

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE COATED LATEX PARTICLES BY ADMICELLAR POLYMERIZATION

4.1 Abstract

This work tried to overcome the limitations of Natural Rubber (NR) due to poor conductivity by coating thin-film of polypyrrole over rubber latex particles using admicellar polymerization. Anionic surfactant; sodium dodecylsulfate (SDS) is used to form bilayer as a reaction template. NaCl is added to the system to decrease electrostatic repulsion between headgroups of surfactants. The polymerization of pyrrole monomers was initiated by $\text{Fe}_2(\text{SO}_4)_3$ at low temperature (0°C). The success of synthesis was confirmed by FTIR. The TGA curves revealed the shift to higher decomposition temperature of pure PPy indicating the improvement in thermal property of the admicelled rubbers. The mechanical properties of the admicelled rubbers were also developed to be stiffer than natural rubber. The conductivity of the admicelled rubbers are about 10^{-6} S/cm which are much higher than that of natural rubber by several orders (the conductivity of pure natural rubber is about 10^{-13} S/cm).

4.2 Introduction

Polypyrrole (PPy) is one of the most studied conducting polymers because of its good electrical conductivity, high environmental stability and relative ease of synthesis (Omastova M. *et al.*, 2003)¹. However, its processibility is poor and its flexibility is limited. Natural rubber (NR) is an unsaturated elastomer with some good properties, such as high strength, outstanding resilience, and high elongation at break but its conductivity is low. One method to overcome the limitations of PPy and NR is the thin-film technique referred to admicellar polymerization (Wu J. *et al.*, 1987)². Admicellar polymerization is a fine-coating technique that leads to the formation of ultrathin polymer films on charged surfaces by using a surfactant bilayer as a reaction template (Genetti W.B. *et al.*, 1998)³.

The objectives of this research are to improve mechanical property and thermal property of natural rubber and to investigate the effect of the mole ratio between pyrrole and initiator and weight ratio between pyrrole and natural rubber on the conductivity of admicelled rubber. After admicellar polymerization, the admicelled rubber films were characterized to confirm the success of the admicellar polymerization and the improvement on conductivity.

4.3 Experimental

A. Materials

Natural rubber latex was provided by Rubber Research Institute, ~60% DRC. Pyrrole from Aldrich was stored in refrigerator at 4°C before using in polymerization. Dodecyl sulfate sodium salt from Aldrich Chemical Company, 99.9% sodium chloride from Carlo Erba Reagents and iron (III) sulfate hydrate from Fluka were used without further purification.

B. Purification of the Natural Rubber Latex

60% dried rubber content rubber latex of 2 g was mixed with distilled water 50 ml and centrifuged at 20°C, 10000 rpm for 20 minutes 2 times to removed dissolved impurities. After washing, the particles were resuspended in water pH 3.0.

C. Particle Size Measurement

The particle size of natural rubber was determined by a particle size analyzer, Masterizer X version 2.15 (Malvern Instruments Ltd.). The lens used in this experiment was 45 mm for particle size 0.1-80 μm and active beam length was set at 24 mm. The aqueous solution of latex particles was placed in a sample cell across a laser beam. This machine analyzed the average particle size and standard size distribution from the laser beam depending on the beam length parameter. Consequently, the specific surface area was calculated from the particle diameter with the assumption of constant volume of spherical particle.

A droplet of surfactant was added in a stirring water chamber in order to help the distribution of natural rubber in water. After that, 0.03 vol% of natural rubber aqueous solution was suspended in a stirring water chamber.

D. Electrophoretic Mobility Measurement

The change in the surface charge of latex particles with pH is important to determine the surfactant adsorption. Electrophoretic mobility was used to determine the surface charge of the latex particles at various solution pH (3.0-6.5). The NR colloidal dispersion was diluted in 250 ml distilled water. The pH in the solution was adjusted by 0.1M NaOH or HCl, and was left to equilibrate for 1 day. The electrophoretic mobility of the latex particles was observed at room temperature with a Zeta Meter 3.0.

E. Polymerization of Pyrrole onto Latex Particles

The latex 25 g was separated and resuspended in water pH 3.0 50 ml which is the pH below the point of zero. Then the rubber latex was mixed with surfactant solution 3.2–16 mM, 400 ml stirred over night to let the surfactant molecules form bilayer at the surface of rubber particles. Pyrrole solution 20–100 mM (0.69–3.36 ml) was added and left for 2 hours. Then the aqueous solution of initiator 25 ml was added to initiate the polymerization and to obtain 500 ml of total volume. In this step, the temperature of the system was reduced to 5°C by adding ice. After the polymerization step for 2 hours, the dark emulsion was filtered through the bushner funnel and washed with water 1000 ml followed by methanol 150 ml. Then it was dried in vacuum oven at 70°C for 12 hours to obtain a black sheet with a constant weight. The synthesis of samples with 0.1-0.3M NaCl addition was repeated all steps and salt was dissolved with surfactant solution.

F. Morphology Study

The emulsion of the admicelled rubbers was casted in thin films on glass slides and then dried in vacuum oven for 12 hours at 70°C. The samples were cut into small pieces and adhered on brass stubs by using adhesive tape. The samples on stubs were painted with thin layer of silver. The morphologies of the admicelled rubbers were observe by a scanning electron microscope (SEM, JOEL model JSM-

5200). SEM digitized photographs were obtained with a magnification range between 1,000–5,000 times using an acceleration voltage of 15 kV.

G. Thermal Properties Measurement

Thermal stability, moisture contents, and degradation process of the admicelled rubbers were studied by a thermalgravimetric analyzer (DuPont, model TGA 2950). The samples were weighed at 5–12 mg and put them in a platinum pan. The instrument was set to operate at temperatures from 30 to 600°C at a heating rate 10°C/min under nitrogen atmosphere 100 ml/min.

H. FT-IR Observation

The admicelled rubber films with thickness 0.3–0.8 mm obtained by compression at 160°C under pressure 25 tons for 15 min were determined for their absorptions using the horizontal attenuated total reflection accessories for the FTIR (Nexus 670, HATR module) to measure the spectra of materials. The spectra were recorded in the absorbance mode in a wavenumber range of 400–4000 cm^{-1} . The sample spectra were recorded by using air as a background.

The KBr technique was used to prepare the powder sample of pure PPy for recording spectrum. Specimen of pure PPy was prepared by grinding the powdered PPy with the KBr powder. The mixture was molded in special dies under the pressure 10 tons. The sample spectrum was recorded by using KBr as a background.

I. Mechanical Properties Measurement

The admicelled rubber films from compression with dimension 20x100 mm (thickness 0.3–0.8 mm) were tested following ASTM D882-91 with crosshead speed of 50 mm/min, guage length of 50 mm, and load cell 500 N under room temperature using Lloyd Universal Testing Machine. The test was repeated 3 times.

J. Conductivity Measurement

The admicelled rubber films from compression (thickness 0.3–0.8 mm) were cut into the round edge shape with six inches in diameter and tested for their surface and volume resistivity by using Keithley 8009 Resistivity Test Fixture and Keithley 6517A Electrometer/High Resistance Meter. The dc voltage from 0.1 to 15

volt was applied to the specimen placed in the Keithley 8009 test fixture. Then, the current was read and the surface and volume resistivity were determined.

The resistance, R , of the films was calculated using Eq. (1), the volume resistivity, surface resistivity and the conductivity were found using Eq. (2), (3) and (4), respectively:

$$R = \frac{V}{I} \quad (1)$$

$$\rho_v = \frac{22.9V}{tI} \quad (2)$$

$$\rho_s = \frac{53.4V}{I} \quad (3)$$

$$\sigma = \frac{1}{\rho_v} \quad (4)$$

where R is the resistance (watts), V is the voltage (volts), I is the current (amperes), ρ_v is the volume resistivity (ohm centimeters), ρ_s is the surface resistivity (ohm), t is the film thickness (centimeters) and σ is the conductivity (siemens per centimeter).

The samples were stretched and measured conductivity by using two-point probe under N_2 atmosphere. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The conductivity of the films was calculated using Eq. (5) and (6):

$$R_s = CF \times \frac{V}{I} \quad (5)$$

$$\sigma = \frac{1}{R_s \times \pi \times r} \quad (6)$$

where R_s is the sheet resistivity (ohms), CF is the correction factor which is 2.70 and r is the probe's radius 0.192 cm.

4.4 Results and Discussion

A. Particle Size Distribution of NR Latex

The particle size distribution of NR latex before admicellar polymerization showed the mean diameter 1.1 μm and the mean specific surface area 6.59 m^2 / g . These results indicated the polydispersity of NR latex particles with narrow size distribution (see Fig C.1).

B. Electrophoretic Mobility

The electrophoretic mobility of the colloidal dispersion of the NR latex before admicellar polymerization at various pH of the solution revealed the point of zero charge (PZC) of these NR latex particles at pH 3.8 at room temperature (see T D1 and Fig D.1).

C. Scanning Electron Microscopy

The morphologies of the admicelled rubbers were investigated by scanning electron microscopy. The SEM micrographs of the admicelled rubbers with different PPy concentration reveal round shape of rubber particles with evenly coating of PPy over the particles. The sample with 20 mM PPy shows latex particles coated by PPy layer as a core-shell structure where NR particles are core and PPy is the shell and becomes a continuous or matrix. The samples with 50 and 100 mM of PPy clearly show coating of PPy on each latex particle individually. They also show no phase separation between PPy and NR. This suggests a high level of dispersability of rubber particles and PPy. The average particle diameter was estimated to be between 0.8-1.0 μm , or approximately the same as the value determined by particle size analyzer. This also reveals the very fine nanometer thickness of the PPy shell.

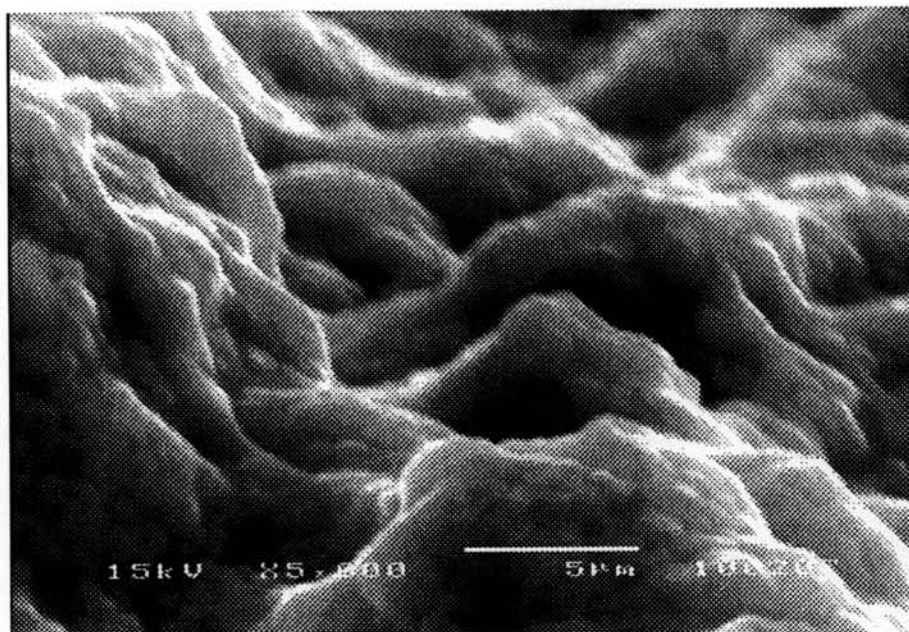


Figure 4.1 Scanning electron micrograph of the admicelled rubber (B20,1-1) magnification 5000/15 kV.

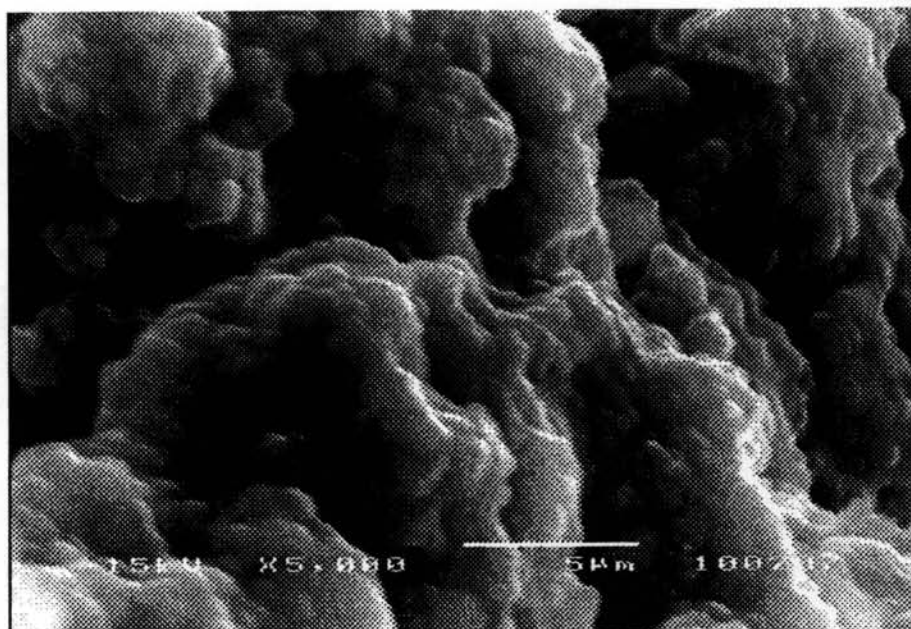


Figure 4.2 Scanning electron micrograph of the admicelled rubber (B50,1-1) magnification 5000/15 kV.

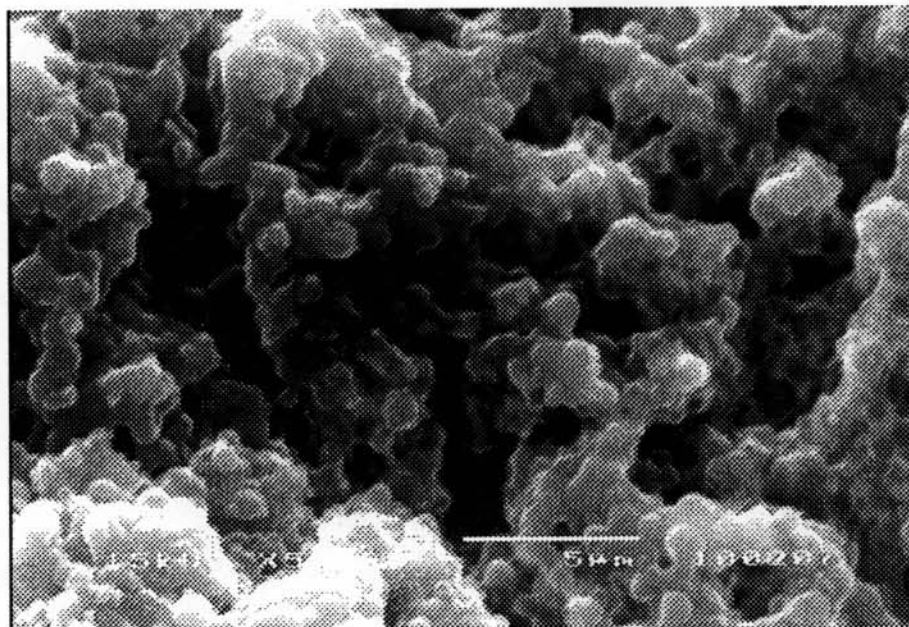


Figure 4.3 Scanning electron micrograph of the admicelled rubber (B100,1-1) magnification 5000/15 kV.

D. Thermogravimetric Analysis

Thermogravimetric analysis results are shown in Figure 4.7 – Figure 4.9. NR shows the major decomposition at 373°C and PPy starts to degrade from temperature 205°C then shows the main mass loss at 260°C. The significant weight loss of the admicelled rubbers start at around 372 to 376°C. They lose about 90% of their weight between 345 and 450°C. This suggests that the admicelled rubbers begin to lose weight at higher temperature compare to that of NR and they also show the shift of major decomposition of pure PPy to higher temperature. (T_d of rubber = 373°C, T_d of PPy = 260°C, T_d of the admicelled rubbers = 372 to 376°C) Compare with result of Shen Y. and Wan M. (1998)⁴, the decomposition temperature of PPy is at 217°C, this indicates better thermostability of admicelled rubbers caused by admicellar polymerization. The DTG curves of the admicelled rubbers follow the shape of the DTG curve of pure rubber during heating from 30 to 600°C. The reason is that the main composition is NR (%wt. of PPy added is about 3-12%, see T A2), indicating that rubber is a dominant factor affecting the thermal stability of the admicelled

rubbers. The curves also demonstrate that char yields of the admicelled rubbers increased from 1% of pure rubber to 3-16% related to content of PPy added. The residual contents of samples with PPy 20 mM (2.61 %wt.) are about 2.28-9.31% (estimate PPy residue = 2.80%), PPy 50 mM (6.29%wt.) are 2.75-16.22% (estimate PPy residue = 5.21%), and PPy 100 mM (11.38%wt.) are 4.39-11.39% (estimate PPy residue = 8.54%). These indicate that an increase of PPy content enhanced the residue remaining (residual content of pure PPy is 66.58%). Moreover, the onset temperatures of admicelled rubbers are higher than that of pure rubber. The decomposition temperatures were also ended at higher temperature (455°C) than that of pure rubber. The higher PPy content, the slower the samples start to degrade. This fact also supports the above-mentioned results that coating PPy by admicellar polymerization improves thermostability of natural rubber.

Table 4.1 The degradation temperature of the admicelled rubbers without salt

Sample	On Set Temp. (°C)	End point Temp. (°C)	Peak temp. (°C)	Residual Content (%)
Rubber	345.4	421.5	373.0	1.09
PPy	204.9	579.3	260.3	66.58
A20,1-1	345.3	454.0	374.1	2.89
A20,2-1	348.9	450.7	373.8	4.55
A20,3-1	341.1	455.4	372.7	2.28
A50,1-1	350.4	450.5	373.0	9.93
A50,2-1	346.2	450.9	372.9	5.77
A50,3-1	347.5	446.9	375.1	5.91
A100,1-1	352.3	448.5	376.2	10.48
A100,2-1	350.5	450.1	372.1	10.21
A100,3-1	350.0	452.7	373.3	4.39

Note Ax,y-z

A,B,C = [NaCl] 0.0, 0.1, 0.3 M, x = [PPy] 20, 50, 100 mM, y-z = [Mo]/[In]

Table 4.2 The degradation temperature of the admicelled rubbers with 0.1M NaCl

Sample	On Set Temp. (°C)	End point Temp. (°C)	Peak temp. (°C)	Residual Content (%)
Rubber	345.4	421.5	373.0	1.09
PPy	204.9	579.3	260.3	66.58
B20,1-1	336.5	450.0	373.2	2.91
B20,2-1	345.4	452.8	374.8	2.32
B20,3-1	342.9	452.8	374.9	3.56
B50,1-1	346.7	440.3	375.9	6.92
B50,2-1	345.8	441.2	376.5	2.75
B50,3-1	345.9	450.0	376.3	3.99
B100,1-1	349.2	444.4	375.2	11.39
B100,2-1	346.0	433.2	375.7	5.85
B100,3-1	337.7	432.7	376.0	5.18

Table 4.3 The degradation temperature of the admicelled rubbers with 0.3M NaCl

Sample	On Set Temp. (°C)	End point Temp. (°C)	Peak temp. (°C)	Residual Content (%)
Rubber	345.4	421.5	373.0	1.09
PPy	204.9	579.3	260.3	66.58
C20,1-1	340.1	444.5	375.8	4.12
C20,2-1	341.9	446.1	374.6	9.31
C20,3-1	342.0	428.4	377.4	3.15
C50,1-1	348.6	440.6	373.7	16.22
C50,2-1	348.5	443.2	376.3	4.14
C50,3-1	346.5	427.7	377.2	7.94
C100,1-1	348.3	426.7	374.4	11.28
C100,2-1	344.0	428.0	373.5	12.48
C100,3-1	339.9	429.6	375.5	7.53

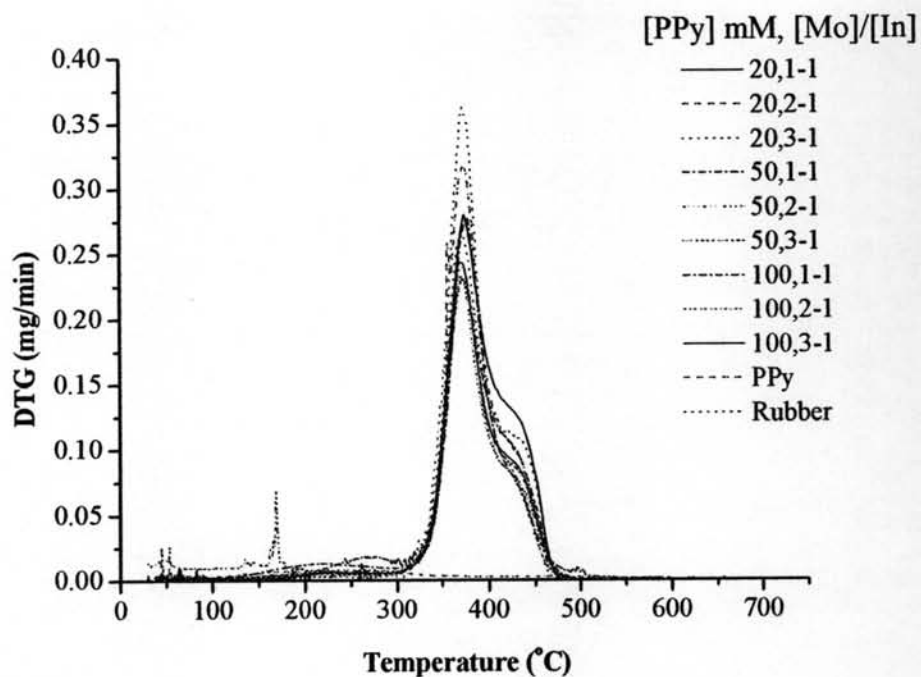


Figure 4.4 DTG thermograms at 10 °C/min of nitrogen atmosphere of the admicelled rubbers without salt.

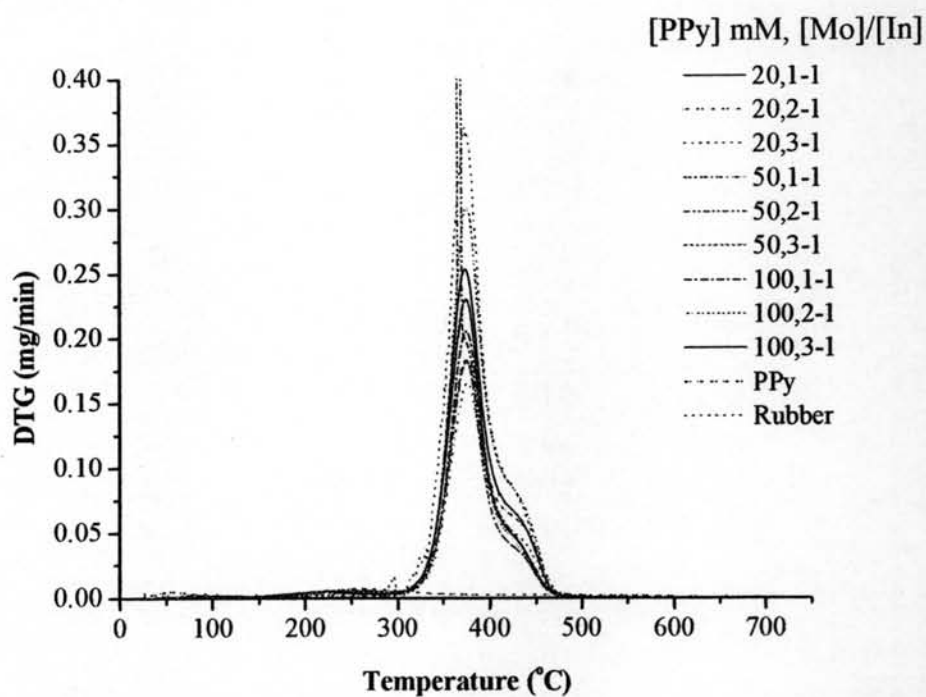


Figure 4.5 DTG thermograms at 10 °C/min of nitrogen atmosphere of the admicelled rubbers with 0.1M NaCl.

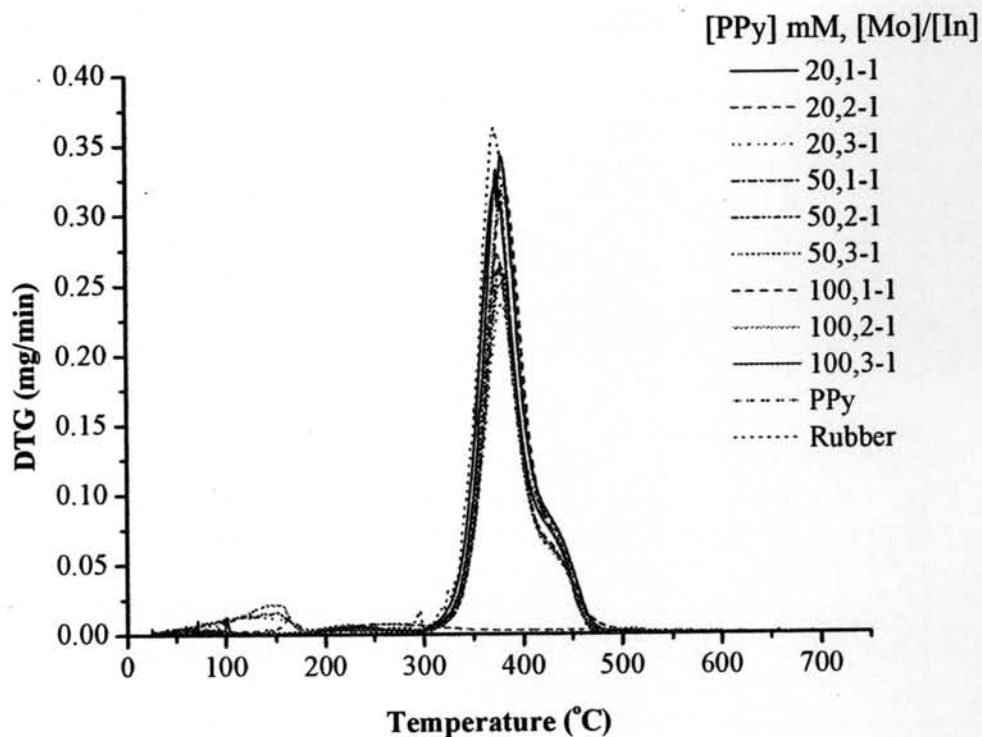


Figure 4.6 DTG thermograms at 10 °C/min of nitrogen atmosphere of the admicelled rubbers with 0.3M NaCl.

E. Fourier-Transform Infrared Spectroscopy of Admicelled NR Latex

The infrared spectra of pure rubber, pure PPy and admicelled rubbers in the region from 4000 to 400 cm^{-1} are shown in Figures 4.11 - 4.14. The obtained spectrum of pure rubber correlates with the IR spectrum reported by Rippel M., *et al.* (2003)⁵. The band at 3035 cm^{-1} corresponds to =C-H stretching. Bands at 2960, 2926 and 2853 cm^{-1} assign to C-H stretching of CH_3 , C-H stretching of CH_2 , and C-H stretching of CH_2 and CH_3 , respectively. The spectrum of polypyrrole is consistent with the results of Liu J. and Wan M. (2001)⁶ and Yan F., *et al.* (1999)⁷. Bands at 1557 and 1476 cm^{-1} correspond to C=C stretching and C-C stretching, respectively. Bands at 1285 and 1193 cm^{-1} belong to =C-H in plane vibration. The band at 1044 cm^{-1} in the spectrum corresponds to N-H in plane deformation vibration and the band of the C-C out of plane ring deformation vibration is situated at 964 cm^{-1} . The bands at 924, 787 cm^{-1} correspond to C-H out of plane ring deformation or C-H rocking. Bands at 684 and 618 cm^{-1} belong to C-C out of plane and N-H out of plane vibra-

tion, respectively. Overlapping of N-H stretching and C-H stretching at 3400 and 3040 cm^{-1} is the proof of the polymerization of polypyrrole (Sahin D., *et al.*, 2002)⁸. The FT-IR spectra of all admicelled rubbers reveal the combined absorption of rubber and PPy. These results confirm the existence of PPy after polymerization in rubber system.

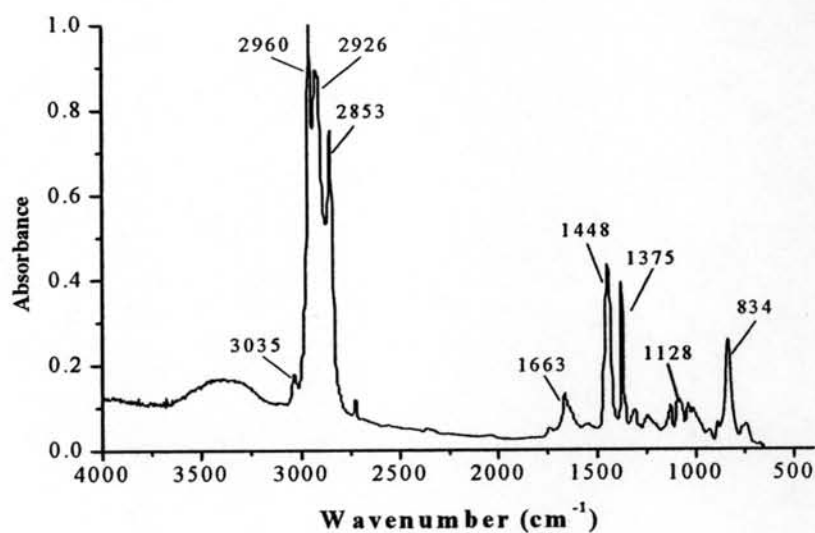


Figure 4.7 FT-IR spectrum of pure NR.

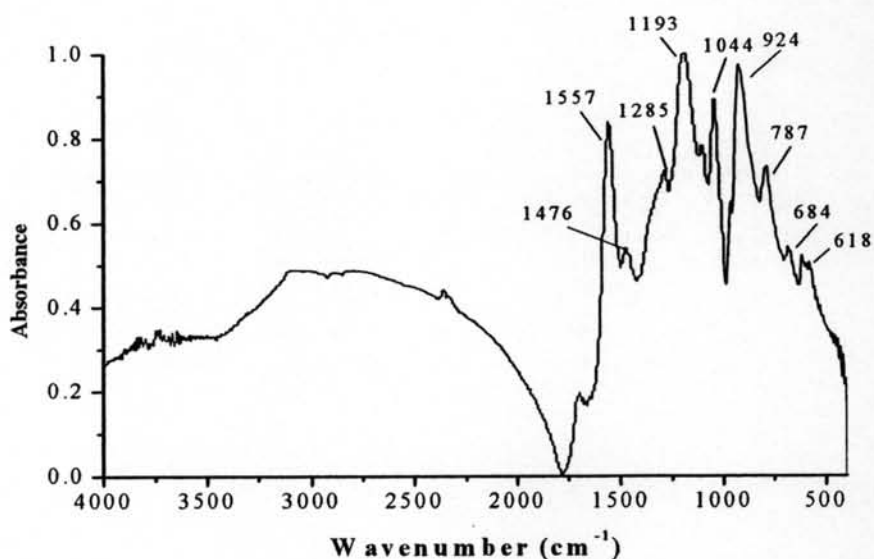


Figure 4.8 FT-IR spectrum of PPy.

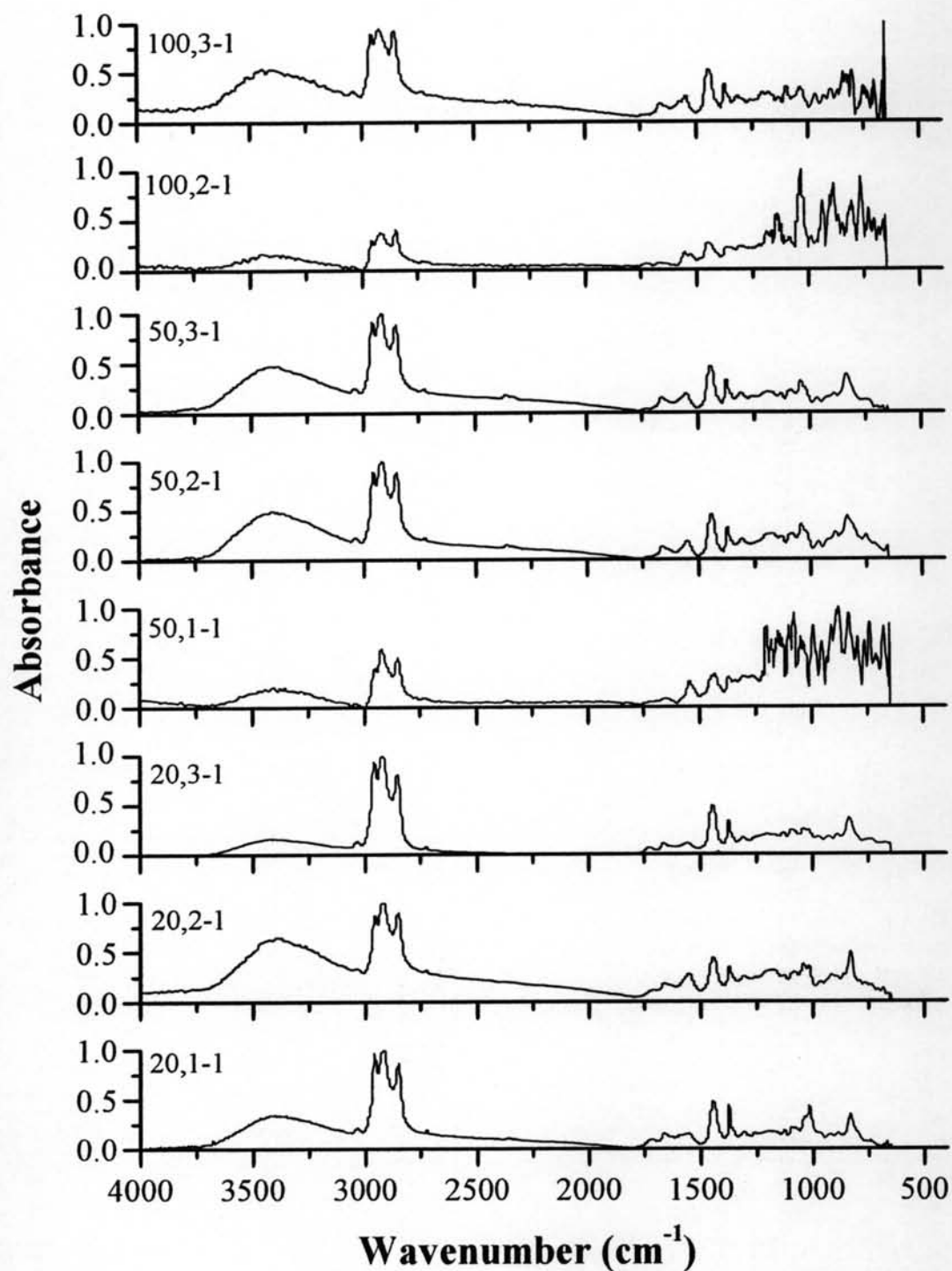


Figure 4.9 FT-IR spectra of the admicelled rubbers without salt (HATR flat plate system with 45 °C ZnSe crystal).

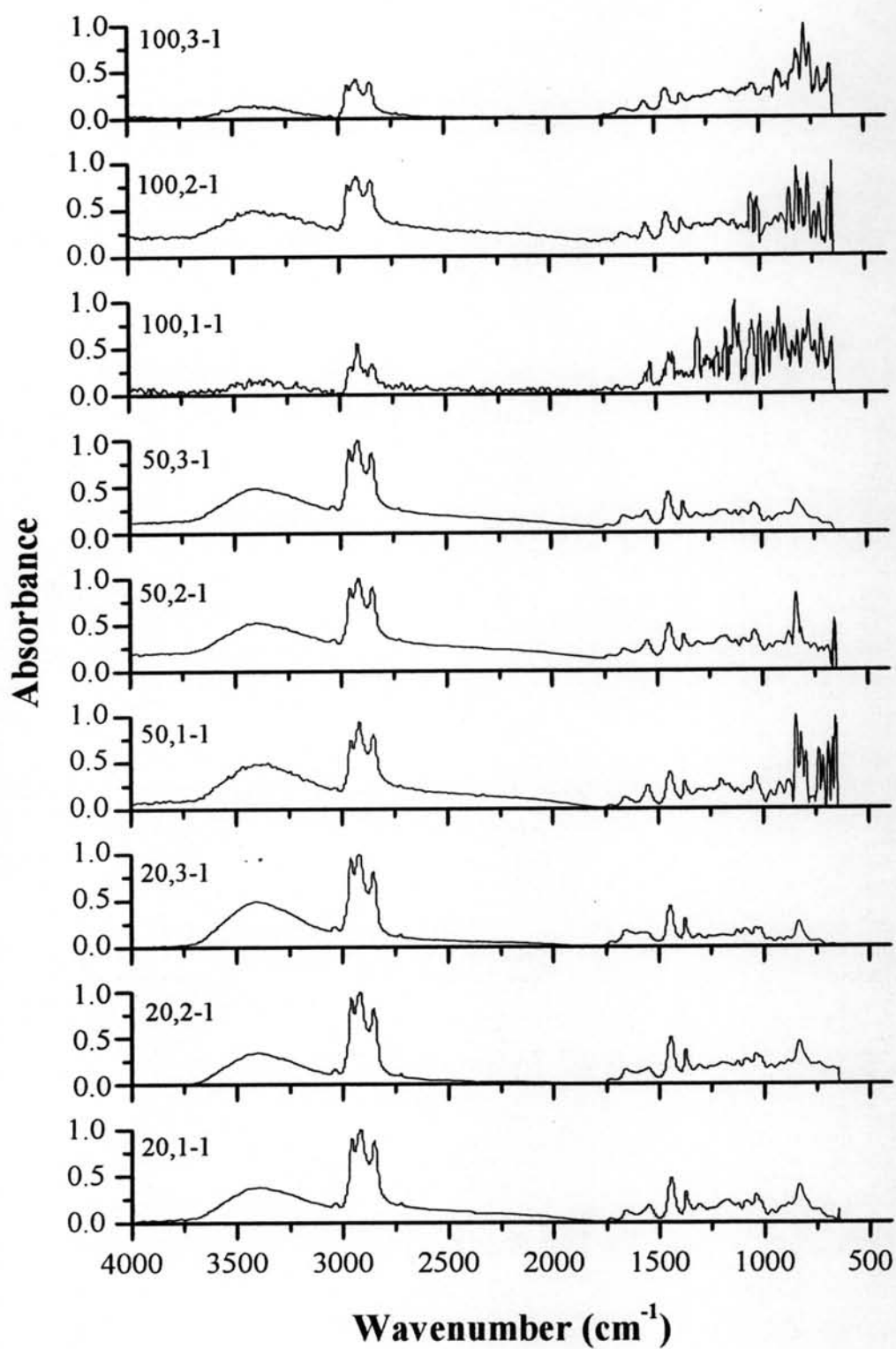


Figure 4.10 FT-IR spectra of the admicelled rubbers with 0.1M NaCl (HATR flat plate system with 45 °C ZnSe crystal).

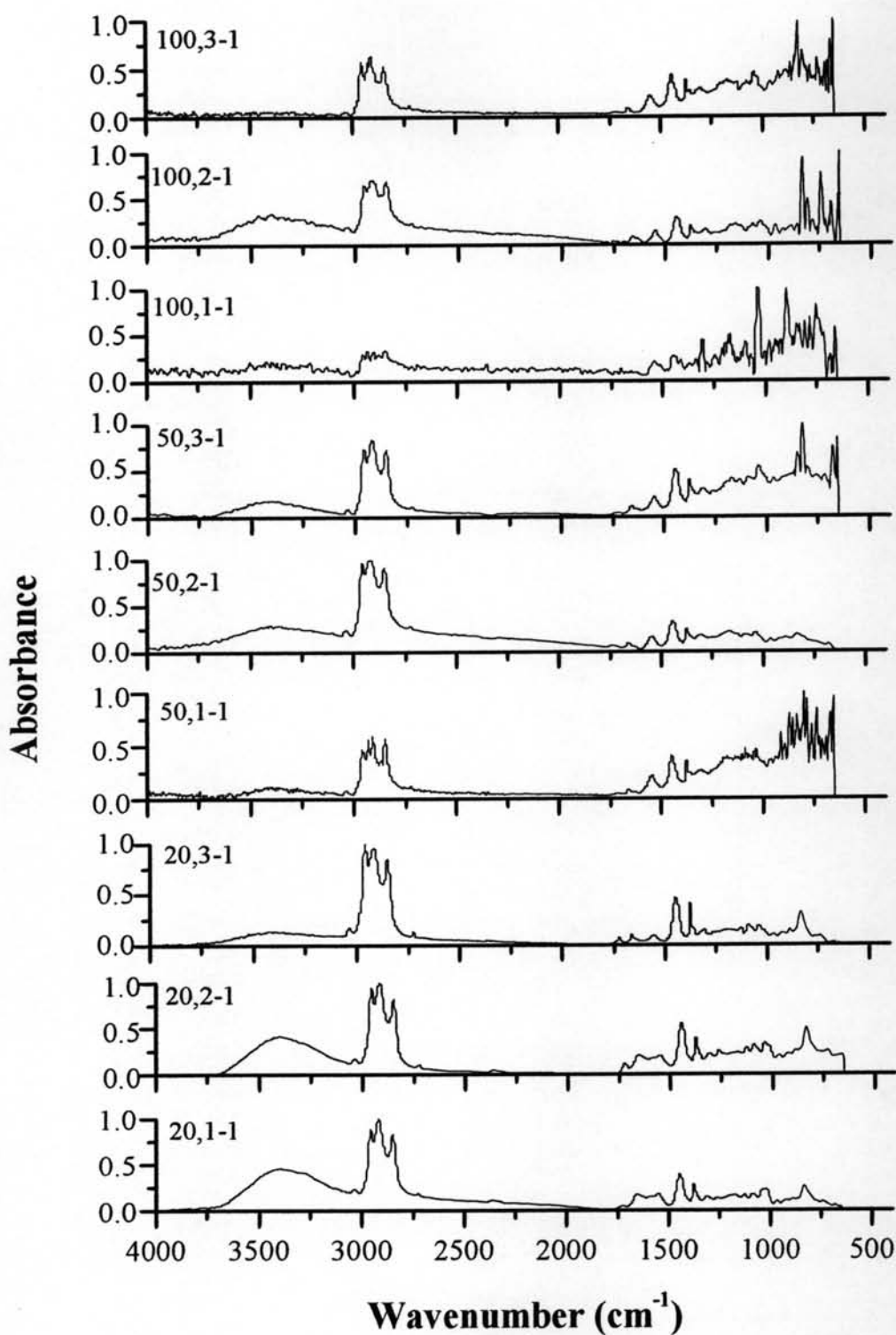


Figure 4.11 FT-IR spectra of the admicelled rubbers with 0.3M NaCl (HATR flat plate system with 45 °C ZnSe crystal).

F. Mechanical Properties Measurement

The admicelled latex films were determined mechanical properties using Lloyd Universal Testing Machine with crosshead speed of 50 mm/min, and guage length of 50 mm under room temperature. The effect of pyrrole concentration on the mechanical properties of admicelled rubber films are shown in Figures 4.12-4.20. Tensile test shows the higher stiffness of the admicelled rubbers compared to natural rubber. The elongation at break of NR is about 450% and the admicelled rubbers are around 50 - 200% which are much lower. The reason is PPy behaves like hard and brittle material. The study of mechanical behavior of PPy by Mano V. *et al.* (1996)⁹ showed elongation at break of pure PPy lower than 5% and breaking out without drawing. Thus, the higher PPy content in the admicelled rubbers, the lower the elongation at break is. Tensile strength of uncrosslinked natural rubber (thickness 1.2 mm) is close to 0 MPa and tensile strength of the admicelled rubbers are around 1 – 9 MPa. The maximum tensile strength of the admicelled rubbers is 9 MPa which is 8 times higher than that of natural rubber. This value is lower compared with the result of Lee J.Y. *et al.* (1995)¹⁰ that tensile strength of PPy doped with DBSA was 17 MPa, (elastic modulus 1945 MPa and elongation at break 0.9%). This is because rubber reduces stiffness of PPy resulting in such a reasonable tensile strength. The Young's modulus of natural rubber is very low, this value is lower than one of uncrosslinked rubber reported by Roy R.V. *et al.* (2006)¹¹ which is about 0.25 MPa. The Young's modulus of the admicelled rubbers are also high compared with pure rubber. This means that the admicelled rubbers are more rigid and their resistance to deformation are higher. The reason is similar to tensile strength which is mentioned above. Since PPy is hard and brittle, the higher PPy content added, the stiffer the materials are.

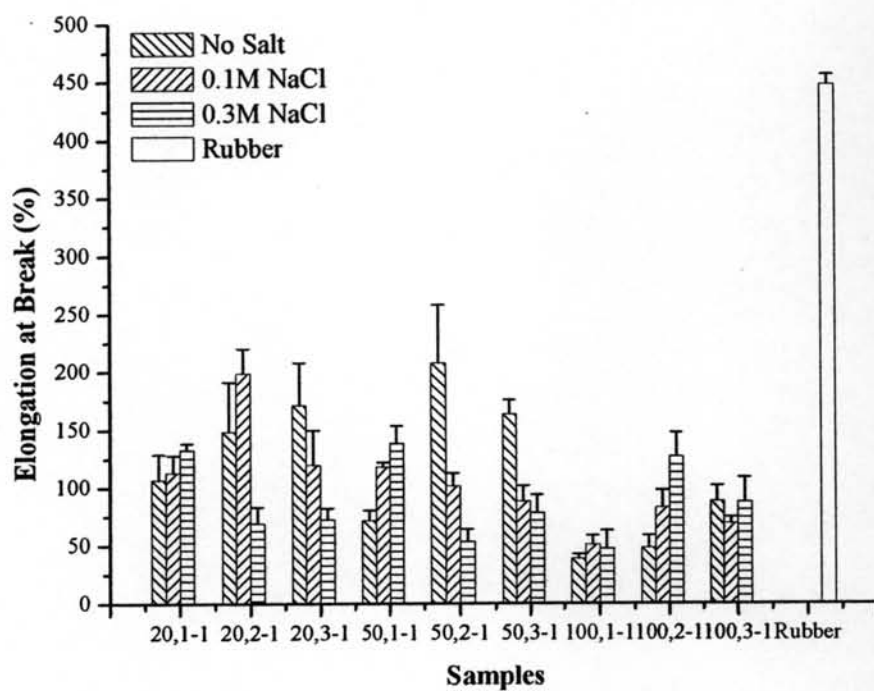


Figure 4.12 Elongation at break of the admicelled rubbers.

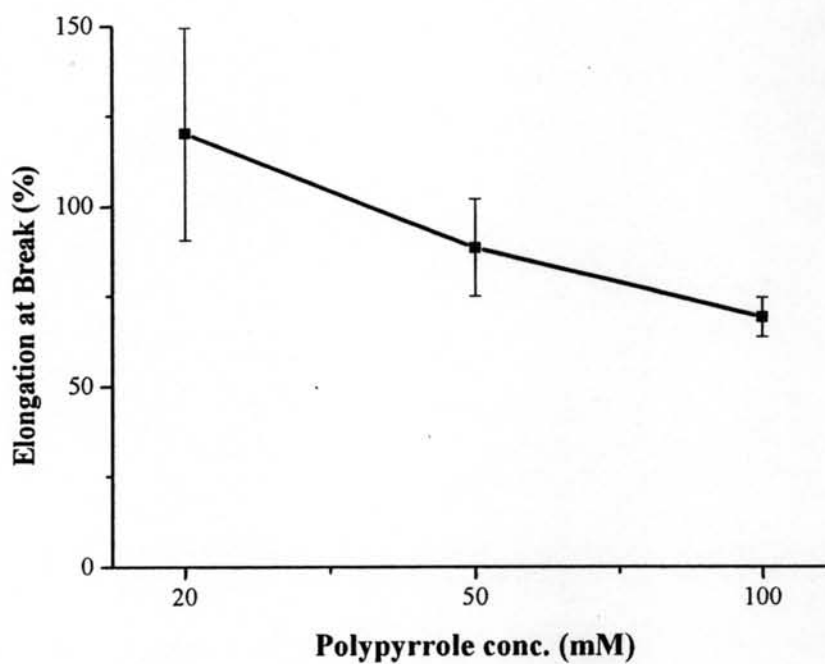


Figure 4.13 Effect of PPy content on the elongation at break of samples with 0.1M NaCl at [Mo]:[In] = 3.

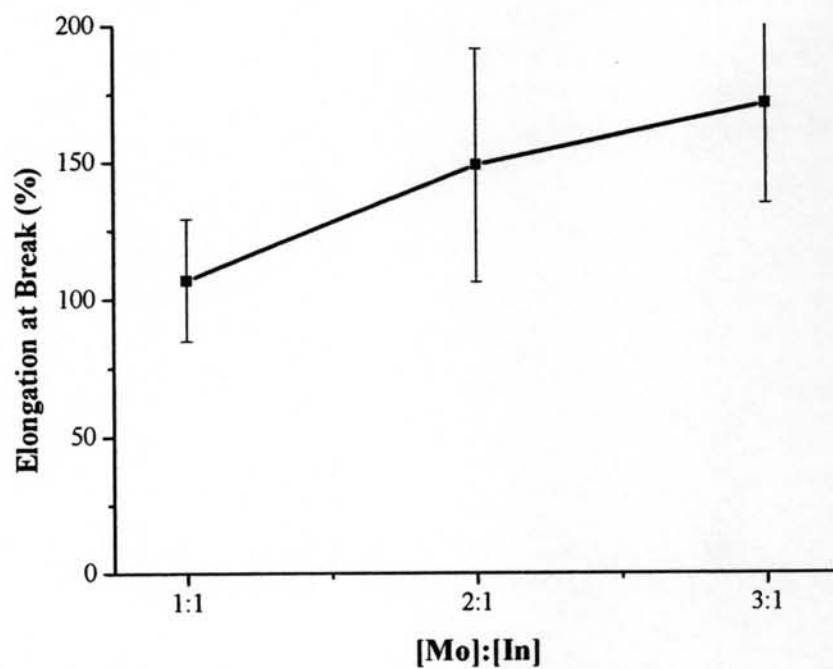


Figure 4.14 Effect of [Mo]:[In] ratio on the elongation at break of samples without salt and [PPy] = 20 mM.

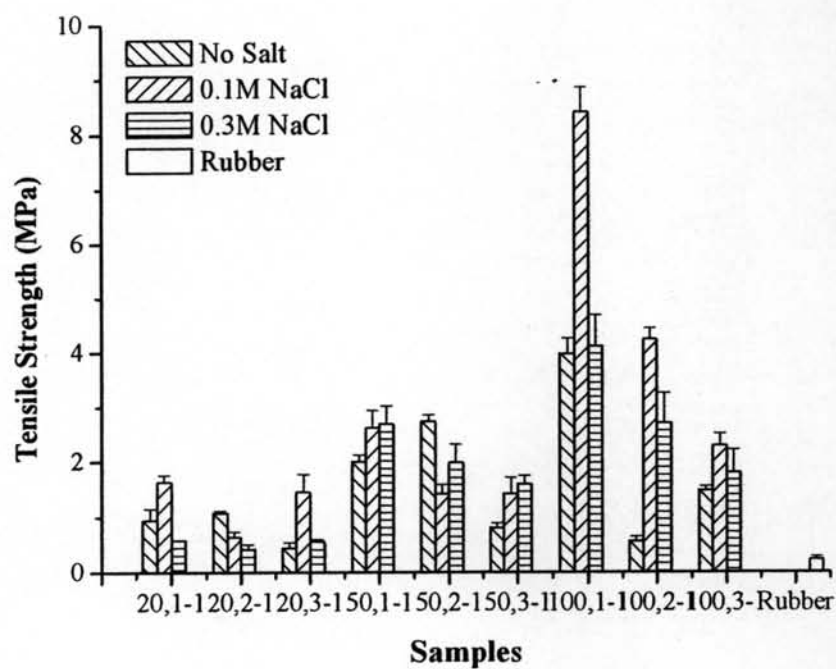


Figure 4.15 Tensile strength of the admicelled rubbers.

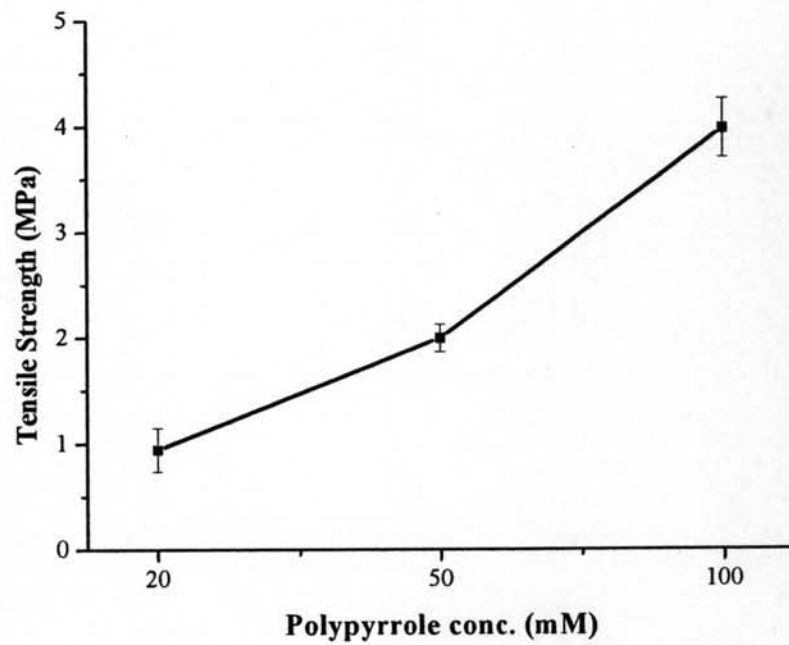


Figure 4.16 Effect of PPy content on the tensile strength of samples without salt at $[\text{Mo}]:[\text{In}] = 1$.

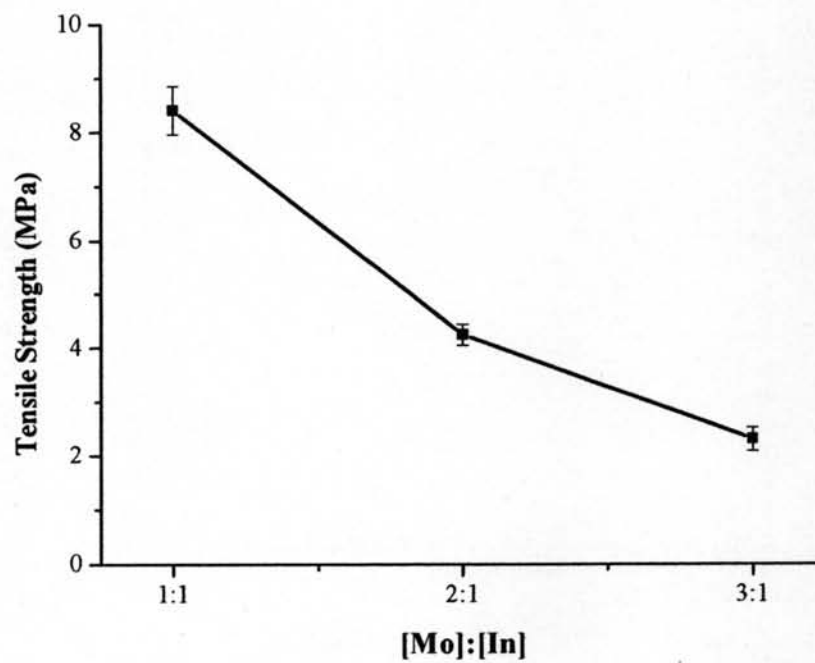


Figure 4.17 Effect of of $[\text{Mo}]:[\text{In}]$ ratio on the tensile strength of samples with 0.1M NaCl and $[\text{PPy}] = 100$ mM.

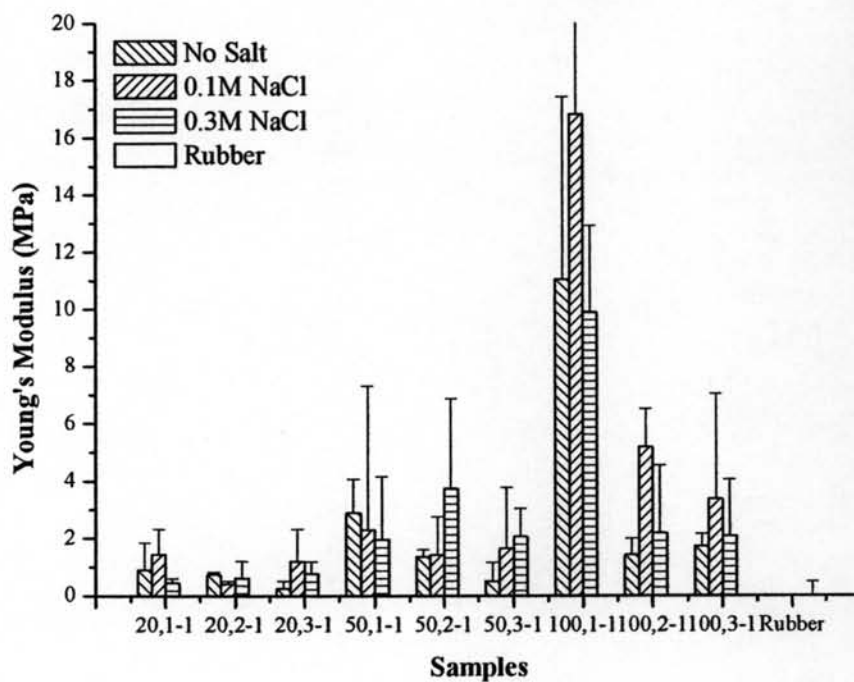


Figure 4.18 Young's modulus of the admicelled rubbers.

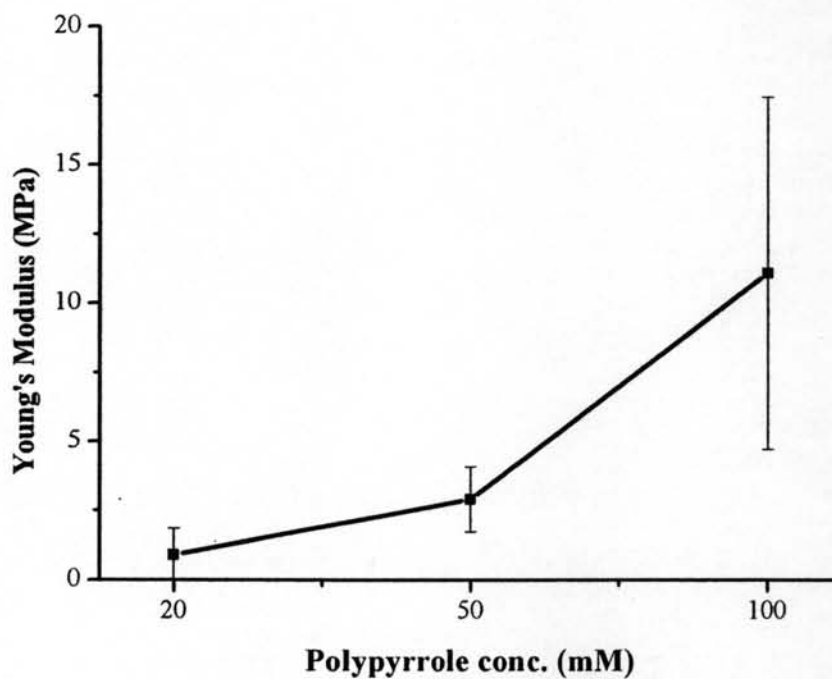


Figure 4.19 Effect of PPy content on the Young's modulus of samples without salt at $[Mo]:[In] = 1$.

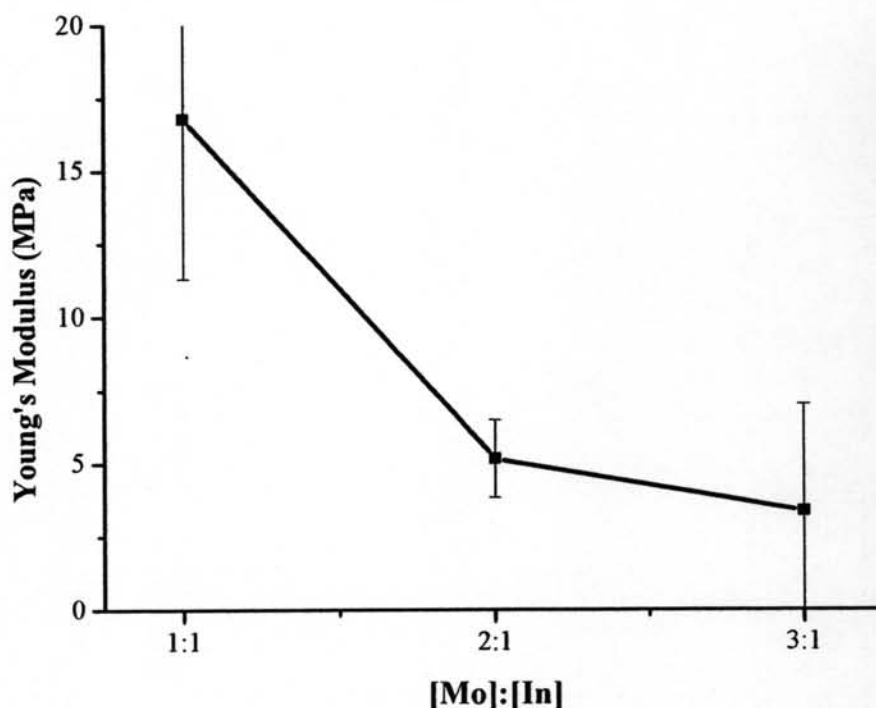


Figure 4.20 Effect of of [Mo]:[In] ratio on the Young's modulus of samples with 0.1M NaCl and [PPy] = 100 mM.

G. Dynamic Mechanical Analysis

Dynamic mechanical test is used to measure the stiffness and loss of the samples. This method reveals the storage modulus E' , loss modulus E'' , and $\tan \delta$ over a range of temperature from $-100\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$. Therefore, glass transition temperatures of the admicelled rubbers can be determined. The results of DMA demonstrate the only one T_g of the admicelled rubbers at about -57 to $-59.5\text{ }^{\circ}\text{C}$ in an intermediate position between glass transition temperatures of pure rubber and pure PPy. (T_g of pure NR is $-70\text{ }^{\circ}\text{C}$ and T_g of pure PPy is $97.32\text{ }^{\circ}\text{C}$ (Vishnuvardhan T.K., *et al.*, 2006)¹²) This suggests that the admicellar polymerization is a unique method to prepare a well miscible core-shell structure of PPy-NR. The results also indicate the shift of T_g of pure rubber to higher temperature caused by admicellar polymerization. This means that the hardness and brittleness of PPy improve rigidity of natural rubber. Moreover, the rubbery modulus increases as the increase of PPy content,

however, there is no effect of salt on T_g of the admicelled rubbers. $\tan \delta$ (E''/E') from Table 4.4 suggest that increasing [Mo]:[In] ratio leads to lower chain mobility and decreasing storage modulus at 25°C or 100°C. This suggests that there are less number of chains or higher molecular weight PPy were formed giving less mobility and softer.

Table 4.4 The glass transition temperature of the admicelled rubbers

Sample	T _g from Peak in Tan δ (°C)	Ratio E'' in Rubbery region/E' in glassy region	E' at 25 °C (MPa)	E'' at 25 °C (MPa)	E' at 100 °C (MPa)	E'' at 100 °C (MPa)
A20,1-1	-57.1	0.0009	1.43	0.13	1.08	0.15
A20,2-1	-57.9	0.0009	1.87	0.32	1.35	0.31
A20,3-1	-59.1	0.0006	1.64	0.20	1.21	0.19
A50,1-1	-58.8	0.0020	6.41	0.78	3.85	0.71
A50,2-1	-57.9	0.0008	2.30	0.32	1.82	0.37
A50,3-1	-58.5	0.0011	2.29	0.18	1.60	0.17
A100,1-1	-58.6	0.0068	19.13	1.60	10.09	1.09
A100,2-1	-58.9	0.0035	7.43	0.90	4.83	0.82
A100,3-1	-57.5	0.0009	1.98	0.19	1.79	0.23
B20,1-1	-58.0	0.0012	1.70	0.14	1.40	0.19
B20,2-1	-58.3	0.0006	1.51	0.15	1.06	0.18
B20,3-1	-57.8	0.0006	1.65	0.15	1.09	0.14
B50,1-1	-58.7	0.0016	5.19	0.53	3.56	0.62
B50,2-1	-59.2	0.0012	2.39	0.24	1.52	0.27
B50,3-1	-58.4	0.0011	1.81	0.14	1.46	0.19
B100,1-1	-59.3	0.0135	36.67	2.36	21.30	1.20
B100,2-1	-59.6	0.0036	7.90	0.67	5.30	0.72
B100,3-1	-58.6	0.0018	3.91	0.35	2.80	0.38

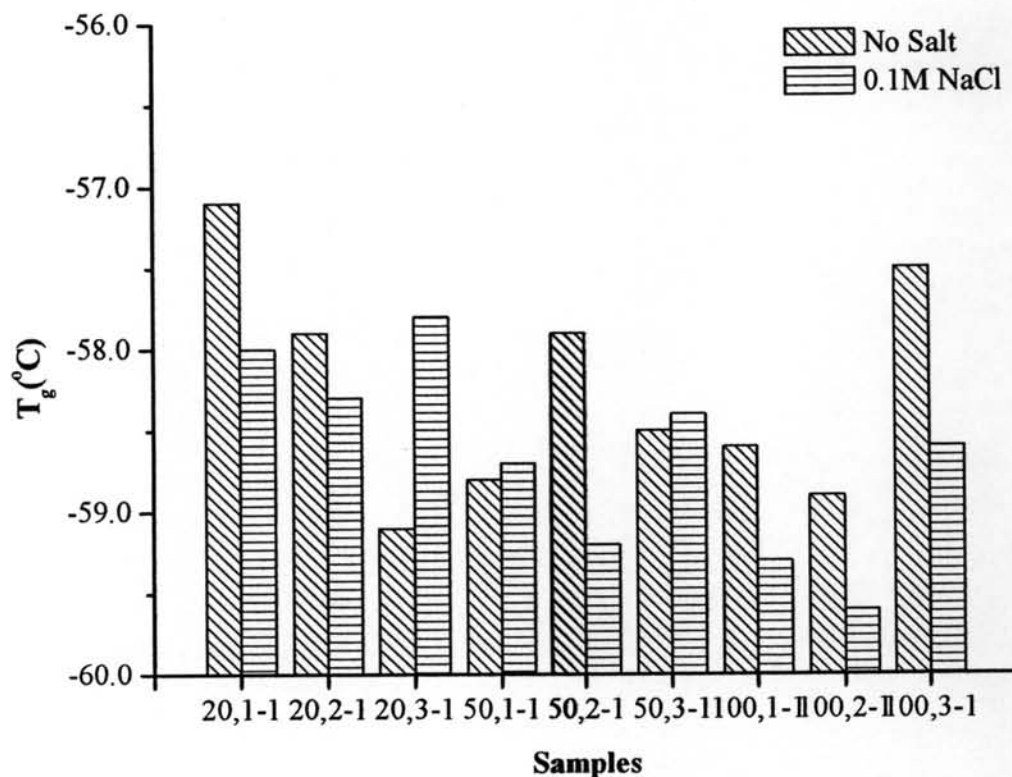
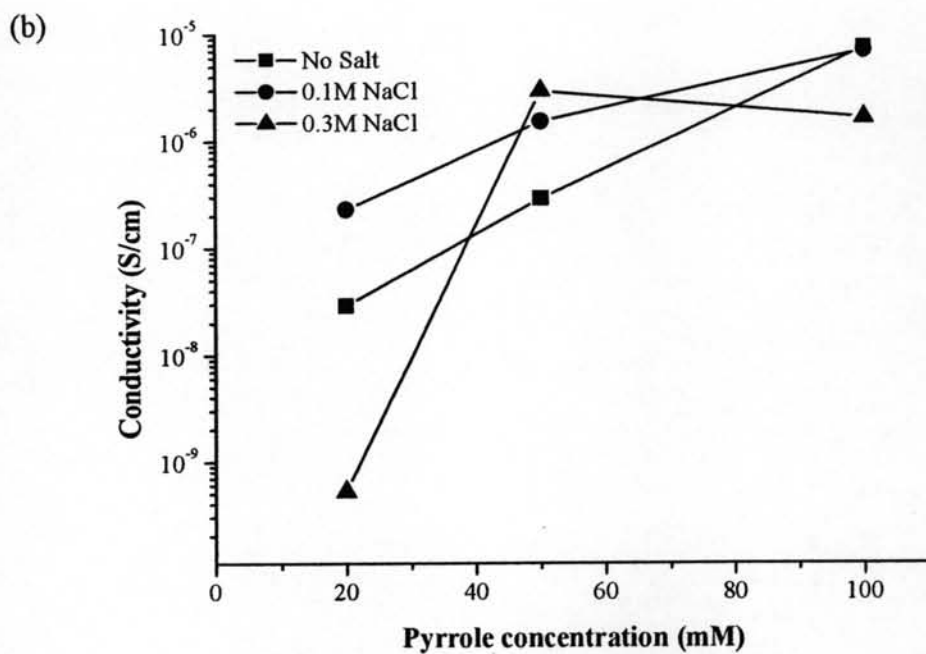
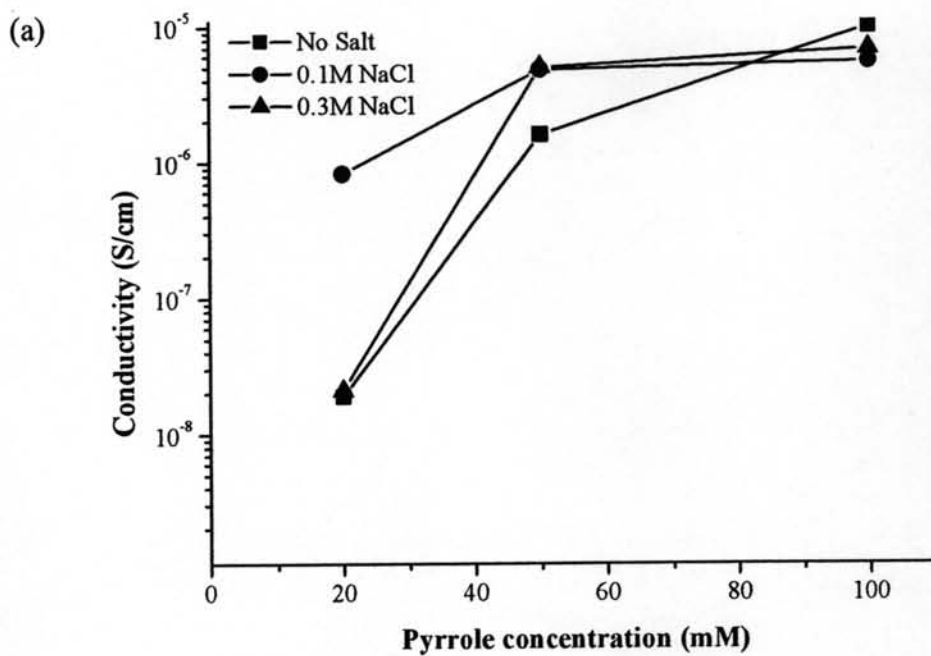


Figure 4.21 Glass transition temperatures from $\tan \delta$ peak of the admicelled rubbers.

H. Conductivity Measurement

Figure 4.22 shows the effect of salt on the conductivity of the admicelled rubbers at different polypyrrole content. It reveals that the addition of salt improves the conductivity. This is consistent with the results of Bunsomsit K., *et al.* (2002)¹³. The increasing surfactant adsorption with increasing salt means higher coverage and the creation of more headgroup sites for adsorbilization. The salt decreases electrostatic repulsion between headgroups, which allow more adsorption and adsorbilization. This leads to homogeneous coating of PPy over rubber surface and enhancement in conductivity. However, the addition of 0.3M NaCl shows lower conductivity than 0.1M NaCl addition because too much salt added is difficult to wash out and that affects the charge carrier path way resulting in lower conductivity. When [NaCl] is high, Cl^- reacts with Fe^{3+} generating FeCl_3 . This limits the oxidize power of Fe^{3+} leading to less number of PPy molecules resulting in low conductivity.

Admicellar polymerization of polypyrrole at lower temperature shows higher conductivity of resulting products than those prepared at 0-30°C as reported by Lee J.Y., *et al.* (1997)¹⁴. At low temperature, the growing sites of the polymer with free radicals are stabilized. The initiation rate is smaller than the propagation rate at low temperature to give the polymer a linear molecular structure with high molecular weight. The oxidant at high temperature decomposes fast to produce many reaction sites, resulting in crosslinking or branching between molecules. It can be seen from the graph that the increase of pyrrole content enhances the conductivity (the conductivity of 20 mM PPy is about 10^{-8} S/cm, the conductivity of 100 mM PPy is about 10^{-6} S/cm). This fact can be supported by the SEM micrographs of admicelled rubber at different pyrrole concentration. At low pyrrole concentration, the coating of polypyrrole film after admicellar polymerization is not as perfect as high pyrrole concentration. At PPy 100 mM, the surface of each rubber particles were covered by PPy film evenly and the connection of each particle forms smooth path way for electron transferring, resulting to the higher conductivity. The effect of monomer to initiator ratio is shown in Figure 4.23. It demonstrates that $[Mo]/[In] = 1$ shows the highest conductivity and the conductivity decreases with increasing of $[Mo]/[In]$ ratio to 3. By the results of Song K.T., *et al.* (2000)¹⁵, the most important factor to control the electrical conductivity and the yield of PPy powder is monomer:initiator mole ratio. This is consistent to the result of Song M.K., *et al.* (2004)¹⁶. This can be explained that when $[Mo]:[In]$ is high, the initiator is less to oxidize much more pyrrole content leading to less polymerization conversion and less number of PPy molecules or shorter chains are produced.



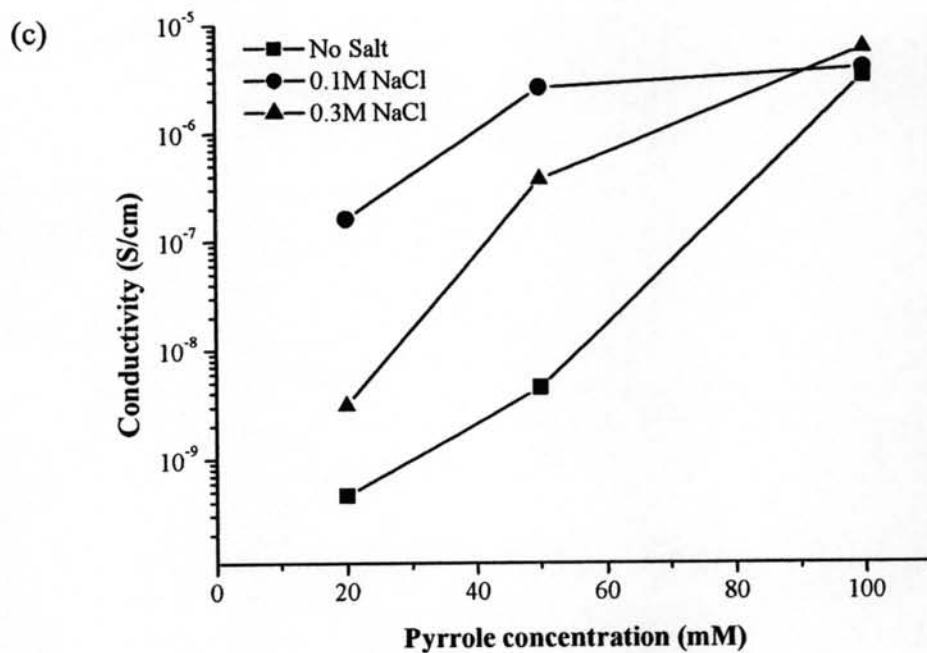
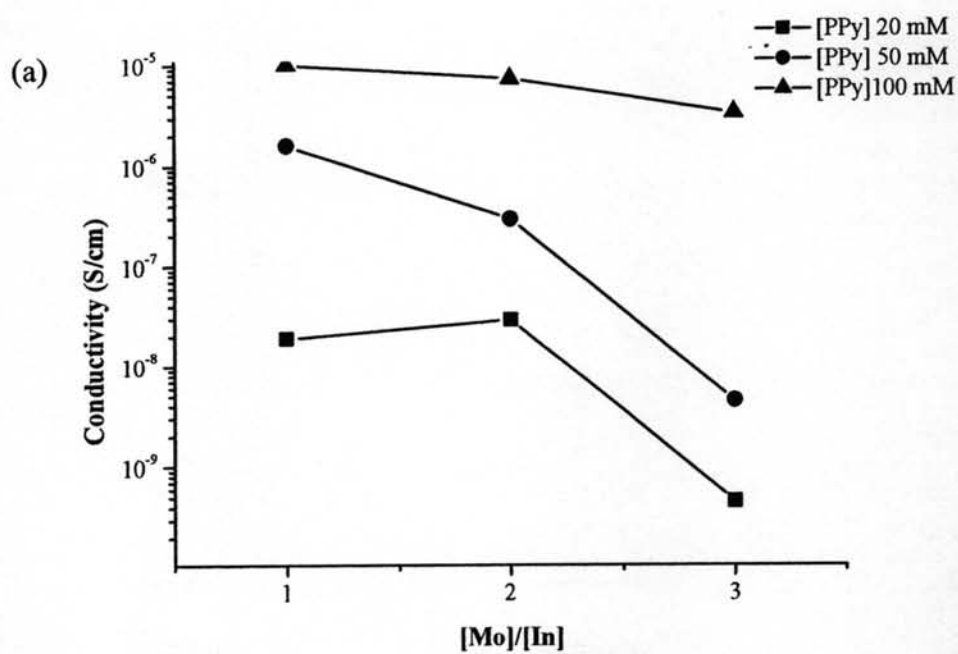


Figure 4.22 Effect of salt on conductivity of the admicelled rubbers at different [Mo]/[In] ratio, (a) [Mo]/[In] = 1, (b) [Mo]/[In] = 2, (c) [Mo]/[In] = 3 (Apply dc 0.1-15 volt).



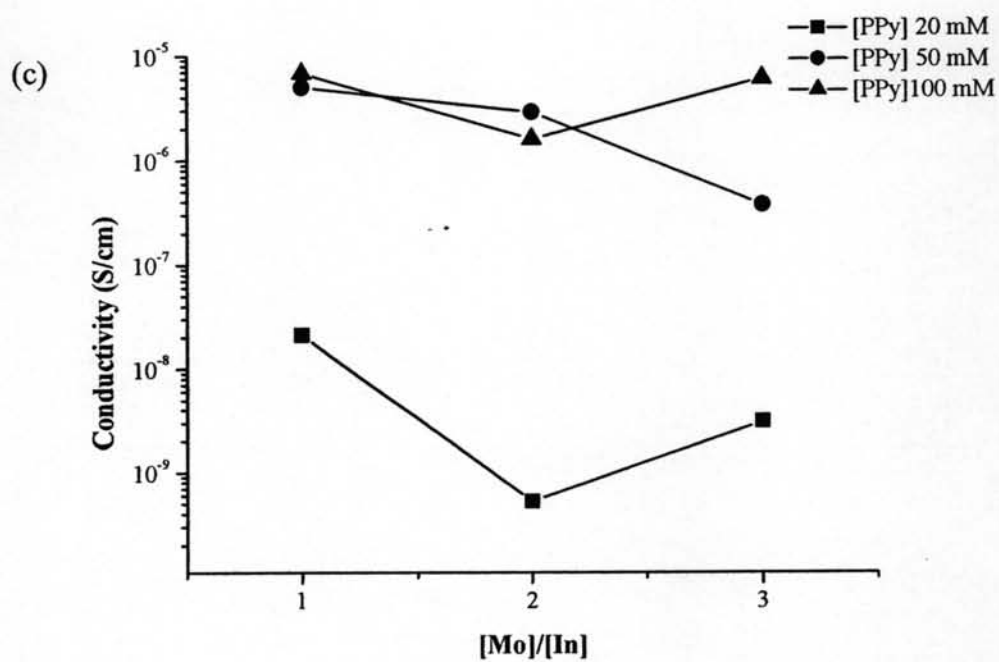
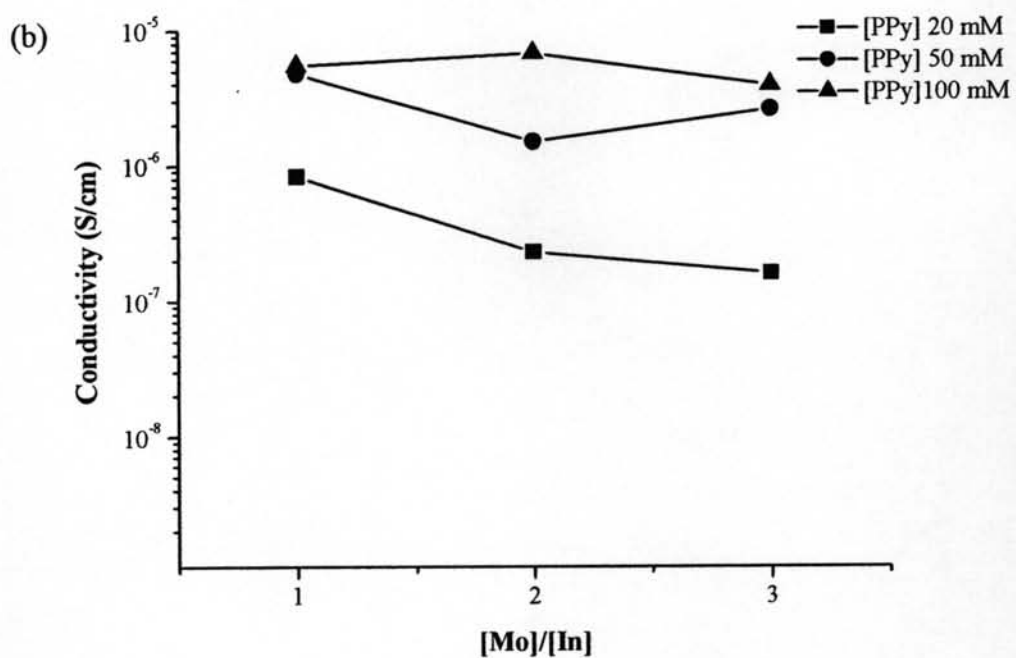


Figure 4.23 Effect of [Mo]/[In] ratio on conductivity of the admicelled rubbers at different salt concentration (a) No salt, (b) 0.1M NaCl, (c) 0.3M NaCl (Apply dc 0.1-15 volt).

The conductivity of the thin stretched admicelled rubber films (thickness 0.28-0.89 mm) at different distance is shown in Figure 4.24. Sample B100,1-1 demonstrates that the conductivity gradually increases with low strain due to the improvement of alignment of polypyrrole. When continue to stretch the film to large strain, the conductivity decreases significantly. The reason is that the large strain disconnects the particle contacts and breaks the path way of charge carrier. The result is similar to silicone rubber/polypyrrole composites, studied by Vilcakova J., *et al.* (2004)¹⁷, that the change in electrical conductivity during deformation results from particle displacement which affects the conducting paths in the material. Sample B100,2-1, the conductivity continually decreases with further extension due to the disrupt of PPy network over rubber particles. B100,2-1 is much softer than B100,1-1 so it is easier to stretch and breaking the PPy network. The conductivity of sample B100,3-1 which is the softest film among the three samples decreases at the beginning then increases with continuing stretching. This result relates to the polyaniline/styrene-butadiene-styrene composites studied by Xie H.-Q. and Ma Y.-M. (1999)¹⁸. At the beginning of the extension, the relative displacement of conductive polymer chains increases the distance between the conductive components, resulting in a decrease of conductivity. During further extension, the conductivity begins to increase, because the cross section square of the sample decreases; thus, the contact probability between the longer conductive components begins to increase with the extension (Aneli J. N. *et al.*, 1999)²⁰. This suggests that the number of chains is a major controlled parameter for increasing conductivity; however, if number of chains is less but the length of chain is longer, the conductivity can be raised upon stretching.

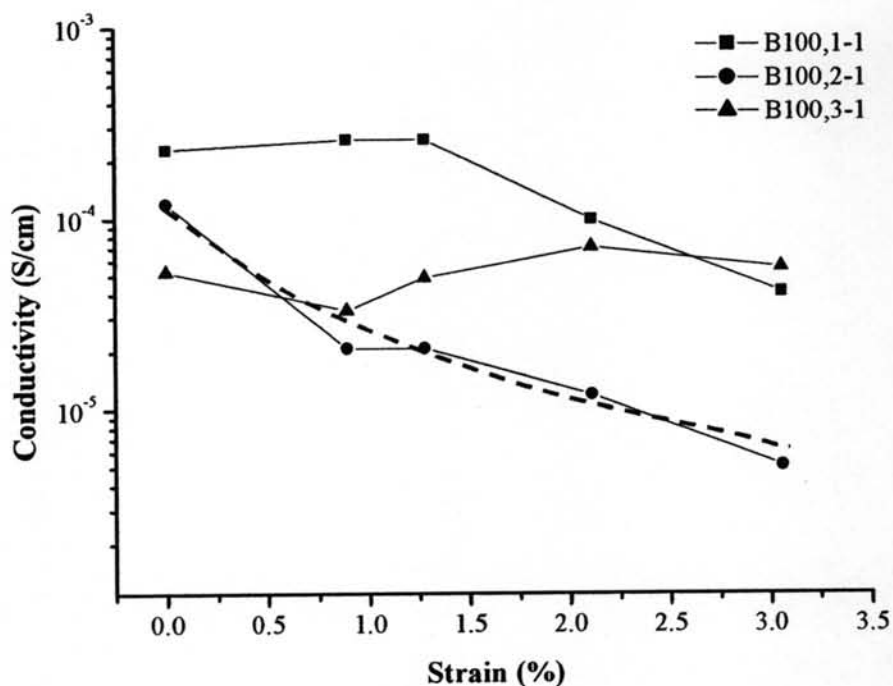


Figure 4.24 Effect of stretching on conductivity of the admicelled rubbers (Apply dc 0.1-15 volt) under N₂ atmosphere.

4.5 Conclusions

The success of the admicellar polymerization of polypyrrole coated latex particles was investigated by using FTIR, SEM, TGA, and DMA. From the FTIR study, the admicelled rubbers showed the characteristic peaks of polypyrrole which confirmed the existence of PPy after the polymerization. The SEM micrographs revealed the evenly coating of PPy over latex particles and they showed core-shell structure of PPy and NR. By the results 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 to higher temperature. The DTG curves also demonstrated the increase of char yields of the admicelled rubbers. As PPy content increased, the residual remaining enhanced and the degradation of the admicelled rubbers was slow down as well. These indicated that the admicelled rubbers were more thermostability than natural rubber. The mechanical properties of

the admicelled rubbers were investigated by using DMA and tensile testing. DMA results showed only one T_g of the admicelled rubbers in between the T_g s of pure rubber and pure PPy. This suggested that the admicellar polymerization was a unique method to prepare a well miscible core-shell structure of PPy-NR. The mechanical properties from tensile testing showed the increase of Young's modulus of the admicelled rubbers. This indicated the higher stiffness of the admicelled rubbers compared to natural rubber. Since PPy behaves like hard and brittle material, the stiffer of the materials increased as PPy content increased. The results of conductivity measurement revealed that the addition of salt improved the conductivity since salt decreased electrostatic repulsion between headgroups, which allowed more adsorption and adsolubilization leading to homogeneous coating of PPy over rubber surface. However, too much salt is not good to stabilize the oxidant leading to inefficient low conductivity to generate PPy. The increase of PPy content enhanced the conductivity because the coating of PPy was more perfectly at higher concentration as supported by SEM micrographs. The study of effect of monomer to initiator ratio on the conductivity indicated that $[Mo]:[In] = 1$ showed the highest conductivity and the conductivity decreased with the increasing of $[Mo]:[In]$ ratio to 3. Higher number of polymer chains was obtained when $[In]$ content is high to abstract electron from pyrrole and enhance free radical polymerization, resulting in higher conductivity. The conductivity of the stretched admicelled rubbers at different distance in low strain region was investigated. It demonstrated that the conductivity increased with low strain due to the improvement of alignment of polypyrrole but the conductivity decreased significantly when continuing to stretch the film to larger strain, because the particle contacts and the path ways of charge carrier were disconnected. However, in case of low number of PPy molecule (high $[Mo]:[In]$), the conductive chains can come to better contact upon stretching and these restore the increase in conductivity.

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