVP weight ratios were varied from 0.1 to 0.8 in methanol. Table 4.9 shows the electrical conductivity of the synthesized polypyrrole at various pyrrole ratios.

Table 4.9 Conductivity of dispersion polypyrrole depends on pyrrole: PVP ratio

Sample code	Pyrrole: PVP ratio	Conductivity (Scm^{-1})
PVP01	0.1	0.15
PVP02	0.5	0.24
PVP03	0.8	1.16

It can be seen that the electrical conductivities of these samples were very low when PVP was added to the reaction even though the high amount of pyrrole was present. The highest conductivity is only 1.16 Scm^{-1} although 0.8 pyrrole ratio was used. This result indicates that the polymerization of polypyrrole in methanol solution containing PVP cannot make the high conductivity product, dissimilar to the synthesis of polypyrrole in the same conditions, which can successfully prepared the very high conductivity polypyrrole [5]. It can be proposed that the use of stabilizer in the methanol system lead to the low conductivity PPy. This result corresponds to Digar's report [43]. They proposed that dispersion PPy prepared in nonaqueous media like ethanol or methanol mixture showed much lower conductivity than those prepared in aqueous media.

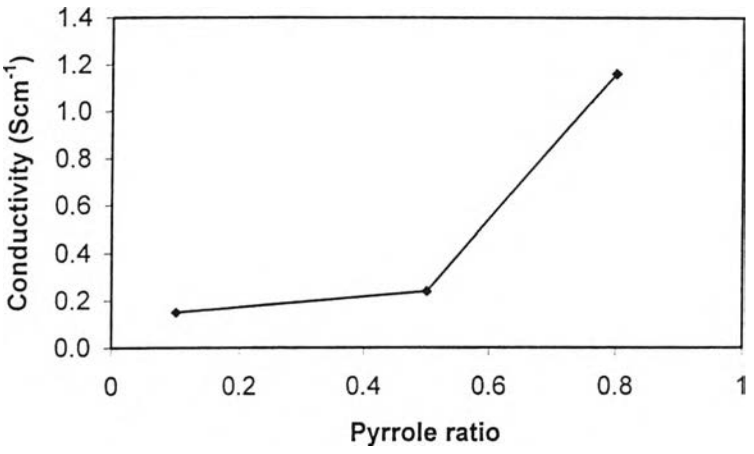

Figure 4.20 The conductivity of dispersion PPy versus pyrrole ratio

The relationship of conductivity with the amount of pyrrole added to the reaction is shown in Figure 4.20. It can be proposed that the conductivity of synthesized PPy depend on the amount of pyrrole. When pyrrole ratio increases conductivity of PPy increases also. However, although the conductivities of PPy in the presence of PVP are very low but the effect of monomer concentration on the conductivity is analogous to those prepared without stabilizer.

4.8.2 Effect of solvent

The effect of solvent was studied by carrying the experiment in various solvent systems. Water, methanol, and 50% methanol/water were used for the investigation. The other parameters were kept constant, i.e. 2.5 M $FeCl_3$ concentration, 0 °C reaction temperature, and 1 hour polymerization time. Table 4.10 shows the electrical conductivity of prepared PPy.

Table 4.10 Conductivity of dispersion polypyrrole depends on the solvent

Sample code	Pyrrole: PVP ratio	Solvent	Conductivity(Scm^{-1})
PVP01	0.1	Methanol	0.15
PVP02	0.5		0.24
PVP03	0.8		1.16
PVP04	0.1	Water	15.98
PVP05	0.5		6.53
PVP06	0.8		2.87
PVP07	0.1	50% Methanol/water	41.99
PVP08	0.5		15.64
PVP09	0.8		0.90

Form Table 4.10, the aqueous solvent can synthesize the high conductivity PPy. It can be proposed that the reaction of polypyrrole polymerization might be achieved in the water system. However, in 50% methanol/water system the conductivity can reach higher because the suitable oxidation potential from methanol can make the high conductivity PPy. For absolute methanol system, PVP in the solution may be hindering the polymerization of pyrrole monomer. Therefore, the conductivity level of dispersion PPy is become low. This is analogous to the use of ethanol and ethanol 50% aqueous solution by Digar [43]. They reported the very low conductivity in absolute ethanol while the higher conductivity was obtained in 50% ethanol system.

The surprising feature of conductivity is observed in the aqueous system. The conductivity at low pyrrole ratio is higher than at high pyrrole ratio. The highest conductivity was obtained of 42 Scm^{-1} at 0.1 pyrrole ratio in 50% methanol/water solvent. This result cannot be explained now and need the additional study to understand its behavior in the future.

The conductivities of PPy powder in different solvents are shown in Figure 4.21. It clearly exhibits that the conductivity decreases as the pyrrole ratios increase. The highest conductivity was obtained when the polymerization was carried out in 50% aqueous methanol. From this result, it can be concluded that 50% methanol/water is the best solvent for the preparation of dispersion PPy.

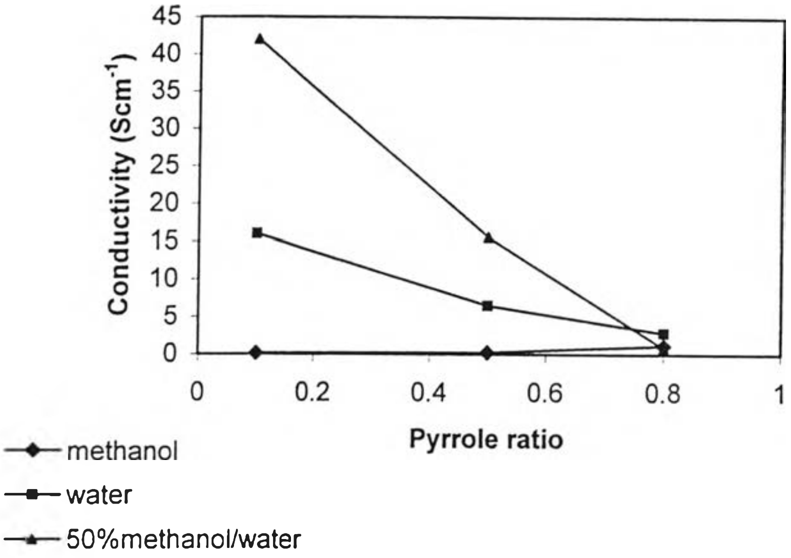

Figure 4.21 The conductivity of dispersion PPy versus pyrrole ratio in various solvents

To understand the morphology of dispersion polypyrrole in the different solvent system, the powder samples were investigated by using scanning electron microscope to obtain the surface photograph. Scanning electron micrograph of polypyrrole powder, which was polymerized in the methanol solvent, was shown in Figure 4.22.

The morphology of PPy powder that was polymerized in methanol and 50% methanol/water are shown in Figures 4.22 and 4.23, respectively. Figure 4.22 shows the character of PPy powder, which was prepared in methanol. It can be seen that it was no dispersity, dissimilar to PPy polymerized in 50%methanol/water solvent, which fully have the dispersity character. However, it cannot be concluded that the dispersion PPy from this experiment is good because PPy particles are agglomerated.

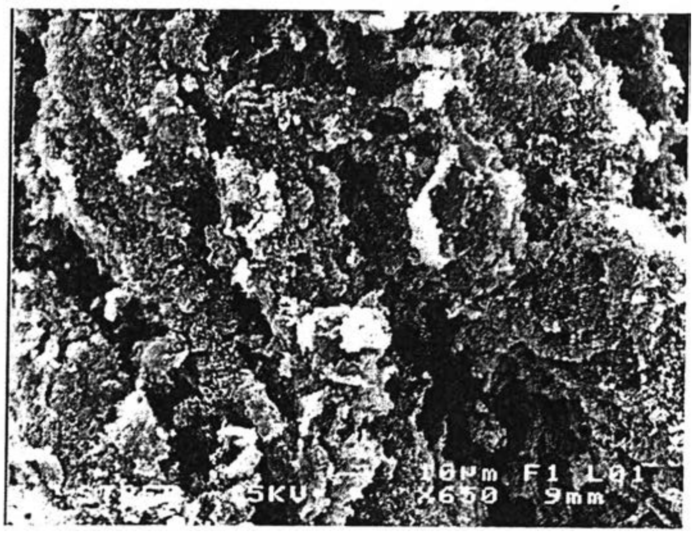

Figure 4.22 Scanning electron micrograph of dispersion PPy polymerized in methanol

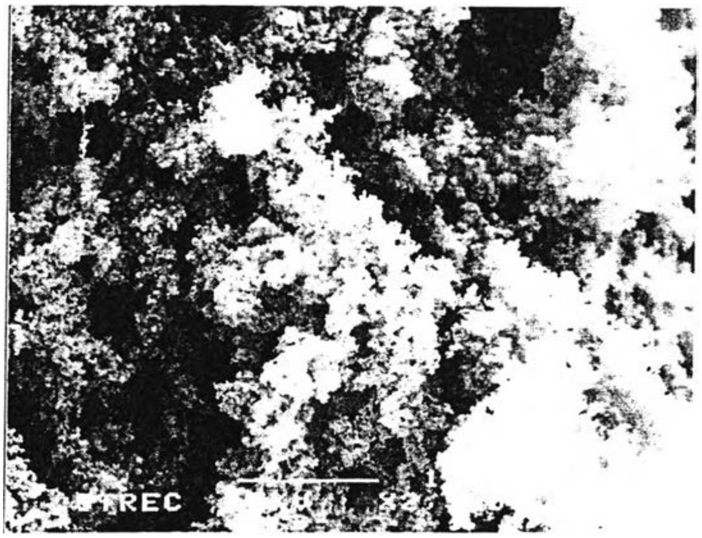

Figure 4.23 Scanning electron micrograph of dispersion PPy polymerized in 50% methanol/water

The agglomeration of PPy powder was explained by Armes et al. [45] who concluded that the coating stabilizing becomes non-uniform when sample was dried. The non-uniform coverage also helps the particles to adhere together so those agglomerations are found in the electron micrograph. So, the redispersion occurs easily when the isolated particles are not dried.

4.8.3 Effect of reaction time

The polymerization reaction of the dispersion PPy was accomplished at various reaction times from 1 to 3 hours. These reactions employed 0.5 pyrrole: PVP weight ratio. Table 4.11 shows the dependence of the electrical conductivity on the reaction time while the other parameters were kept constant, i.e. the 0 °C reaction temperature, 1 hour reaction time, and 2.5 M $FeCl_3$ aqueous solution.

Table 4.11 Conductivity of dispersion PPy depends on the reaction time

Sample code	Reaction time (hour)	Conductivity(Scm^{-1})
PVP05	1	6.53
PVP10	2	7.33
PVP11	3	14.88

Table 4.11, suggests that the electrical conductivity of PPy products increases when the reaction time increases. It seems that the higher conductivity can be observed at longer reaction time. Nevertheless, the reaction time over 3 hours is almost not practical because the mixture in the reactor began to condense. So, in this experiment, the reaction had to be stopped not more than 3 hours. It is noted that the conductivities increase as the reaction times increase in the

dispersing system. This seems to be the effect of PVP in the reaction system. The presence of PVP in the solution could hinder the electrical transport among PPy particle, which is significant at the initial stage. Other researchers used the very long polymerization time to proceed the reaction in mild oxidant concentration. The polymerization of dispersion PPy was successful at 24 hours and low conductivity PPy was obtained [38,39].

The study of dispersion PPy is the additional study of this research. The experiment involved the preparation of dispersion PPy is at the initial stage. The attempt now is only the improvement of electrical conductivity. Thus, various properties of these products are not yet determined, i.e. particle feature, conductivity, and processability. These properties are very interesting in dispersion PPy synthesis. In the future work the synthesis of dispersion polypyrrole to improve the particle shape and conductivity should be investigated.

4.9 The effect of reaction temperature on the Polystyrene/Polypyrrole composite synthesis

As well known, the reaction temperature is an important factor for the synthesis of PPy. Most PPy syntheses were carried out in the low temperature environment, especially, near 0 °C temperature. However, in the case of PPy composite, the polymerizations at the temperature lower than 0 °C had been never exhibited. In order to obtain the suitable temperature for the chemical polymerization of PS/PPy composite, the reaction temperatures at 0, -5, -10, -20 °C were studied. So, to keep those temperatures in the reaction, dry ice in ethanol was used.

Table 4.12 shows the electrical conductivity of PS/PPy depends on the reaction temperature lower than 0 °C. The other parameters were kept constant, i.e. 0.5 pyrrole: PVP weight ratio, 2.5 M $FeCl_3$ solution in absolute methanol, 1 hour reaction time.

Table 4.12 Conductivity of PS/PPy composite depends on the reaction temperature

Temperature(°C)	Conductivity(Scm^{-1})
0	7.57
-5	4.02
-10	2.86
-20	-

The results show that the lower reaction temperature can reduce the conductivity of PS/PPy composite. The conductivity decreases as the reaction temperature decreases. It can be seen that at -20 °C, the conductivity cannot be obtained since the polymerized PPy was not occurred after the polymerization was allowed to proceed at 1 hour. The color of mixture in flask could be used to show the occurrence of polymerization. It can be seen that brown color of the oxidant solution had not changed at the end of reaction in the -20 °C system. These show that the polymerization was only occurred when the temperature closes to 0 °C. It is participate with dark black color of the mixture when the reaction temperature is high. This can prove that the very low temperature is not suitable for the preparation of PS/PPy composite. The polymerization of pyrrole monomer was not occurred at very low temperature. This result corresponds to the synthesis of PPy in Tanawadee's research [5]. Thus, it can be concluded that the much lower temperature, <0 °C is not good for the synthesis of PS/PPy and other composites.