

CHAPTER VI
VARIOUS PROPERTIES COMPARISON OF NATURAL RUBBER COATED
POLYPYRROLE AND POLYTHIOPHENE

6.1 Compared reaction time and mass of PPy and PTh on NR

The success of admicelled polymerization of PPy and PTh coated natural rubber latex was investigated. The polymerization reaction was carried out via admicellar polymerization of rubber with various Pyrrole and Thiophene concentrations (20-800 mM) using the electrochemical method at 9V, 25°C. Table 6.1 and Table 6.2 show the dependence of %yield and reaction times on the monomer concentration.

Table 6.1 Effective of PPy content on % yield and reaction times at 9 V

PPy (mM)	20	50	100	200	500	800
NR (g)	25 *	25	25	25	25	25
PPy(g)	0.67	1.67	3.34	6.68	16.70	26.72
SDS (g)	2.307	2.307	2.307	2.307	2.307	2.307
Mass at anode (g)	23.22	24.17	27.43	29.83	35.61	45.31
%yield	90.45	90.62	89.55	86.58	85.39	87.61
Times (hr)	35	32	20	15	13	10

When : $\%yield = \frac{M_{total} \times 100}{(M_{NR} + M_{PPy})}$; M_{sds} is not calculate due to it can remove by water.

Table 6.2 Effective of PTh content on % yield and reaction times at 9 V

PTh(mM)	20	50	100	200	500	800
NR (g)	25	25	25	25	25	25
PTh(g)	0.841	2.104	4.027	8.414	21.035	33.656
SDS (g)	2.307	2.307	2.307	2.307	2.307	2.307
Mass at anode (g)	23.67	24.23	25.81	29.70	39.43	48.91
%yield	91.59	89.39	88.92	88.88	85.65	83.38
Time (hrs)	30	27	26	25	24	23

When : $\%yield = \frac{M_{total} \times 100}{(M_{NR} + M_{PTh})}$; M_{sds} is not calculate due to it can remove by water.

* 25g = 18.30 g dry rubber

According to Table 6.1 and 6.2, It is obvious that the %yield and reaction times of admicelled rubber were decreased along with the PPy and PTh concentration increased. This technique is efficient: % yield ~83-91%. The studies found that the reaction time at the higher amount of PPy and PTh, the faster reaction was. At lower amount of monomers, it takes much long reaction time (35-30 hrs) to synthesize. However, the reaction of Pyrrole monomer seems to be faster at higher conversion than Thiophene. The reason can cause by the change in band structure of PPy and PTh subsequent to doping (Nathalie K. 2007)⁴. There are many factors that influence the band gap (the distance between conducting band and valence band (Bredas,J.L. ,1985)⁴¹), including dopant, oxidation level/doping percentage, synthesis method and temperature (G. Wallace (2004)⁴⁵. The amount of anions found in each material is governed by the level of oxidation of the polymer. The anion contents for the various films are listed in Table 6.3.

Table 6.3 Anion content of conducting film

Film	Oxidation level	Anion Content (%by wt)
Polypyrrole	0.25-0.33	25-30
Polythiophene	0.06	7-25
Polybithiophene	0.22	12
Azlene	0.25	15-28
Pyrene	0.45	-
Carbazole	0.45	21
Indole	0.2-0.3	15-20
Furan	-	26

From Table 6.3, PPy has higher amount of oxidation level and anion content than PTh. Higher concentration of PPy results in the rapid, which polymerization of pyrrole faster than PTh and hence, the complete covering of PPy on NR particles. The morphology obtained after 6 hrs of reaction are shown in the Figure 6.1.

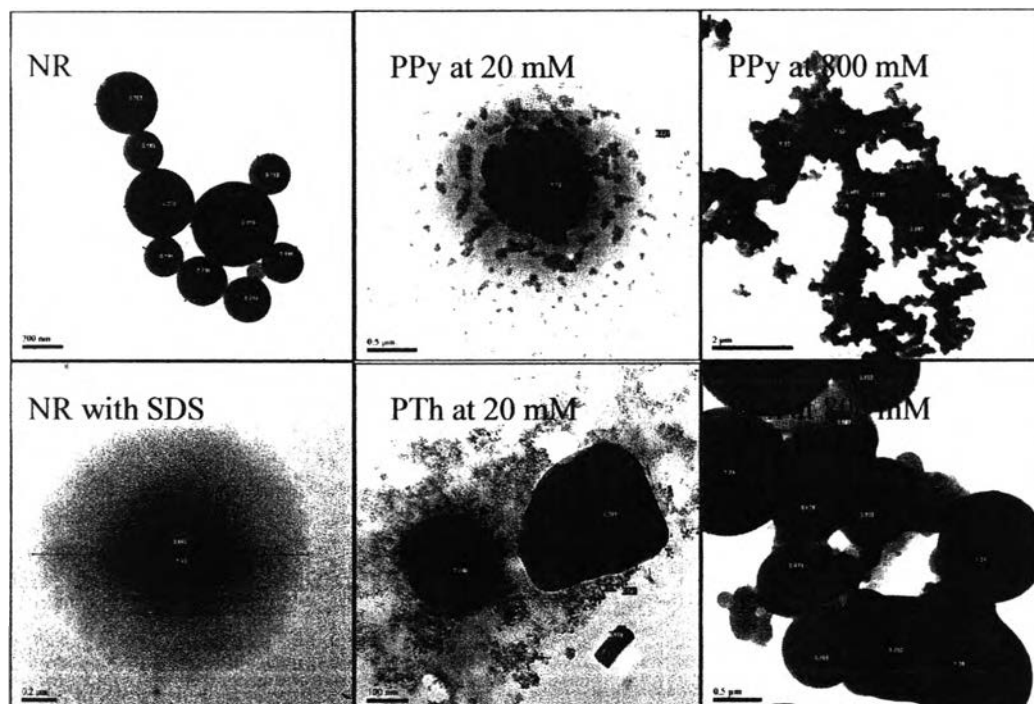


Figure 6.1 Transmission electron microscope (TEM) of the monomer coating by using the admicelled technique.

6.2 The particle size distribution of particle

The particle size distribution of NR latex before admicellar polymerization showed the mean diameter $1.05 \mu\text{m}$ and the mean specific surface area $6.874 \text{ m}^2 / \text{g}$. These results indicated the polydispersity of NR latex particles with narrow size distribution (Figure 6.2). The average core particle diameter was estimated to be between 0.5 to $0.9 \mu\text{m}$ and the coating particles were between 0.8 and $2 \mu\text{m}$.

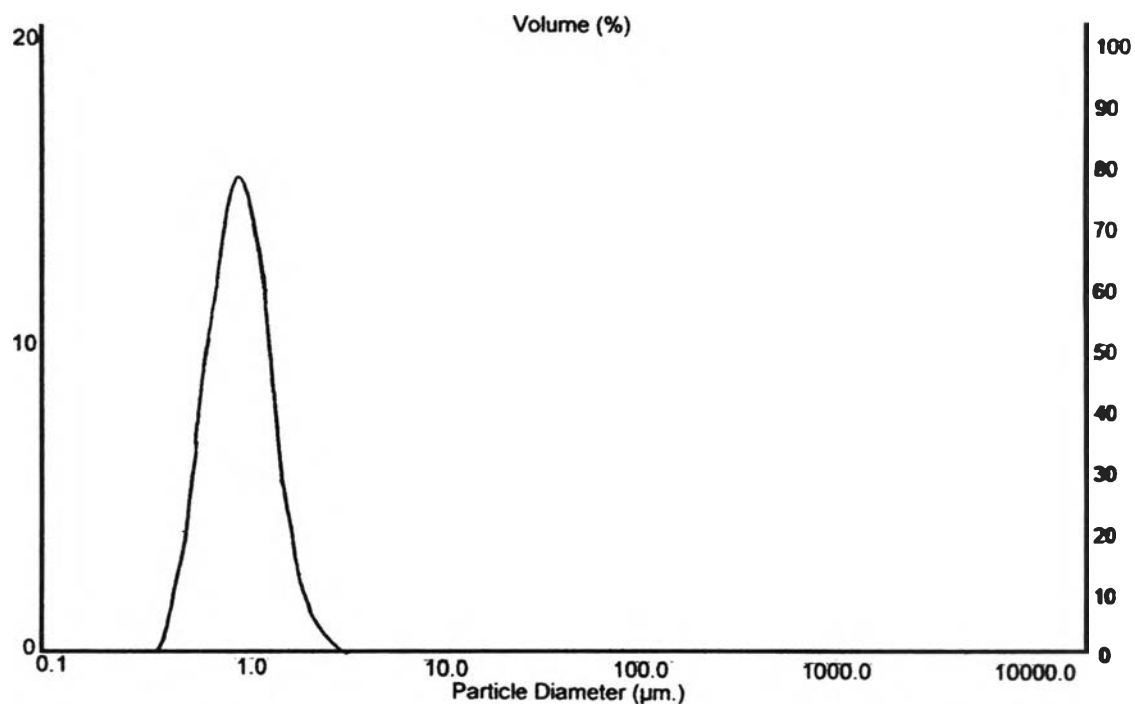


Figure 6.2 Histogram showing the particle size distribution by volume of the natural

However, The particle size distribution of NR by particle size analyzer was differ from TEM results. The diameter of NR particle can be smaller than 0.5 μm or larger than 1.5 μm (Figure 6.3).

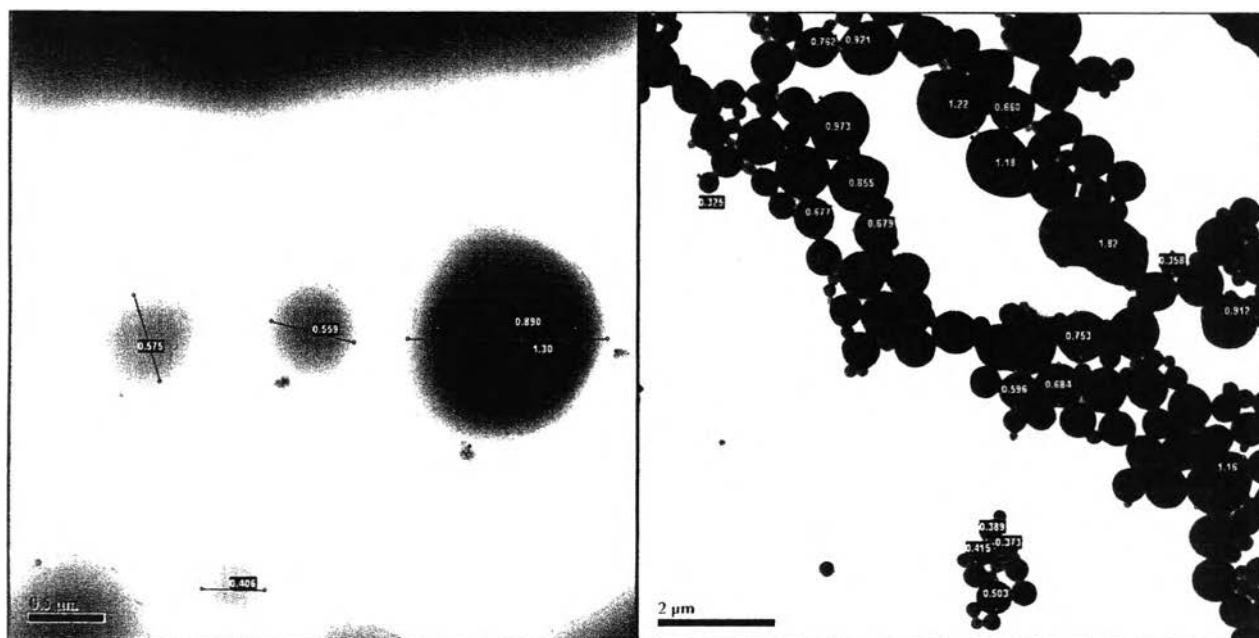


Figure 6.3 Transmission electron microscope (TEM) of the natural rubber latex.

6.3 Morphology

SEM result can confirm the presence of polypyrrole in the admicelled natural rubber. As observe in Figure 6.4 (a) a grained texture, coaser cauliflower are presented. Figure 6.4 (b) the morphology PTh can be demonstrated in several shapes e.g. globules, fibrils, ribbon whereas NR exhibited the smooth surface without any coating as shown in Figure 6.4 (c).

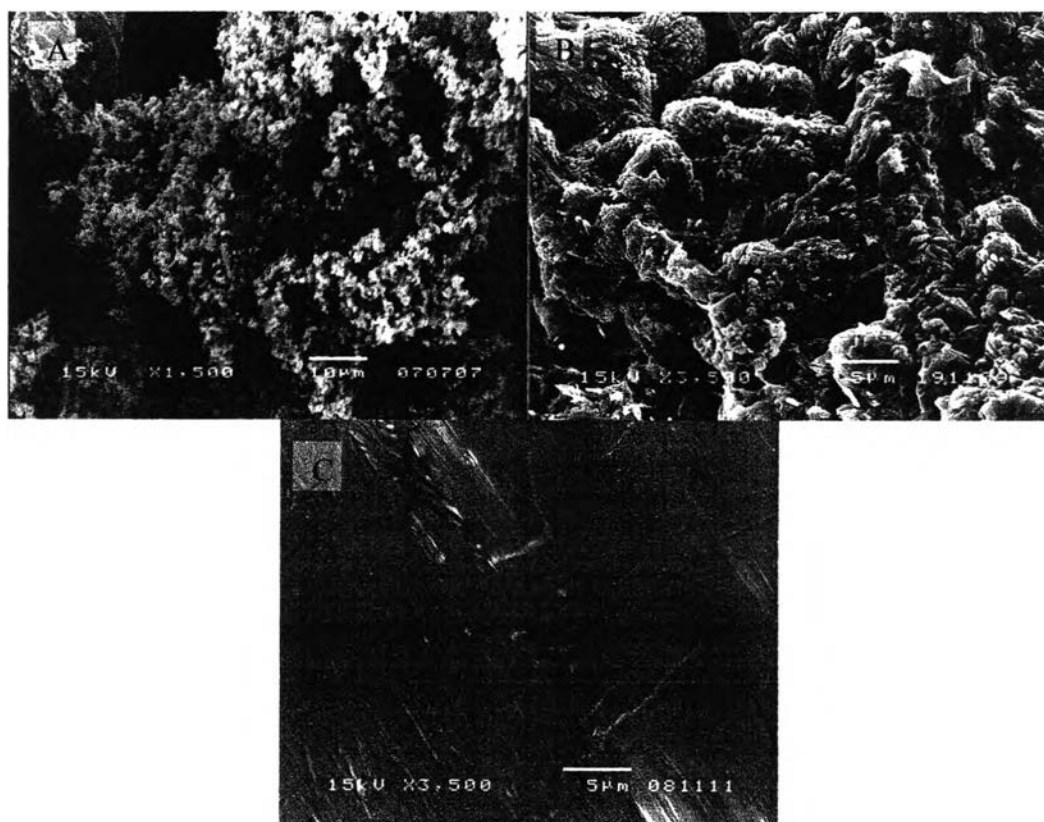


Figure 6.4 Scanning electron micrograph of the coating with (a) polypyrrole (b) polythiophene (c) natural rubber by using electrochemical method magnification 1,500-3,500 /15 kV

The SEM micrographs of PPy and PTh are compared according to the various concentrations as shown in Figure 6.5 and 6.6 respectively. The SEM micrographs of PPy on admicelled rubber with different monomer concentration reveal round shape of rubber particles with evenly coating over the particles.

In this work, the synthesized PTh appears as the aggregates of tiny ribbons which are similar to those found by Gok.A, making its surface much rougher than NR surface. The admicelled PTh/NR morphology in the dry state is rather like the

morphology of PTh; i.e. there is no clear appearance of round NR particle aggregates but it shows, at 20 mM thiophene, the protruding of rigid rods (about 1 micron wide or less) and the aggregates of rigid rods that becomes finer like needles and denser like pads as monomer concentration increases. It also shows pores between needles. However, the pad like structure at high monomer concentration is attributed to the smooth PTh shell covering the NR core particles so that good particle connection is obtained.

The morphology of pure PPy can be varies with the synthesized methods. As observed in Figure 6.5, a grained texture is present and must be compared with the coarser cauliflower structure which is commonly found. The morphology of PPy in the presence of anionic surfactant was studied by Osmastova.M (2003) [22-25]. PPy-DBSNa showed significantly tiny particles (globules), and it showed that the presence of the anionic surfactant in the polymerization mixture strongly influenced the morphology of PPy preparation, which formed irregular aggregates whereas NR exhibited the smooth surface without any coating as shown in Figure6.4. The admicelled PPy/rubber with different PPy concentrations reveals latex particles coated by a PPy layer as a core-shell structure (NR core and PPy shell). The samples with 50, 100, 200, 500, and 800 mM of PPy clearly show the coating of PPy whose morphology changes from tiny globular aggregates to continuous smooth connection of particles, which is shown in Figures 6.5 (c-h).

Both of PTh and PPy coating on NR show no phase separation suggesting good compatibility and dispersability of rubber particles and conductive polymer. As is known, the morphology and electrical properties of the conductive polymers are strongly related. The smooth shell surface (no pores) obtain at high monomer concentration can be reason for the higher density as well as better conductivities. Thus, a higher concentration of PPy (≥ 100 mM) in admicelled PPy/NR results in the change in morphology from tiny globule packing dense packing, as a result, the rough surface coating become smooth coating surface such that the conductivity can be enhanced. Conductivity of high content PTh (500-800 mM) NR was also enhanced.

They also show no phase separation between the PPy and the NR. This suggests a high level of dispersability of rubber particles and PPy. The average particle diameter was estimated to be between 0.6-1.6 μm , or approximately the same as the value determined by the particle size analyzer. This also reveals the very fine nanometer thickness of the PPy shell.

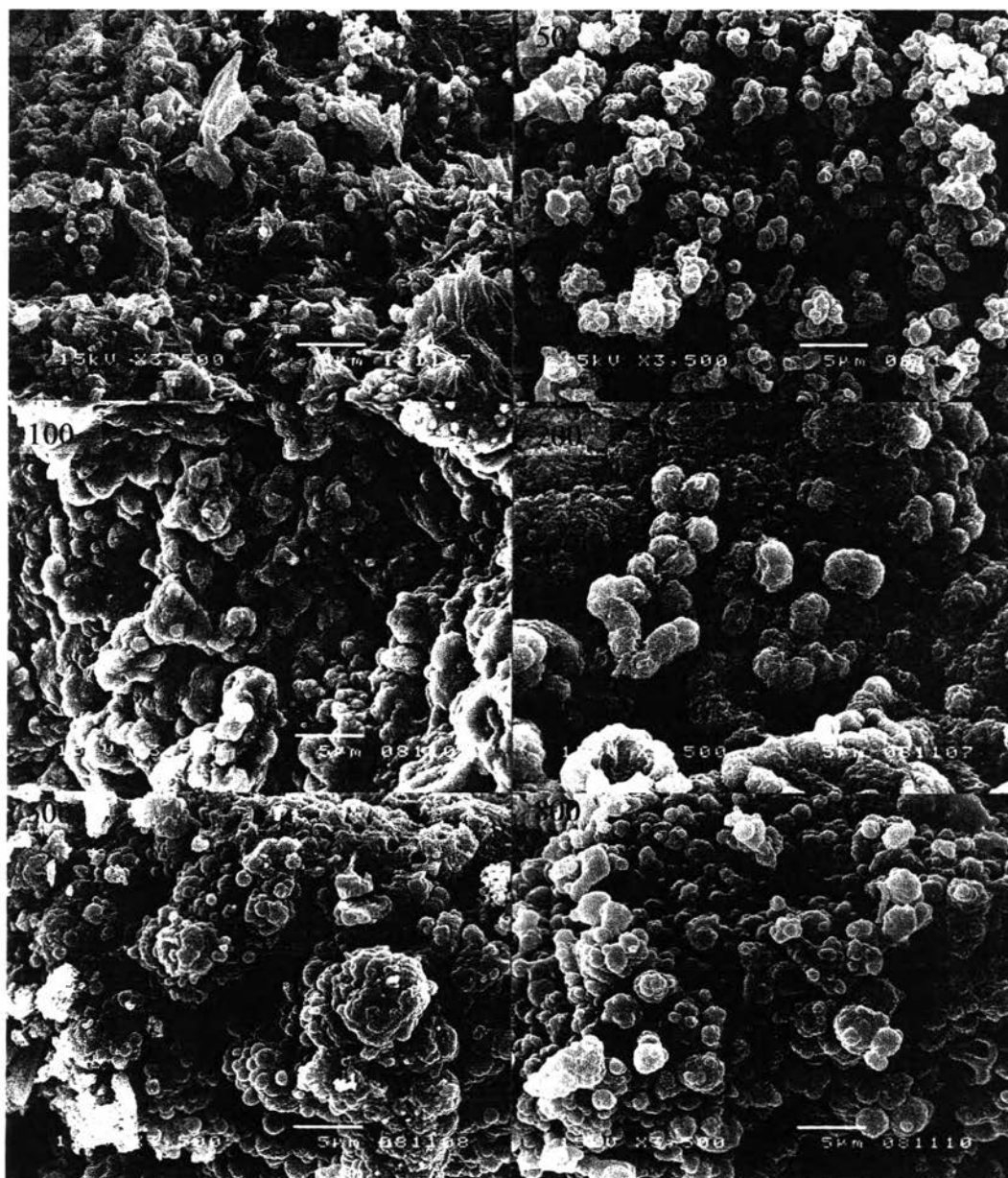


Figure 6.5 Scanning electron micrograph of the coating admicelled rubber (with various content of PPy) by using electrochemical method magnification 3,500/15 kV.

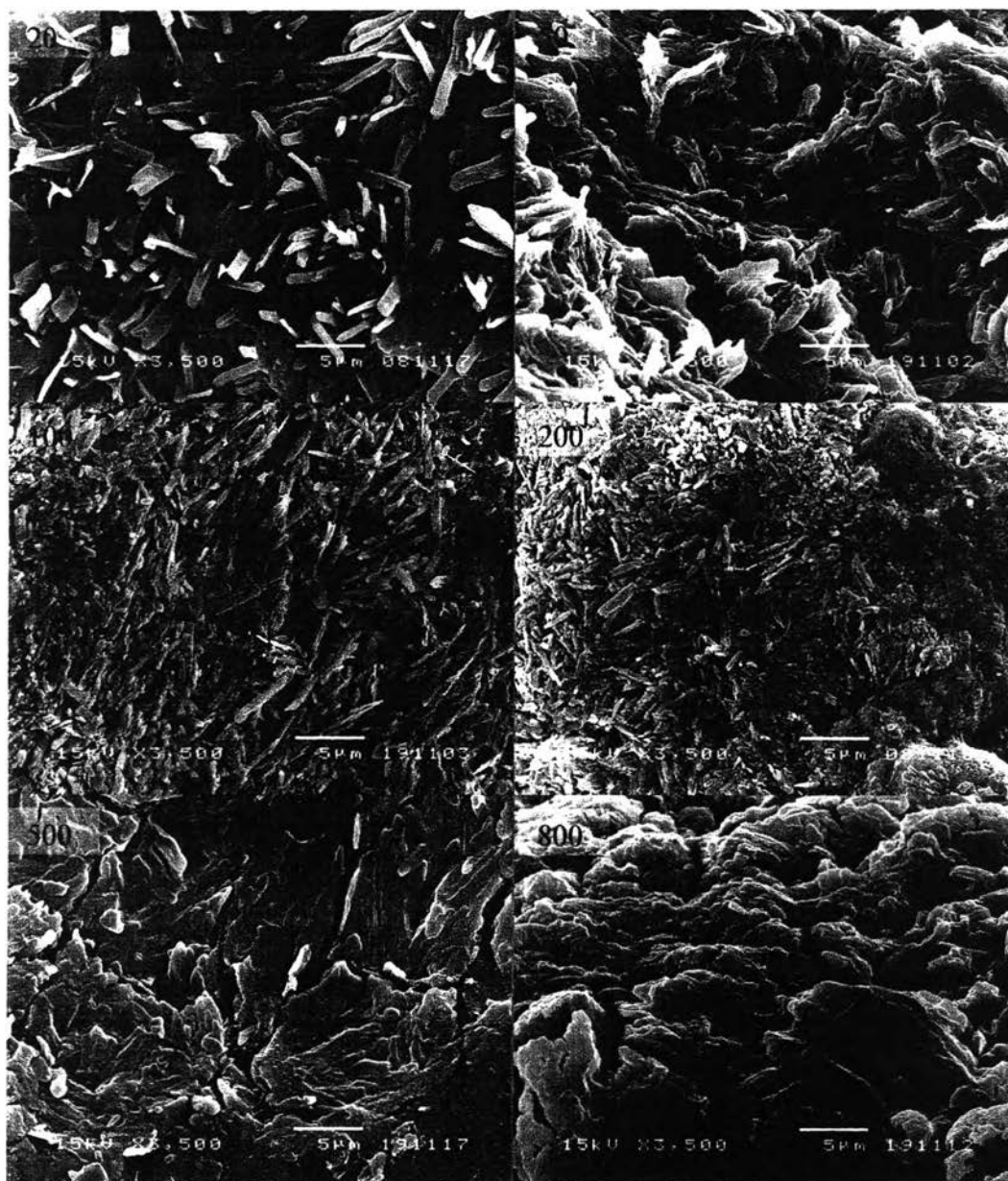


Figure 6.6 Scanning electron micrograph of the coating admicelled rubber (with various content of PTh) by using electrochemical method magnification 3,500/15 kV.

6.4 Thermogravimetric behavior of samples

Thermal behavior of samples was compared between PPy and PTh contents by using Thermogravimetric-Differential Thermal analyzer (Perkin Elmer, Pyris Diamond). The effect of both monomers was explained more details in chapter4 and chapter5.

Table 6.4 comparison the degradation temperature of the admicelled rubbers

Sample	Onset Temperature	End point Temperature	Peak temperature	residual content (%)
Rubber	351.6	471.9	373.6	1.1
20 mM PPy	348.9	481.5	369.4	4.9
50 mM PPy	347.8	485.3	368.6	11.1
100 mM PPy	349.2	493.9	370.2	16.8
200 mM PPy	352.8	496.6	373.5	17.9
500 mM PPy	353	505.9	374.5	19.2
800 mM PPy	352.2	521.1	374.4	22.3
PPY	204.9	579.3	260.3	66.58
20 mM PTh	347.6	473.5	370.3	1
50 mM PTh	348.3	475.1	372.1	1.7
100 mM PTh	348.5	476.3	374.5	2.9
200 mM PTh	348.4	476.6	374.8	3.2
500 mM PTh	348.6	478.9	375	3.4
800 mM PTh	350.8	480.9	378.7	3.9
PTH	194,8	597,46	211,4	16.1

From Table 6.4 and Figures 6.7 to 6.10, the amount of PPy or PTh has hardly affect on decomposition temperature of NR and decomposition about 200 mM PPy or 100mM PTh comparable to NR. These demonstrate that char yields of admicelled rubber increased with related to content of monomers added.

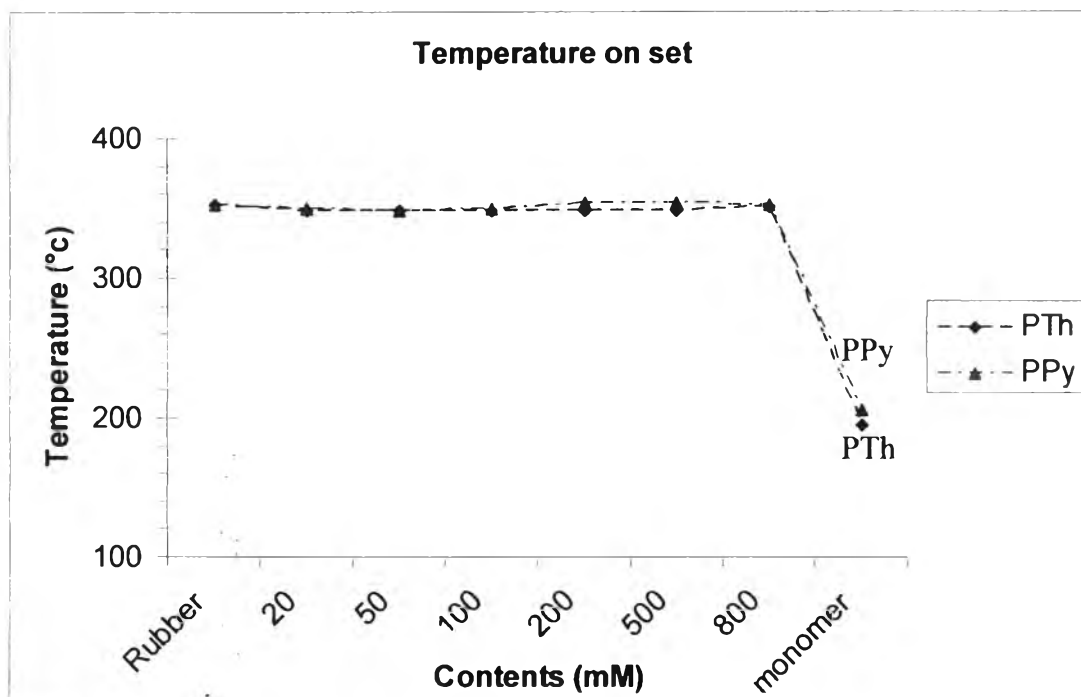


Figure 6.7 Thermogravimetric analysis thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.

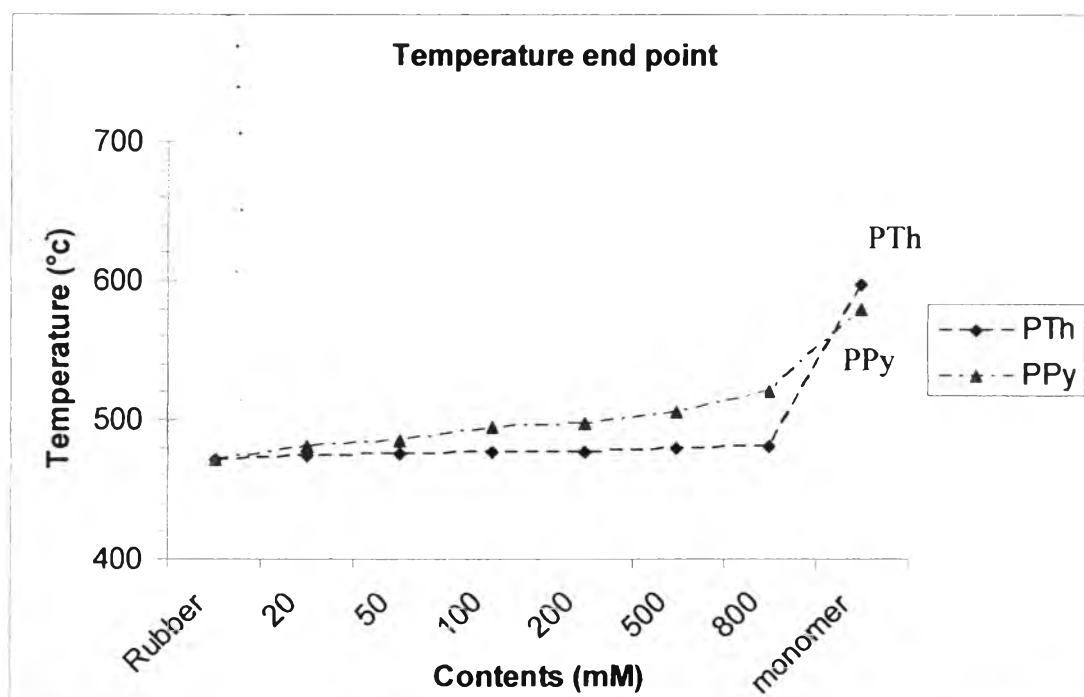


Figure 6.8 Thermogravimetric analysis thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.

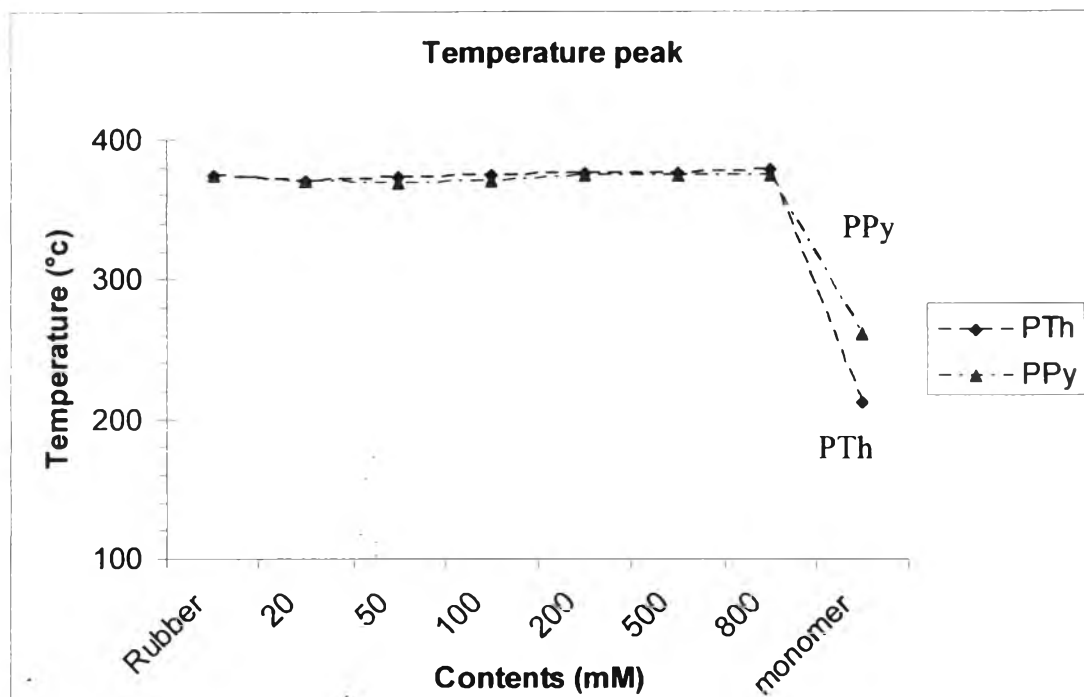


Figure 6.9 Thermogravimetric analysis thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.

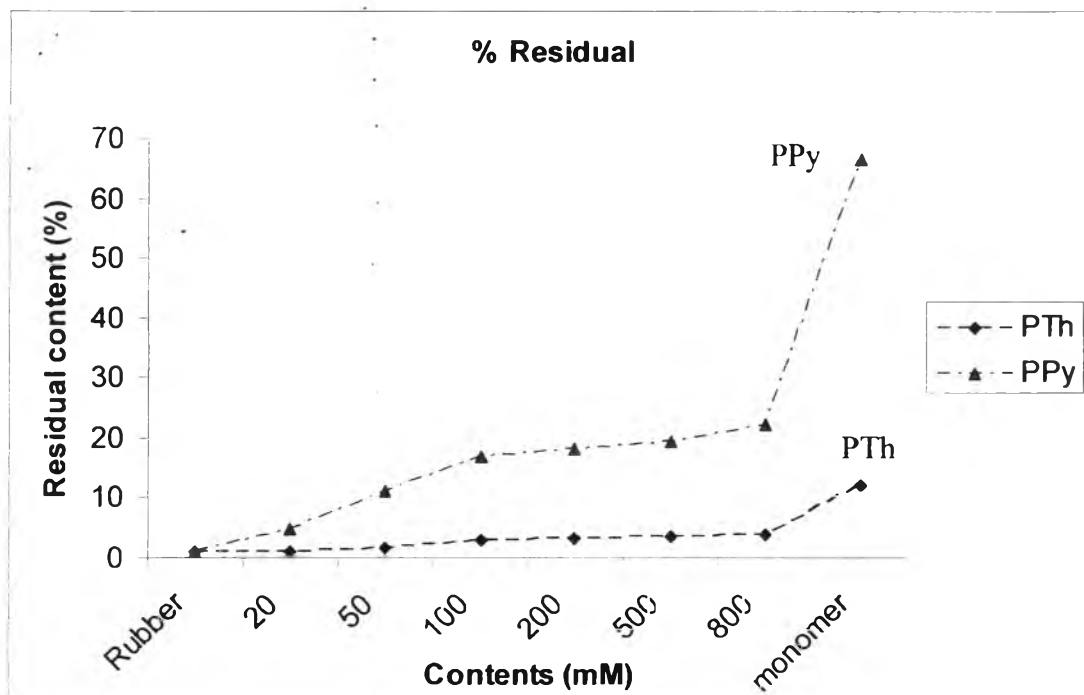


Figure 6.10 Thermogravimetric analysis thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.

Indeed, the higher concentrations can be improved the thermostability of NR. This can support the hypothesis as mention in the objective of this research topic.

6.5 Mechanical properties measurement

The mechanical properties were determined for two specimen types with one type is a dimension 20x100 mm (thickness 0.3-0.8 mm) the test were prepared from compression molding. The test were following ASTM D822-91 with crosshead speed of 50 mm/min, gauge length of 50 mm, and load cell 500 N under room temperature using Lloyd Universal Testing Machine, model :LRX. The test was repeated 5 times.

The Tensile Strength Test uses two clamps to hold the testing strip. When secured, the testing strip will be pulled, with a specified force, apart. The yield point and/or breaking point will be measured. (Figure 6.11)

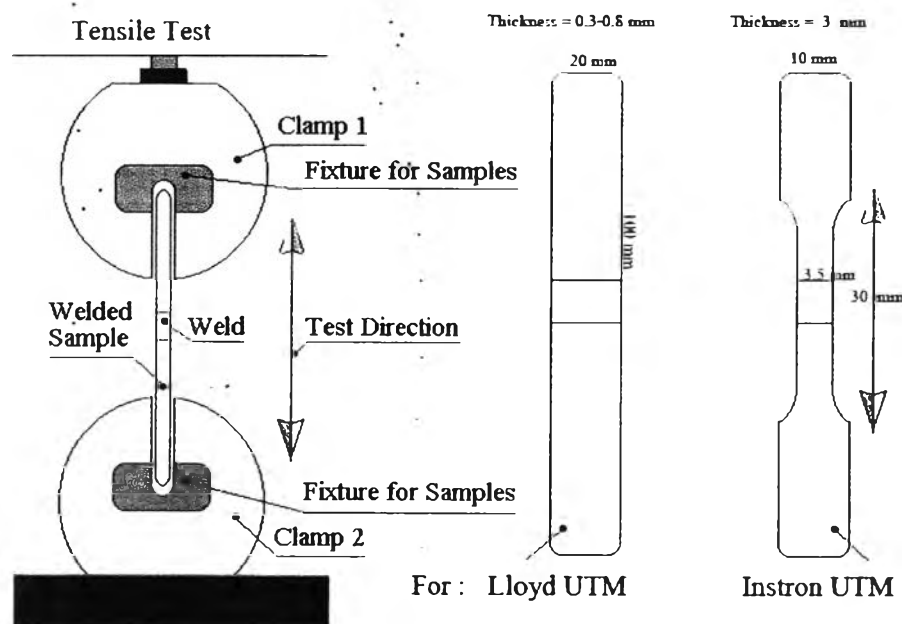


Figure 6.11 preparation samples for tensile test.

Another type is the dumbbell shape, which has thickness larger than 3 mm, the specific sample size (Figure 6.11) were cut by using the pneumatic punch following ASTM D638M-91a. The samples were tested by using the Instron Universal Testing machine with crosshead speed 50 mm/min gauge length of 13 mm, and load cell 100 kN under room temperature. The test was repeated 5 times.

6.5.1 Lloyd universal machine

The admicelled latex films were determined mechanical properties (Lloyd universal machine) as shown in the Chapter 4 and 5. A comparison of the mechanical properties corresponding to the various concentration of PTh and PPy as shown in Table 6.5.

Table 6.5 Composition and properties of (PPY,PTH)/NR (Lloyd universal machine)

Sample (mM)	Elongation at break (%)	Tensile strength at break (MPa)	Work to Break (J)	Young's modulus (MPa)	
NR	311.75 ± 6.23	0.48657 ± 0.002	0.6724 ± 0.013	0.1667 ± 0.013	
PPy	20	180.95 ± 9.05	0.56688 ± 0.006	0.5571 ± 0.027	1.11 ± 0.022
	50	144.91 ± 10.14	0.98323 ± 0.033	0.5110 ± 0.086	1.25 ± 0.025
	100	118.83 ± 11.18	0.92941 ± 0.018	0.4912 ± 0.049	1.60 ± 0.032
	200	90.06 ± 9.01	0.9441 ± 0.0192	0.3824 ± 0.038	2.00 ± 0.040
	500	73.47 ± 16.16	1.3561 ± 0.0190	0.2623 ± 0.018	2.50 ± 0.050
	800	88.87 ± 6.22	1.8792 ± 0.0266	0.2413 ± 0.016	2.85 ± 0.057
PTh	20	312.73 ± 15.378	0.2036 ± 0.0283	0.746 ± 0.0402	0.2857 ± 0.006
	50	198.80 ± 9.141	0.2952 ± 0.0501	0.561 ± 0.0678	0.4000 ± 0.008
	100	139.34 ± 8.512	0.2501 ± 0.02501	0.269 ± 0.0301	0.5714 ± 0.011
	200	129.01 ± 13.113	0.2963 ± 0.0338	0.249 ± 0.0237	0.5142 ± 0.010
	500	83.77 ± 14.896	0.9661 ± 0.0749	0.244 ± 0.0091	1.710 ± 0.034
	800	69.60 ± 5.143	1.3385 ± 0.0898	0.236 ± 0.0205	2.850 ± 0.057

The elongation is shown in Figure 6.12, that pure NR film was soft, tough and high elastic material, with high elongation at break (311.75 %), higher value for work to break (0.672 J) in Figure 6.14, but low tensile strength at break (4.8657×10^5 Pa) in Figure 6.13 and Young modulus (0.16 MPa) in Figure 6.15.

Conversely the mechanical properties of PPy and PTh change from soft and elastic to hard and brittle material, depending on the amount of monomer incorporation. Increasing the concentration of monomer to NR, it leads to harder and more brittle. The tensile strength at break can be improved from 4.8657×10^5 Pa (NR) to 18.792×10^5 Pa (800mM PPy) and 13.385×10^5 Pa (800mM PTh) in Figure 6.13. This indicate of PPy incorporated into NR by admicelled technique can be improved

tensile strength higher than PTh. It might be caused by the bonding of the structure. The micrographs from SEM and TEM can suggest the core-shell structure where NR particle are core and PPy / PTh is shell. Young modulus in Figure 6.15 is also similar trend to tensile strength. However, PTh can enhance the elongation higher than that of PPy in Figure 6.12.

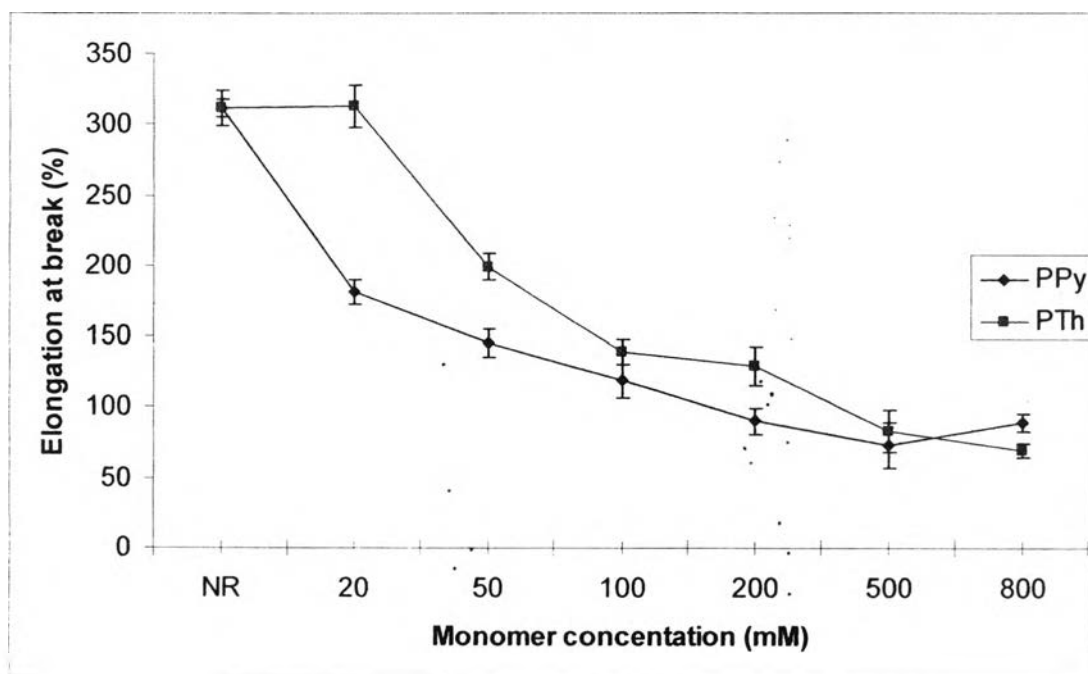


Figure 6.12 Elongation vary the concentration of monomer (Lloyd UTM)

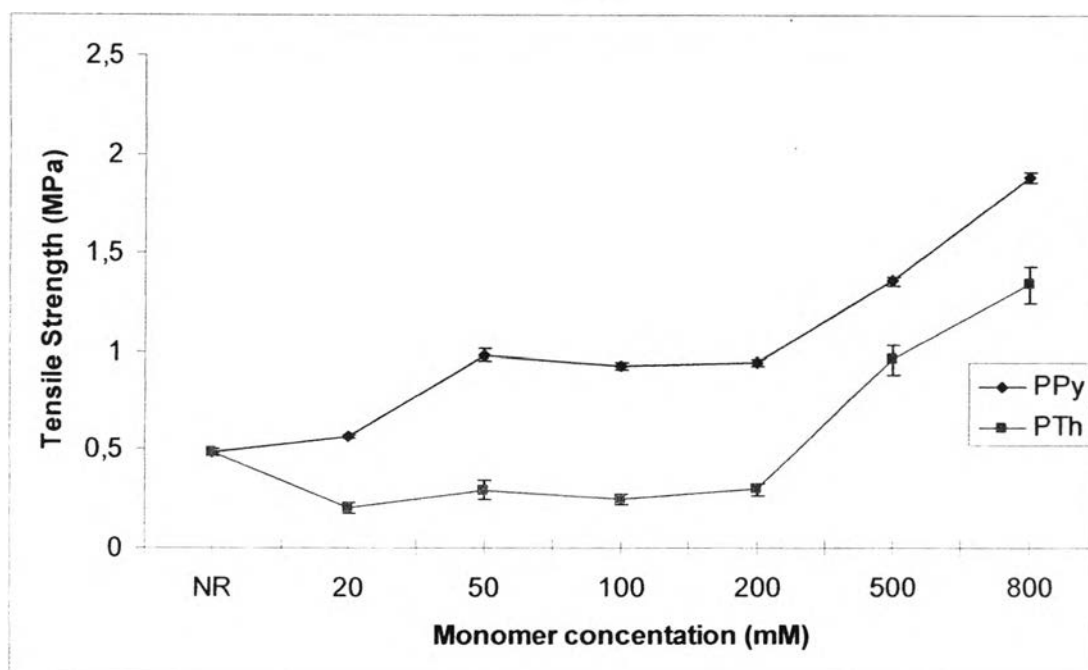


Figure 6.13 Tensile strength vary the concentration of monomer (Lloyd UTM)

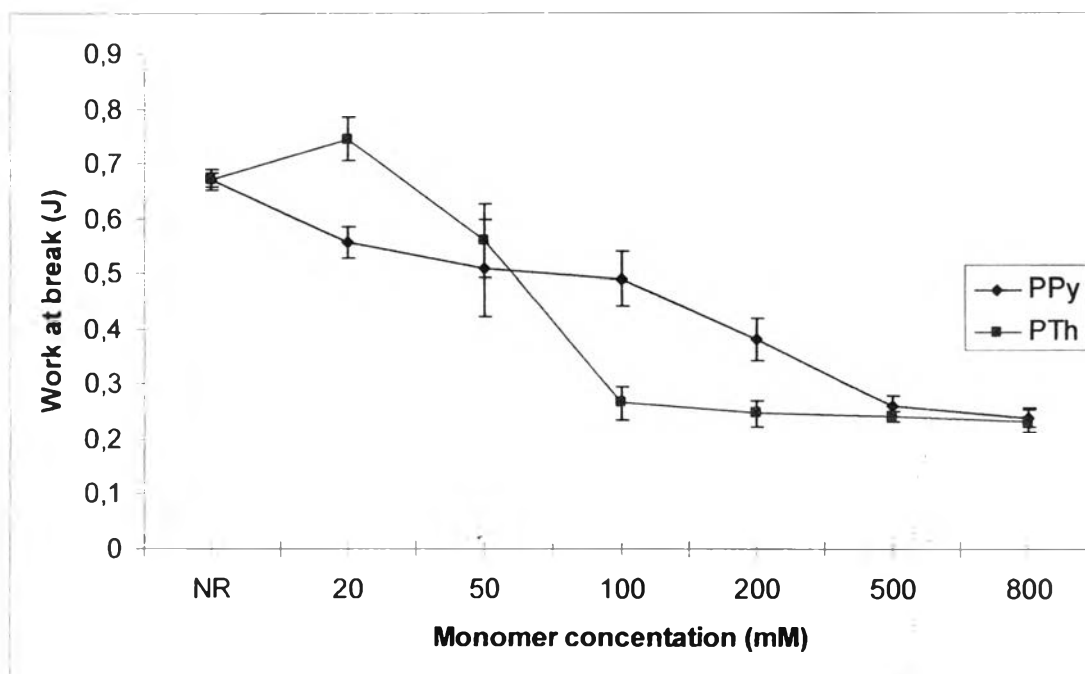


Figure 6.14 Effect of monomer concentration to the energy at break (Lloyd UTM)

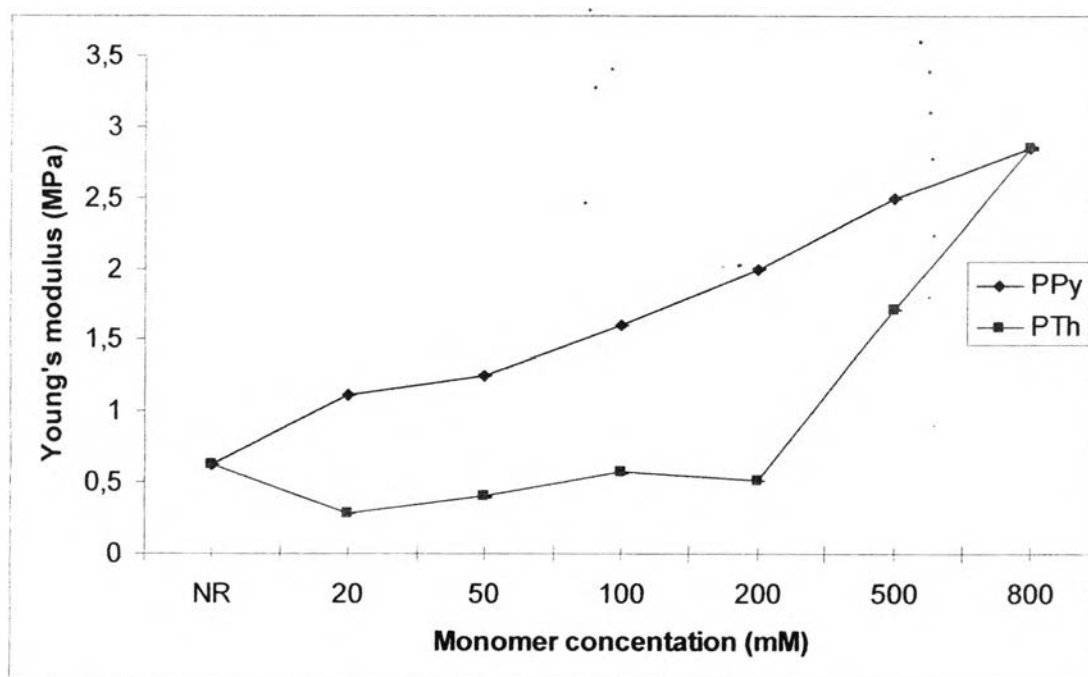


Figure 6.15 Effect of monomer concentration to Young's modulus (Lloyd UTM)

6.5.2 Instron universal machine

Another type was the dumbbell shape, the admicelled latex films were also determined mechanical properties (Instron universal machine) as shown in the Chapter 4 and 5. A comparison of the mechanical properties corresponding to the various concentration of PTh and PPy as shown in Table 6.6.

Table 6.6 Composition and properties of Monomer/NR

Sample (mM)	Elongation at break (%)	Tensile strength at break (Mpa)	Work to Break (J)	Young's modulus (Mpa)	
NR	831.46 ± 16.63	1.3011 ± 0.026	1.0181 ± 0.020	0.333 ± 0.006	
PPy	20	655.28 ± 32.21	1.5021 ± 0.075	0.9984 ± 0.049	0.266 ± 0.005
	50	521.94 ± 36.53	1.7012 ± 0.289	1.0593 ± 0.180	0.04 ± 0.001
	100	392.34 ± 39.23	1.9839 ± 0.198	0.6848 ± 0.068	0.533 ± 0.011
	200	380.13 ± 38.01	2.0512 ± 0.205	0.6746 ± 0.067	0.60 ± 0.012
	500	226.86 ± 49.90	3.0112 ± 0.211	0.5654 ± 0.039	1.333 ± 0.027
	800	221.67 ± 15.51	3.5175 ± 0.246	0.4581 ± 0.032	1.667 ± 0.033
PTh	20	664.28 ± 33.21	1.1041 ± 0.171	0.3861 ± 0.029	0.166 ± 0.003
	50	567.57 ± 31.87	2.9181 ± 0.212	0.3920 ± 0.110	0.333 ± 0.006
	100	431.31 ± 29.23	2.9113 ± 0.218	0.3645 ± 0.058	0.370 ± 0.007
	200	420.86 ± 21.78	5.8101 ± 0.125	0.3123 ± 0.027	0.833 ± 0.016
	500	375.08 ± 18.10	8.7012 ± 0.141	0.2901 ± 0.049	1.176 ± 0.023
	800	302.31 ± 16.11	11.6101 ± 0.179	0.2817 ± 0.012	5.405 ± 0.108

The result is similar trend to test with Lloyd universal machine. However, both experiments differ in their shapes and upon ASTM.

The elongation is shown in Figure 6.16, that pure NR film was soft, tough and high elastic material, with high elongation at break (831.46 %), higher value for work to break(1.0181 J) in Figure 6.18, but low tensile strength at break (1.30MPa) in Figure 6.17 and Yong modulus (0.16 MPa) in Figure 6.19.

Conversely the mechanical properties of PPy and PTh change from soft and elastic to hard and brittle material, depending on the amount of monomer incorporation. Increasing the concentration of monomer to NR, it leads to harder and more brittle in Figure 6.13. Young modulus in Figure 6.15 is also similar trend to tensile strength. However, PTh can enhance the elongation higher than that of PPy in Figure 6.12.

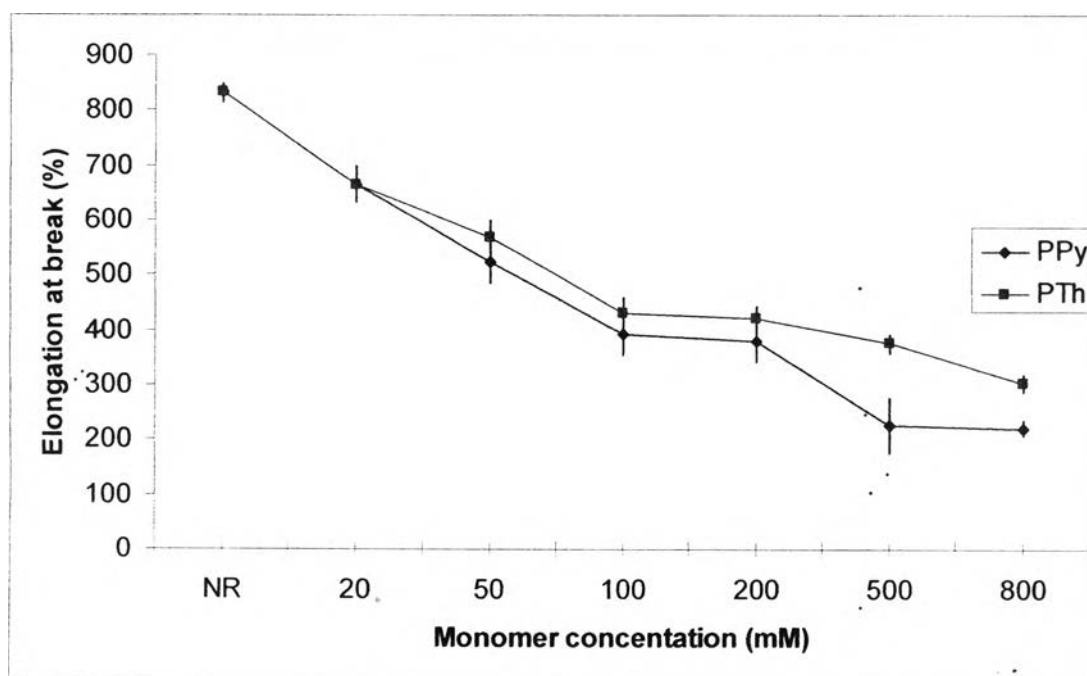


Figure 6.16 Elongation vary the concentration of monomer (Instron UTM)

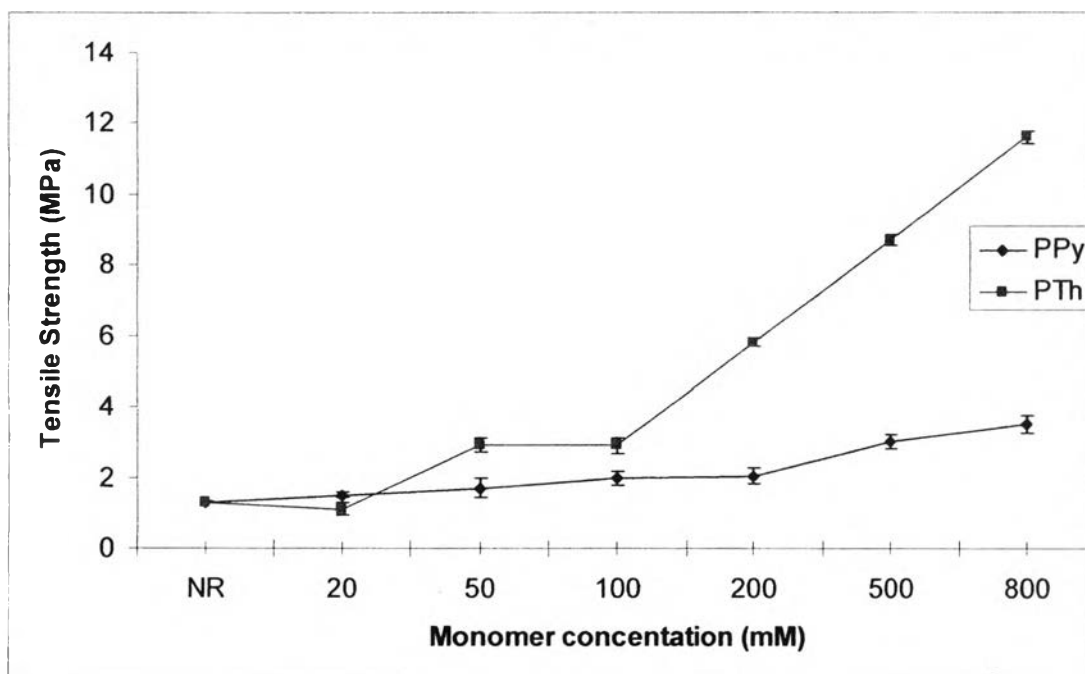


Figure 6.17 Tensile strength vary the concentration of monomer (Instron UTM)

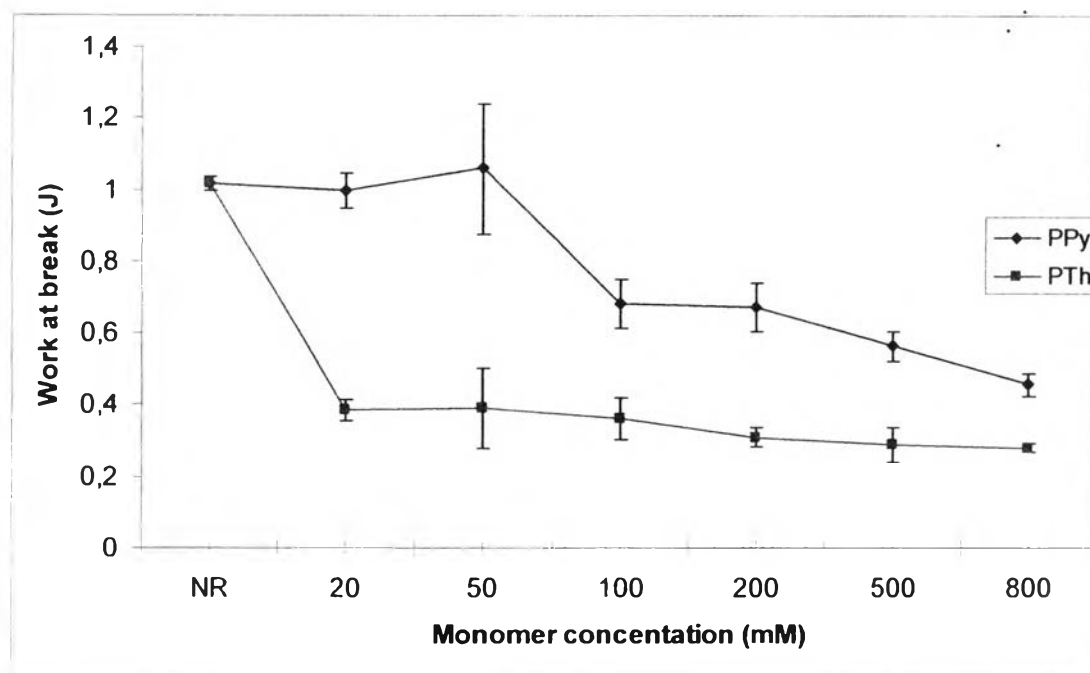


Figure 6.18 Effect of monomer concentration to the energy at break (Instron UTM)

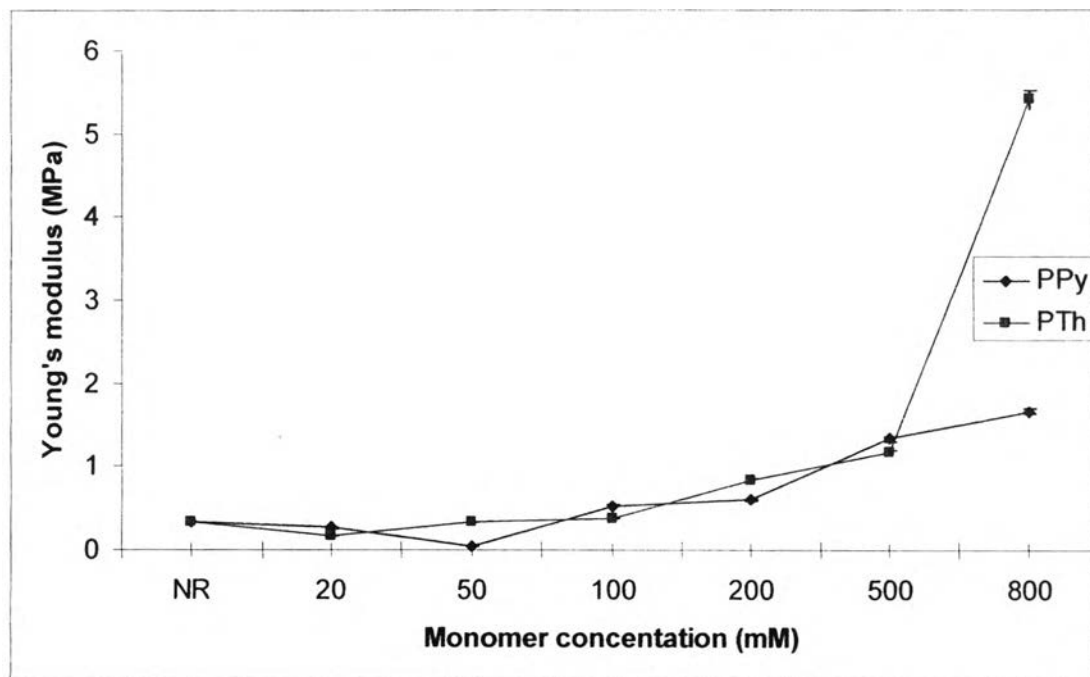


Figure 6.19 Effect of monomer concentration to Young's modulus (Instron UTM)

6.6 Hardness properties measurement

The shore A and shore D hardness of Admicelled rubber are presented more details in chapter 4 and 5. The shore hardness values for the samples are presented in Table 6.7 The variation of hardness of the samples is similar to that of tensile strength as shown in the Figures 6.20-6.21.

In general, elongation of the admicelled rubber decreases whereas the hardness of increases. From Table 6.7, the hardness increased from 22.46 shoreA (NR) up to over value of detecting machine, >90 shoreA (800mMPPy) and 88.67 shoreA(800mPTh). Thus, the hardness was measured by hardness shoreD which increased from less than 10 (NR) to 25.16 shoreD (800mMPPy) and 16.9 ShoreD (800mPTh). PPy demonstrated the higher of hardness than PTh as showed in Figure 5.20 and 5.21. Therefore, hardness of admicellar rubber was corresponding to the monomer concentration. The increasing amount of monomer can lead to having good interfacial adhesion between the matrix and monomer as core-shell structure (S. Lopez, 2004)¹¹⁹. These are strongly evidences which improve their hardness properties.

Table 6.7 Shore hardness with concentration for admicellar rubber^{18,19,20}

Sample (mM)		Hardness (SHORE A)	Hardness (SHORE D)
NR		22.46	<10
PPy	20	30.87	<10
	50	30.85	10.16
	100	65.71	12.33
	200	83.71	14.50
	500	95.33 (>90)	17.83
	800	128.33 (>90)	25.16
PTh	20	18.28571	<10
	50	25.28571	<10
	100	26.85714	<10
	200	36.28571	<10
	500	66.5	13,2
	800	88.66667	16,9

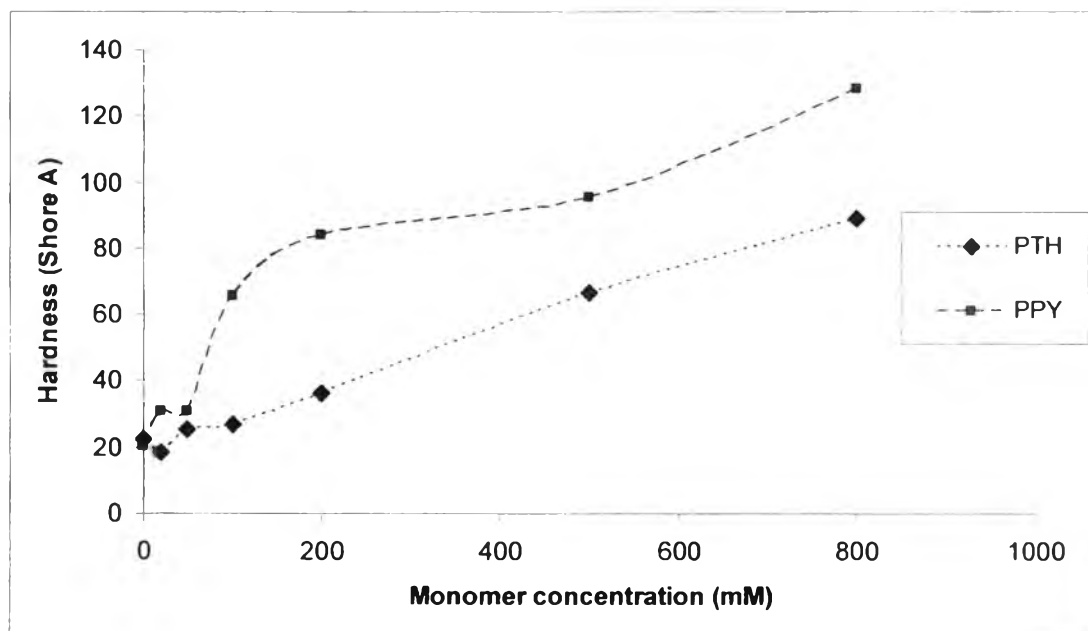


Figure 6.20 Variation of hardness shoreA with conductive polymer for admicellar rubber

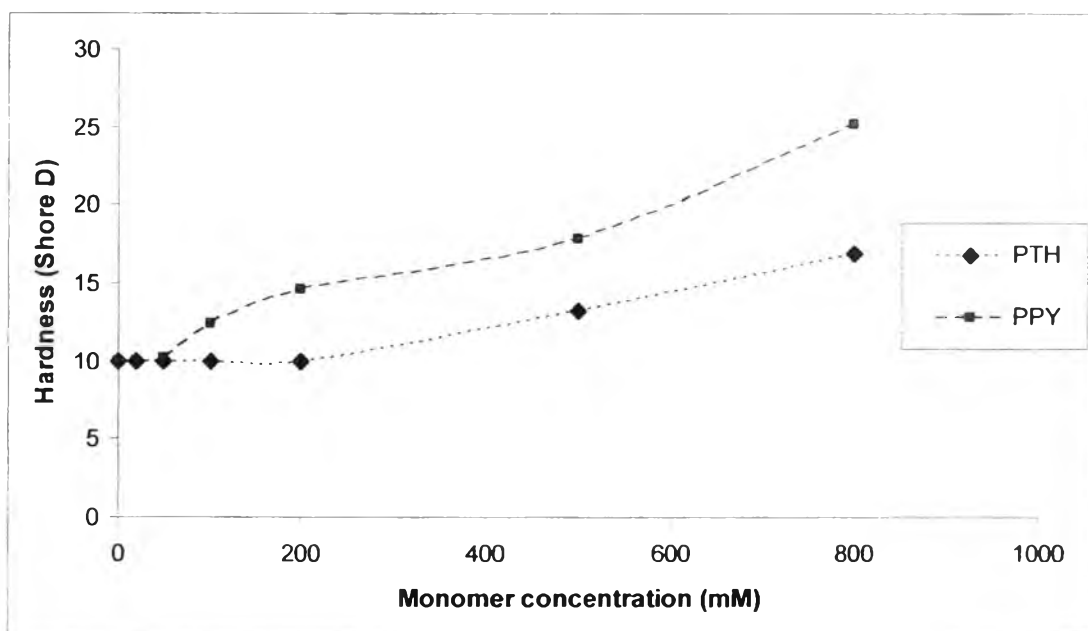


Figure 6.21 Variation of hardness shoreD with conductive polymer for admicellar rubber

6.7 Conductivity properties measurement

The conductivity of admicellar rubber were tested by using Keithley 8009 Resistivity Test Fixture and Keithley 6517A Electrometer/ High Resistance Meter. The dc voltage from 1 to 15 volts was applied to the specimen, placed in the Keithley 8009 Test Fixture. After the current was read, the surface and the volume resistivity were determined. The conductivity of Admicelled rubber is presented more details in chapter 4 and 5.

Figure 6.22 and Table 6.8 show the effects of monomer (pyrrole and thiophene) contents on the electrical conductivity admicelled rubber. The electrical conductivity as high as $3.19 \times 10^{-4} \text{ S/cm}$ (800mM PPy) and $8.26 \times 10^{-6} \text{ S/cm}$ (800mM PTh) could be obtained by using electrochemical polymerization technique. They promoted an increase of ninth to eleventh orders of magnitude on the conductivity of NR, ranging from 10^{-15} to 10^{-6} S/cm . Therefore, as monomer content increased the conductivity was also increased because the coating of monomer (PPy, PTh) was more perfectly at higher concentration as supported by TEM and SEM micrographs and the resulting of TGA.

The increasing of PPy has greater conductivity than PTh can caused by many factors such as the influence of band gap, dopant, oxidation level, doping percentage, synthesis method and temperature (G.Wallace,2004)⁴⁵. Moreover, the conductivity of admicelled increased with increasing strength of the electron-withdrawing force of the substitute. Futhermore, the potential incorporation of a surfactant into conducting polymer is likely to improve the electrical, theromoxidative and hydrolytic stability due to the introduction of bulky hydrophobic component. To improved properties of PPy and PTh can caused by incorporation of anionic surfactant into the PPy/PTh as the dopant. The electron-withdrawing substitute of the phenol derivative seems to prevent undesirable side reactions and to improve the regularity of the PPy|PTh backbone (M.Omastova,2003)⁹⁰. From the conductivity PPy-NR and PTh-NR in SDS, compared the doping level and properties of conductive polymers in several surfactant in the Table 6.9.

In addition, the higher number of polymer chains was obtained when content is high to abstract electron from pyrrole and enhance free radical polymerization, resulting in higher conductivity and higher in their density (Figure6.23).

Table 6.8 conductivity of natural rubber sheet prepared at 25°C, 9V various to monomer content.

Sample (mM)	σ_v PPy S.cm ⁻¹	σ_s PPy S	Thickness (cm)	σ_v PTh S.cm ⁻¹	σ_s PTh S	Thickness (cm)
Rubber	7.18E-15	2.46E-15	0.3336	7.18E-15	2.46E-15	0.334
20	1.49E-10	2.30E-10	0.3140	2.52E-12	1.85E-12	0.387
50	5.99E-08	3.94E-09	0.2940	2.57E-10	1.41E-11	0.394
100	3.10E-06	1.63E-06	0.2925	2.86E-08	1.31E-08	0.395
200	3.79E-06	1.03E-06	0.2821	8.94E-08	1.40E-08	0.391
500	3.11E-05	3.07E-05	0.2823	5.35E-07	2.77E-07	0.490
800	3.19E-04	3.83E-04	0.3095	8.26E-06	2.61E-06	0.413

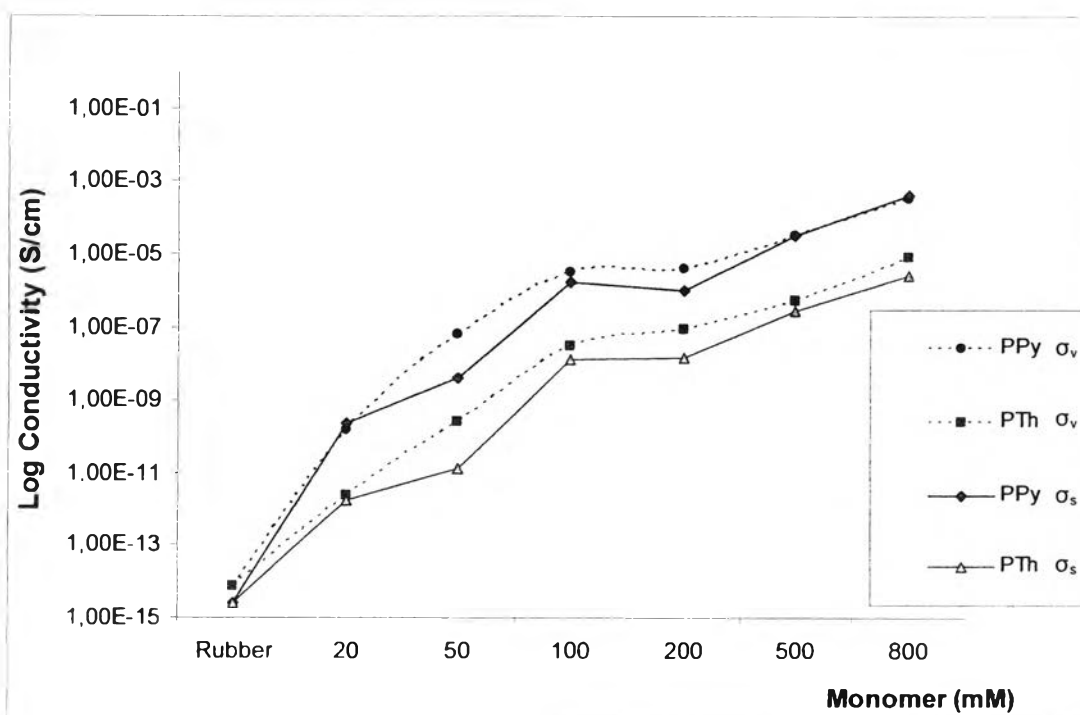


Figure 6.22 Electrical conductivity as a function of monomer content in composites with natural rubber latex (Apply dc 0.1-20 volt).

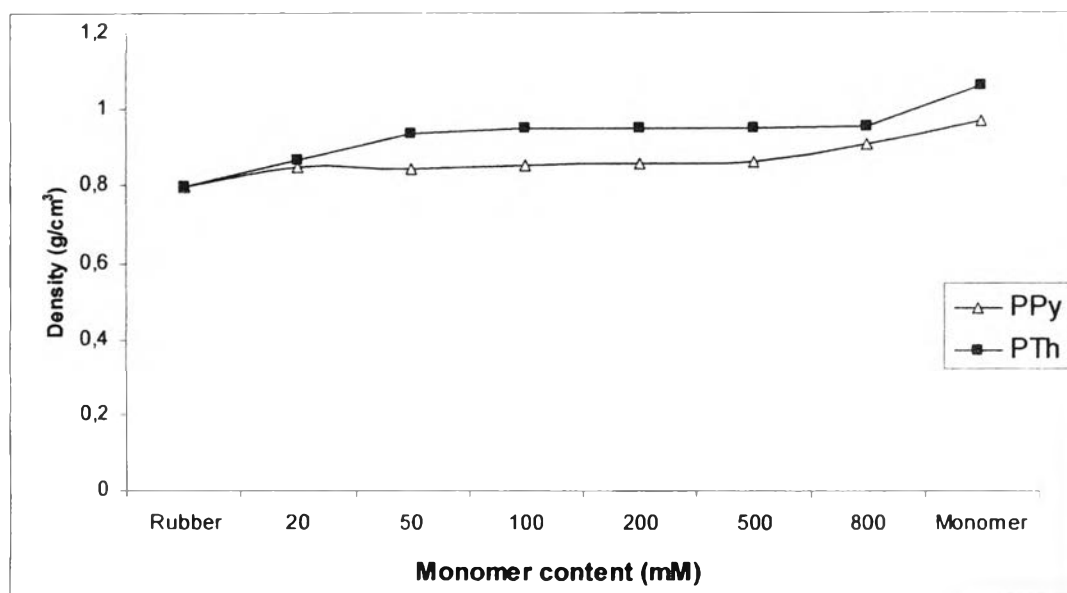


Figure 6.23 Variation of density with monomer concentration for admicellar rubber

Table 6.9 elemental composition (wt.%), conductivity of polythiophene and polypyrrole prepared in the presence of surfactant

Polymer	Type	C	H	N	S	Conductivity (S/cm)	Contents of monomer	ref
NR	-	-	-	-	-	7.18×10^{-15}	-	*
PTh ^{ref}	-	53.51	2.22	-	36.99	5	5.4 mM	[133]
PTh-DBSNa	Anionic	48.81	2.58	-	29.40	5.1×10^{-5}	~24 mM	[92]
PTh-SDS	Anionic	47.57	2.40	-	29.21	4.5×10^{-5}	~24 mM	[92]
PTh-TTAB	Cationic	51.76	2.15	-	36.11	8.4×10^{-5}	~24 mM	[92]
PTh-Tween20	Non-ionic	47.03	3.46	-	23.10	4.6×10^{-5}	~24 mM	[92]
PTh-SO ₄	-	51.13	2.13	-	34.13	8.66×10^{-3}	~24 mM	[92]
PTh-SDS-NR	-					1.85×10^{-12} 2.61×10^{-6}	20mM 800mM	*
PPy ^{ref[133]}	-	55.82	3.57	16.15	-	20	5.4 mM	[133]
PPy-DBSNa	Anionic	64.43	7.39	5.96	5.68	8.3	50 mM	[90]
PPy-SDS	Anionic	62.29	7.15	7.48	5.49	5.5	50 mM	[90]
PPy-TTAB	Cationic	52.42	4.07	13.77	4.85	0.76	50 mM	[90]
PPy-Tween20	Non-ionic	56.45	4.26	12.61	4.75	0.034	50 mM	[90]
PPy-SO ₄	-	50.61	3.32	14.54	4.97	0.049	50 mM	[90]
PPy-SDS-NR	-					2.3×10^{-10} 3.83×10^{-4}	20mM 800mM	*

* = It had done in this experiment.

6.8 Conclusions

The success of the admicellar polymerization of polypyrrole and polythiophene coated latex particles were compared in this chapter. This technique is efficient, % yield in the range between ~83-91%. The %yield and reaction times of admicelled rubber were decreased along with the PPy and PTh (monomer) concentration increased. At lower amount of pyrrole, it takes longer reaction times (35-30 hrs) to synthesis than PTh at beginning. However, the reaction of Pyrrole monomer seems to be faster at higher conversion than Thiophene. The reason can cause by the change in band structure of PPy and PTh subsequent to doping. The TEM and SEM micrographs revealed the even coating of monomer over latex particles and they showed core-shell structure of monomer and NR. It also confirmed the faster polymerization at higher amounts of monomer. SEM result can confirm the presence of polypyrrole in natural rubber. PPy are presented as a grained texture, coaser cauliflower. However, PTh demonstrated spong-like, porous structure and globular structure whereas NR exhibited the smooth surface without any coating. As the result of TGA, the admicelled rubbers began to lose weight at higher temperature compare to that of NR and they also showed the shift of major decomposition of pure PPy and pure PTh to higher temperature. The DTG curves also demonstrated the increase of char yields of the admicelled rubbers. The higher amount of PPy and PTh, can consequently slower the samples degraded temperature from 373.6°C (NR) to 374.4°C (800mM PPy) and 378.7°C (800mM PTh). Furthermore, coating with PTh (20-800mM) can enhance the peak temperature of admicelled rubber, a little more than PPy. However, the end temperature, PTh (20-800mM) has a little lower than PPy. Moreover, the residual content of PPy is significantly higher than PTh. These demonstrate that char yields of admicelled rubber increased with related to content of monomers added. The mechanical properties from tensile testing showed the increased of tensile strength and young modulus of the admicelled rubbers. This indicated the higher stiffness of the admicelled rubbers compared to natural rubber. Since the PPy and PTh behaved like a hard and brittle material, the stiffness of the materials increased as PPy or PTh content increased.

The effect of conductivity measurement revealed that the addition of polypyrrole at the same condition, 9V, 25°C, pH ~3, which allowed more adsorption and adsolubilization leading to homogeneous coating of monomer(PPy,PTh) over rubber surface. However, too much voltage is not good to stabilize leading to the contamination in admicellar rubber due to corrosion copper. The electrical conductivity as high as 3.19×10^{-4} S/cm(800mM PPy) and 8.26×10^{-6} S/cm(800mM PTh) could be obtained. They promoted an increase of ninth to eleventh orders of magnitude on the conductivity of NR, ranging from 10^{-15} to 10^{-6} S/cm. The electrical conductivity as high as 3.19×10^{-4} S/cm(800mM PPy) and 8.26×10^{-6} S/cm(800mM PTh) could be obtained by using electrochemical polymerization technique. They promoted an increase of ninth to eleventh orders of magnitude on the conductivity of NR, ranging from 10^{-15} to 10^{-6} S/cm. Therefore, as monomer(PPy,PTh) content increased the conductivity was also increased because the coating of monomer was more perfectly at higher concentration as supported by TEM and SEM micrographs and the resulting of TGA. The higher number of polymer chains was obtained when content is high to abstract electron from pyrrole and enhance free radical polymerization, resulting in higher conductivity and higher in their density.

6.9 Acknowledgements

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