

## CHAPTER IV



### RESULTS AND DISCUSSION

#### 4.1 Preparation of IPNs product

In this research, the effects of initiator concentration, emulsifier concentration, reaction temperature, reaction time, and monomer content on the properties of NR/PMMA composites were investigated. The composite latex particles based on prevulcanized natural rubber latex have been synthesized to yield materials which may be formally regarded as interpenetrating polymer networks (where both prevulcanized natural rubber latex and PMMA were crosslinked) and semi-interpenetrating polymer networks (where only prevulcanized natural rubber latex was crosslinked). Methyl methacrylate was added to a carefully stabilized prevulcanized natural rubber latex and polymerized *in situ* using an amine-activated initiator, *tert*-butyl hydroperoxide. The bipolar redox system and *tert*-BuHP/TEPA were used to promote a core-shell arrangement. The appropriate conditions were studied in order to obtain high percent conversion.

The composite prevulcanized NR latex particles possess a polar PMMA shell around the rubber core in order to compatibilize the rubbery particles with different polymer matrices. A hard shell, which is encapsulating the soft rubber core, is needed for the continuous blending preparation process in a two-roll mill.

### 4.1.1 Effect of Initiator/Activator Concentration on Monomer Conversion

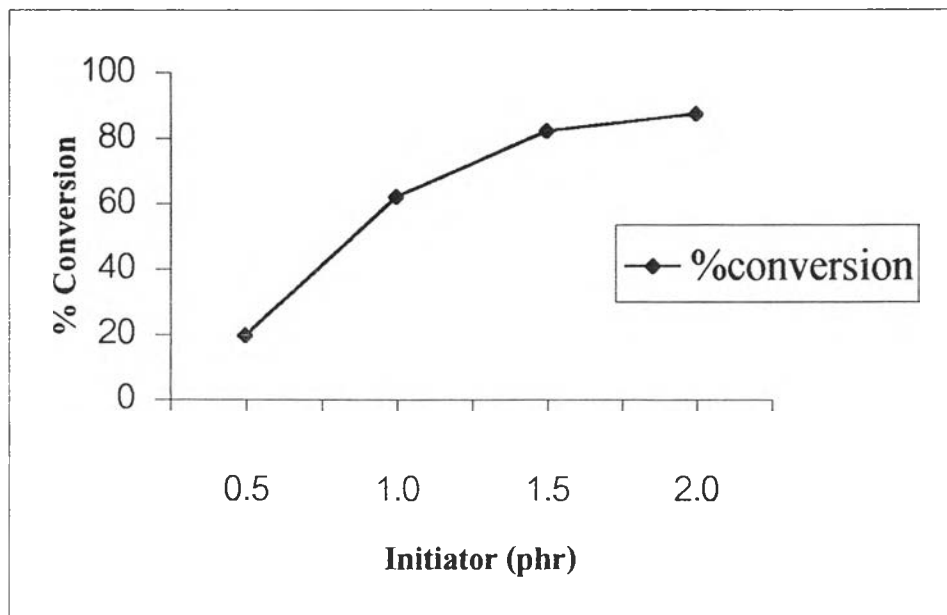
The bipolar redox initiating system was used in this experiment. This system consisted of *tert*-BuHP and TEPA, which promotes a core-shell morphology. The ratio of *tert*-BuHP/TEPA was employed in 1/1 ratio. The effect of initiator concentrations on the degree of monomer conversion was studied by varying the initiator concentrations to 0.5, 1.0, 1.5 and 2.0 phr (parts per 100 part of rubber content). The details are shown in Table 4.1 and Figure 4.1.

The parameters of emulsion polymerization were presented below :

- NR latex/Methyl methacrylate monomer : 70:30
- Crosslinking agent : 0.25 % wt of MMA monomer
- Emulsifier concentration : 1 phr
- Reaction temperature : 50 °C
- Reaction time : 6 hrs

**Table 4.1** Effect of initiator concentration on the percent of monomer conversion

Initiator concentration (phr)	average % Conversion of MMA monomer to PMMA
0.5	20.1
1.0	62.4
1.5	82.6
2.0	87.8



**Figure 4.1** Effect of initiator concentration on the degree of monomer conversion.

The degree of monomer conversion initially increased rapidly with the increasing amount of initiator concentration and slowly increased at high concentration. First, the increase in the initiator concentration produced more radical sites, therefore the degree of monomer conversion could be increased. At higher initiator concentrations, a plenty of initiator radicals are formed and radical recombination can occur to some extent to slightly increase all the reaction properties in terms of increasing conversion. The optimum initiator concentration was 2.0 phr.

### 4.1.2 Effect of Emulsifier Concentration on Monomer Conversion

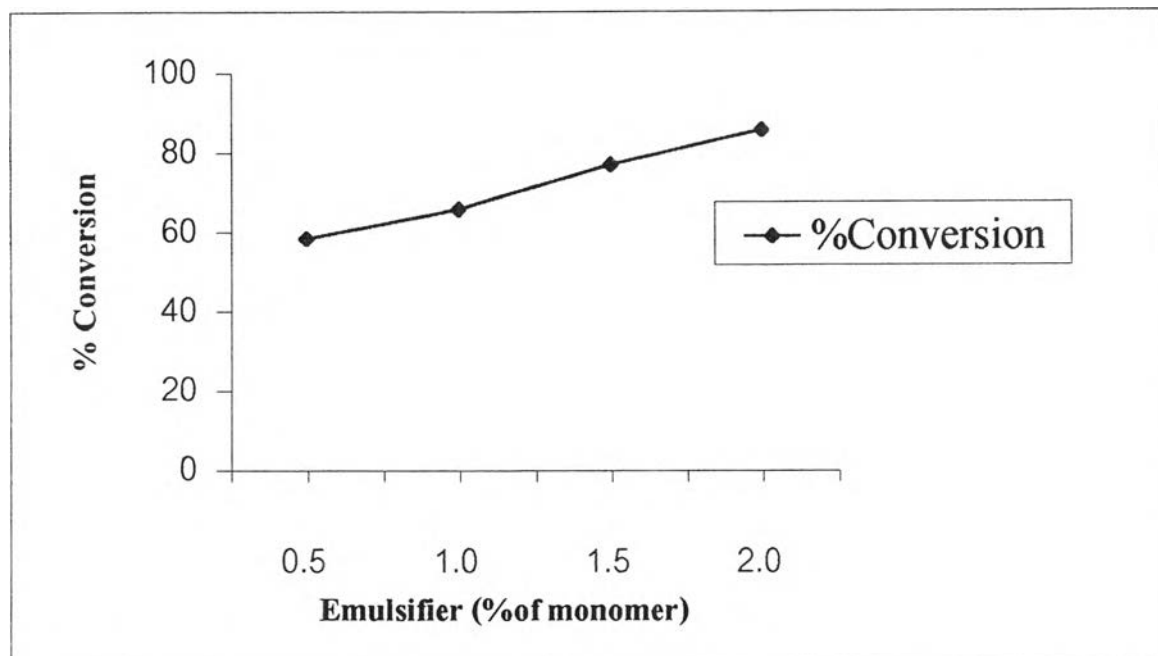
Anionic surfactants are the most commonly used surfactants in emulsion polymerization. In this experiment fatty acid, oleic acid, was used as emulsifiers.  $\text{NH}_4\text{OH}$  was added to stabilize the prevulcanized natural rubber latex.

The effect of emulsifier concentration on the degree of monomer conversion was investigated by varying oleic acid concentration to 0.5, 1.0, 1.5 and 2.0 % wt of methyl methacrylate monomer. The other parameters were kept constant as follows:

- Prevulcanized NR latex/MMA monomer: 70:30
- Initiator/activator : 1.5 phr
- Crosslinking agent : 0.25 % wt of monomer
- Reaction temperature : 50°C
- Reaction time : 6 hrs.

**Table 4.2** Effect of emulsifier concentration on the degree of monomer conversion

Emulsifier concentration (% wt of MMA monomer)	average % conversion of MMA monomer to PMMA
0.5	58.4
1.0	65.9
1.5	77.1
2.0	85.8



**Figure 4.2** Effect of emulsifier concentration on the degree of monomer conversion

It can be seen that the degree of monomer conversion increases with an increase of the emulsifier concentration. At the surfactant concentration above 1.0 % wt of monomer, the degree of monomer conversion was increased slightly. Due to the fact that when the concentration of surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as micelles. The appropriate emulsifier concentration in this emulsion polymerization was found at 1.5% wt of monomer.

### 4.1.3 Effect of the Reaction Temperature on Monomer Conversion

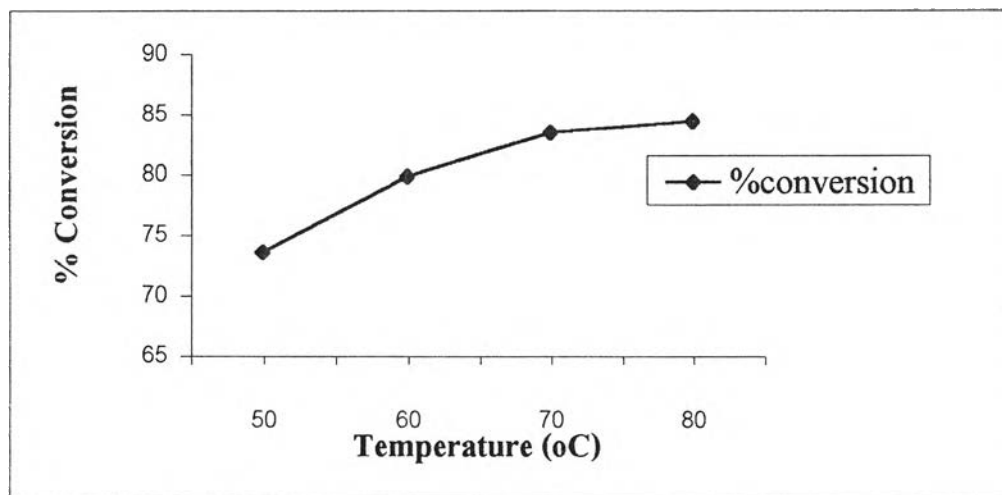
The effect of the reaction temperature on the degree of monomer conversion was investigated by varying the reaction temperature to 50, 60, 70, and 80°C, which are shown in Table 4.3, and Figure 4.3.

Basic formulations for emulsion polymerization of IPNs were prepared as follows:

- Prevulcanized NR latex/MMA monomer: 70:30
- Initiator/activator : 1.5 phr
- Crosslinking agent : 0.25 % wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- Reaction time : 6 hrs.

**Table 4.3** Effect of reaction temperature on the degree of monomer conversion

Reaction temperature (°C)	average % conversion of MMA monomer to PMMA
50	73.6
60	79.9
70	83.6
80	84.5



**Figure 4.3** Effect of reaction temperature on degree of monomer conversion.

The reaction temperature imposed a strong effect on the conversion of monomer, due to the reaction temperature influenced the reactivity ratio of methyl methacrylate monomer in the aqueous phase. When the temperature was increased, the decomposition of the initiator was increased, resulting in an increase number of free radicals and an increase rate of polymerization. At temperatures above 60°C, the degree of monomer conversion increased slightly. The appropriate temperature for this reaction was 60°C.

#### 4.1.4 Effect of the Reaction Time on Monomer Conversion

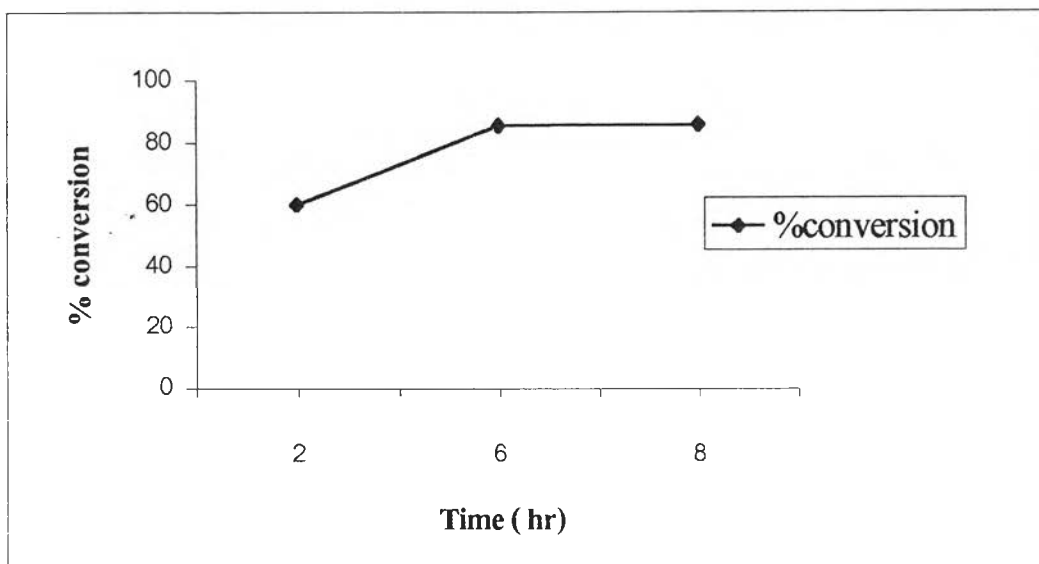
The effect of the reaction time on the degree of monomer conversion was shown in Table 4.4 and Figure 4.4. The other parameters of IPNs product were obtained as follows:

- Prevulcanized NR latex/MMA monomer: 70:30
- Initiator/activator : 1.5 phr
- Crosslinking agent : 0.25 % wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- Reaction temperature : 60°C

**Table 4.4** Effect of reaction time on degree of monomer conversion

Reaction Time (hr)	average % conversion of MMA monomer to PMMA
2	60.1
6	85.5
8	86.1





**Figure 4.4** Effect of reaction time on degree of monomer conversion.

This effects were investigated by varying the reaction time to 2, 6, 8 hrs. In Figure 4.4, it could be seen that when the time was increased the degree of monomer conversion also increased. The reaction was completed within 6 hrs. with the highest monomer conversion of 85.5 %.

## 4.2 The Morphology of NR-PMMA Composite

Core-Shell particle synthesis was prepared by emulsion polymerization. This method applied 1 hr swelling time to achieve a uniform distribution of monomers with the seed latex particles. The high solid content (50%) provided a large total surface area which facilitated the gathering of small particles and the stability of the latex. A core-shell arrangement of the polymer phase was assumed since the bipolar redox initiation system *tert*-BuHP/TEPA was used. Free radicals are produced at the particle/water or monomer droplet/ water interface since the peroxide is soluble in both the monomer and the prevulcanized NR latex particles whereas, the tetraethylene pentamine is water-soluble.

## **4.2.1 Transmission Electron Microscopy (TEM)**

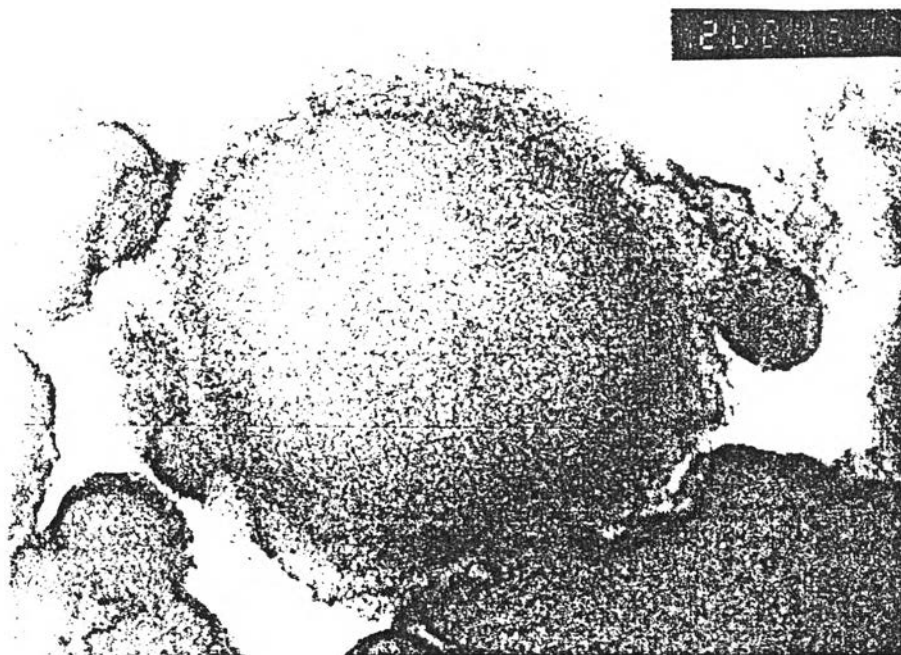
TEM is used to observe ultramicrotome cuts of prevulcanized NR latex particles which have been incorporated into a PMMA matrix. Osmium tetroxide is used to stain the prevulcanized NR latex phase. From the photograph, the prevulcanized NR latex phase is darker than the PMMA phase.

Moreover, TEM was used to identify the size of rubber droplets. The suitable size of rubber droplets to be used as impact modifier is about 3000-5000 angstroms.

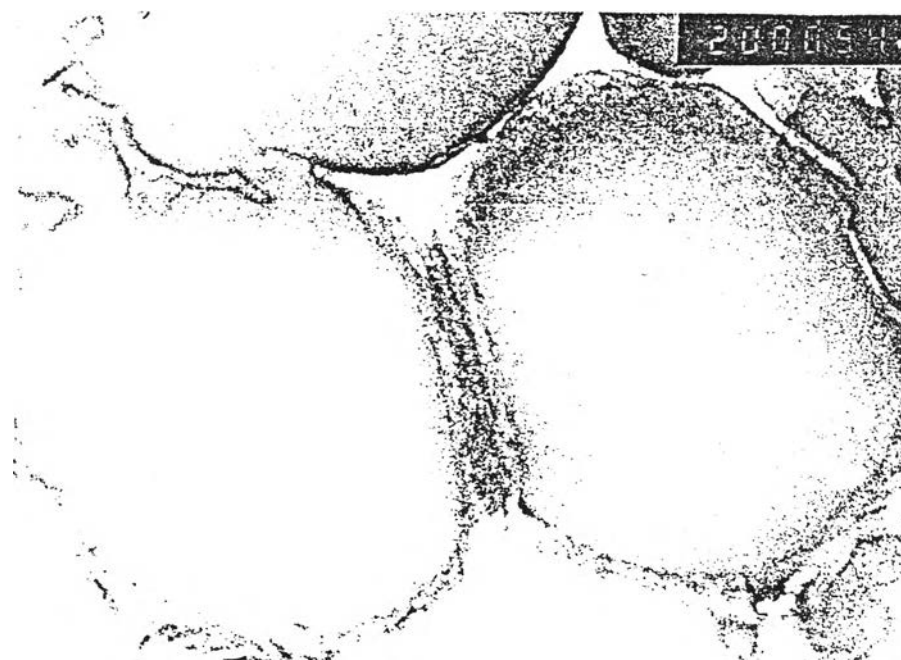
PTA has stained the PMMA shell. The lightly areas represent the PMMA phase. The external region of the shell is formed using pure crosslinked PMMA that penetrated into the prevulcanized NR latex core. A IPNs of prevulcanized NR latex and crosslinked PMMA had been formed. The preparation technique did not allow us to observe the interior of the latex particles.

### **4.2.1.1 Effect of Monomer Content on Particle Morphology**

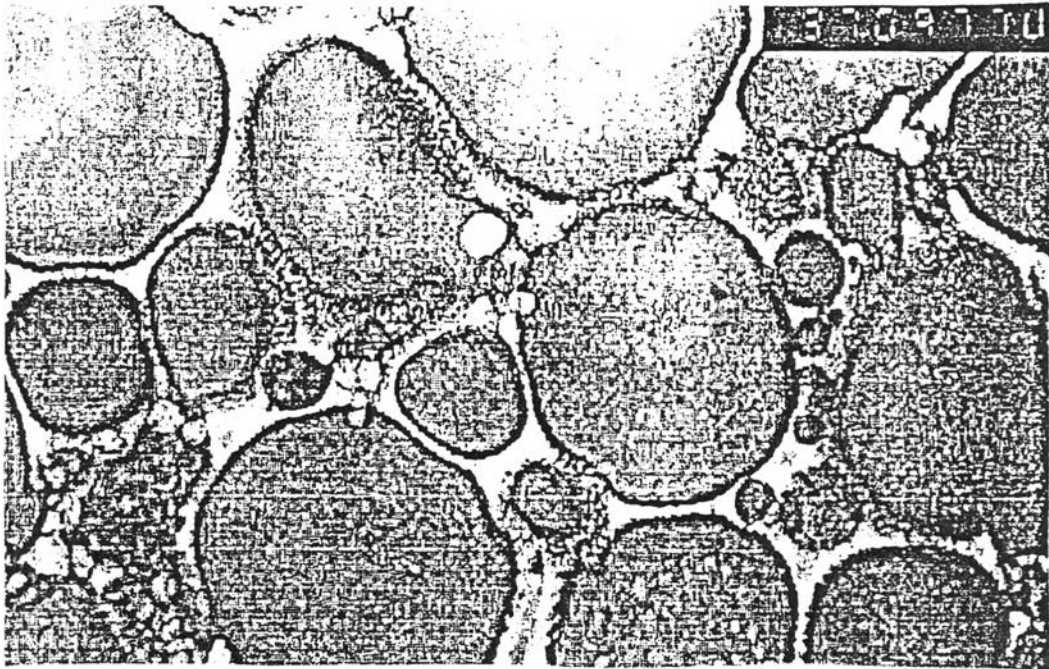
The increase in monomer content decreases the particle size of the prevulcanized NR latex phase. When the monomer content increases, more methyl methacrylate monomer inserts into the prevulcanized NR latex phase. When there is an increase in methyl methacrylate monomer, which polymerizes to polymethyl methacrylate, the prevulcanized NR latex particle size decreases. Figure 4.5, 4.6 and 4.7 show the TEM photomicrograph of NR/PMMA in order from small to large particle sizes, including IPNs 60/40, 70/30 and 80/20.



**Figure 4.5** TEM photomicrograph of NR/PMMA IPNs = 60/40.



**Figure 4.6** TEM photomicrograph of NR/PMMA IPNs = 70/30.

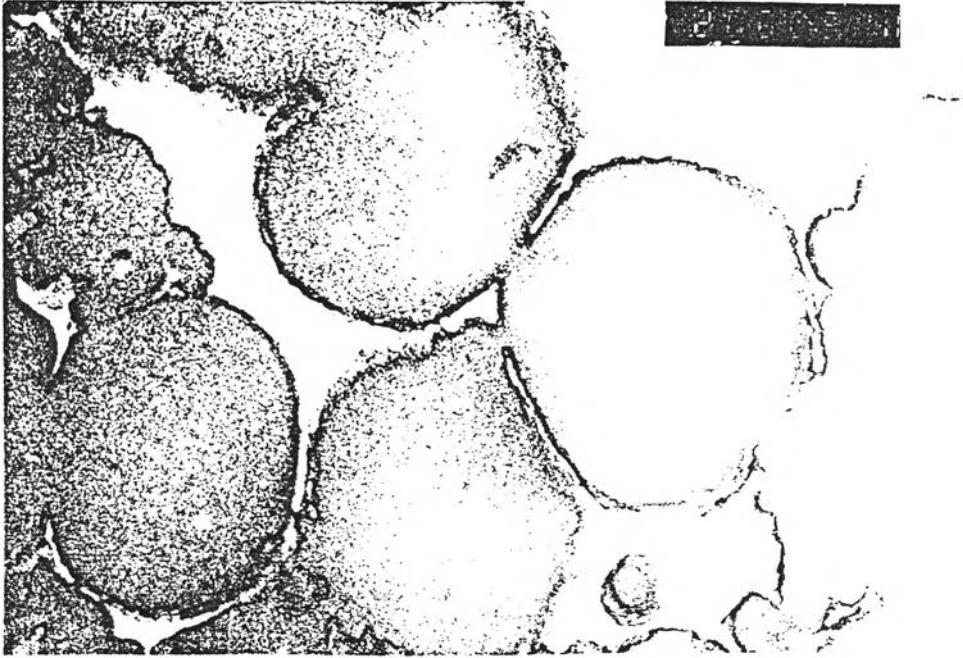


**Figure 4.7** TEM photomicrograph of NR/PMMA IPNs = 80/20

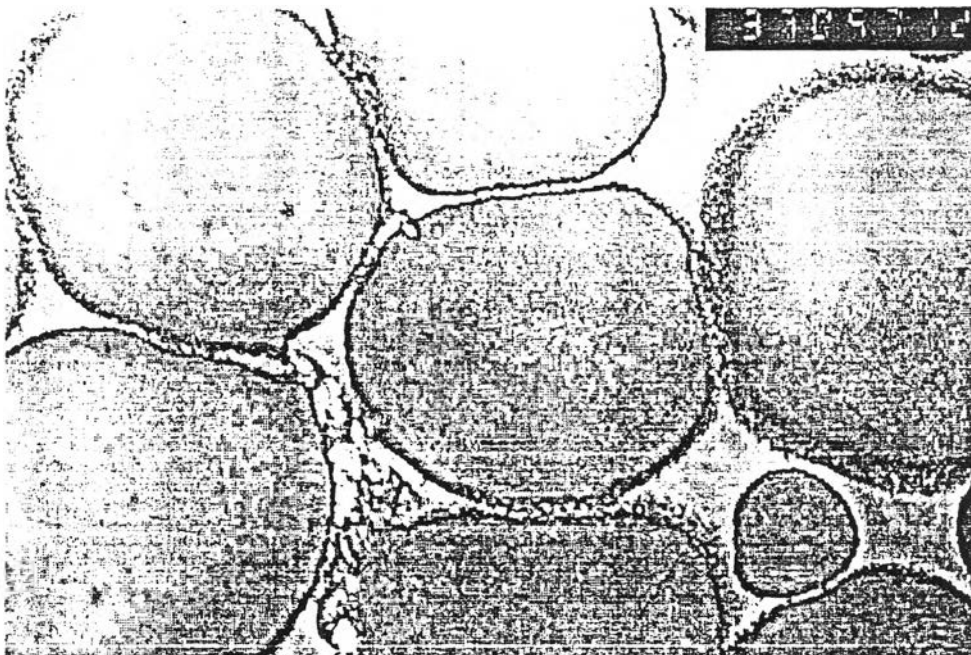
#### **4.2.1.2 Effect of Crosslinking Agent on Particle Morphology**

Figure 4.7 is the photomicrograph of the osmium tetroxide stained ultramicrotome cut of a semi-IPNs of NR/PMMA = 60/40 and IPNs of NR/PMMA = 60/40.

It can be seen that the particle size of prevulcanized natural rubber latex decreases with increasing crosslinking agent. The increase in crosslinking agents of PMMA caused the molecules of PMMA to become crosslinked. For this reason, the prevulcanized natural rubber latex particle size was decreased.



**Figure 4.8** TEM photomicrograph of NR/PMMA of IPNs = 60/40.

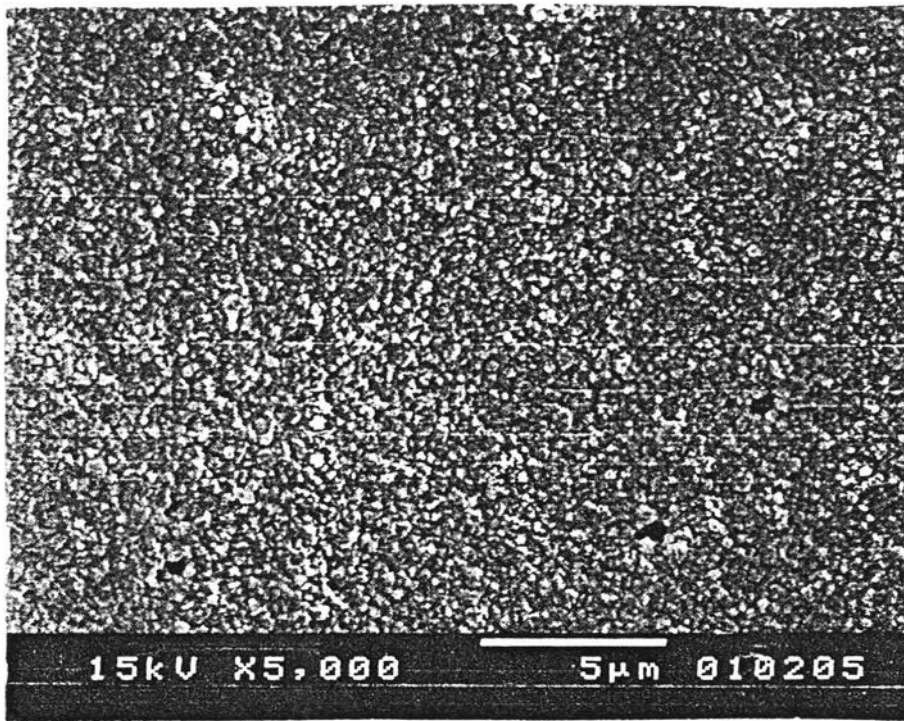


**Figure 4.9** TEM photomicrograph of NR/PMMA of Semi-IPNs = 60/40.

### 4.2.2 Scanning Electron Microscopy (SEM)

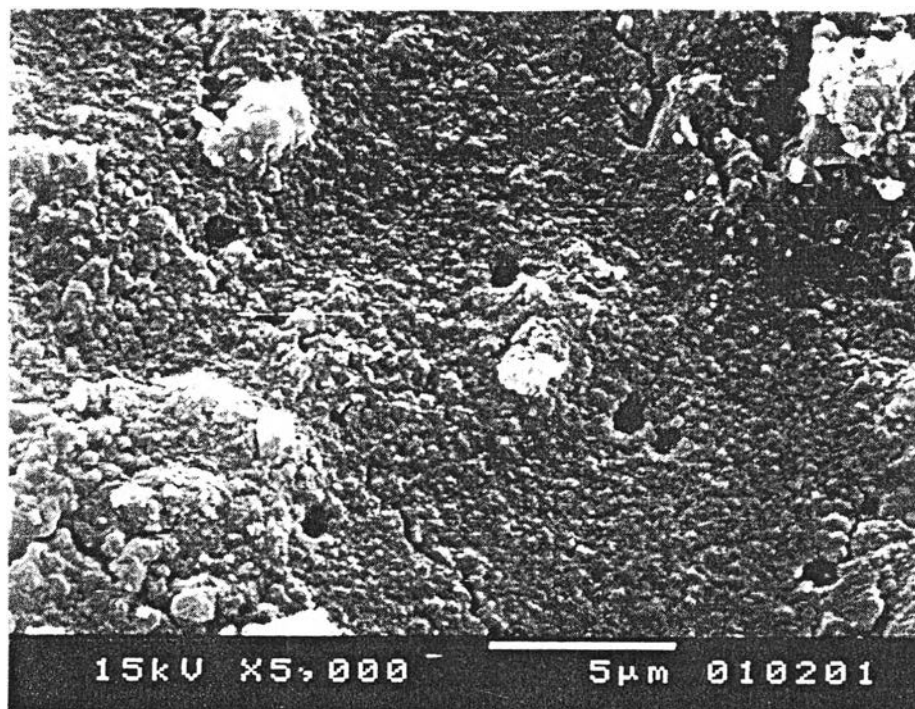
The scanning electron microscope was employed to investigate the particle surface and phase distribution of specimen. In Figures 4.10, 4.11, 4.12, 4.13, 4.14 and 4.15 are the phase distribution of IPNs of NR/PMMA = 60/40, 70/30, 80/20 and semi-IPNs of NR/PMMA = 60/40 , 70/30 and 80/20, respectively.

At 5,000 x magnification, the SEM electron micrographs of IPNs\* semi-IPNs products show the distribution of PMMA and prevulcanized NR latex. The smooth surface as well as the PMMA particle distribution of the specimen can be seen.

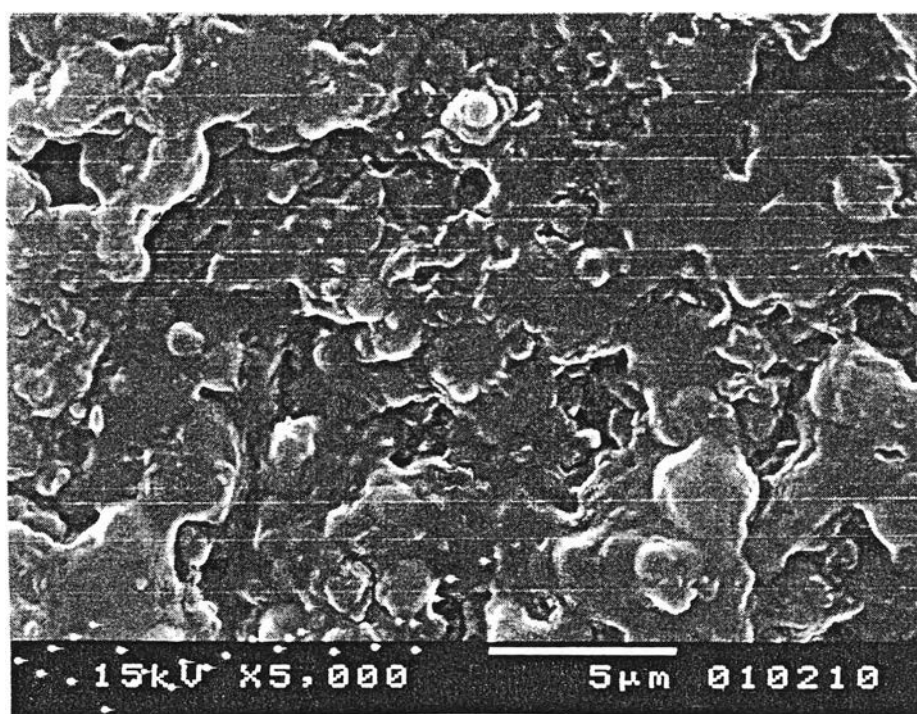


**Figure 4.10** SEM photomicrograph of NR/PMMA IPNs = 60/40.





**Figure 4.11** SEM photomicrograph of NR/PMMA IPNs = 70/30.



**Figure 4.12** SEM photomicrograph of NR/PMMA IPNs = 80/20.

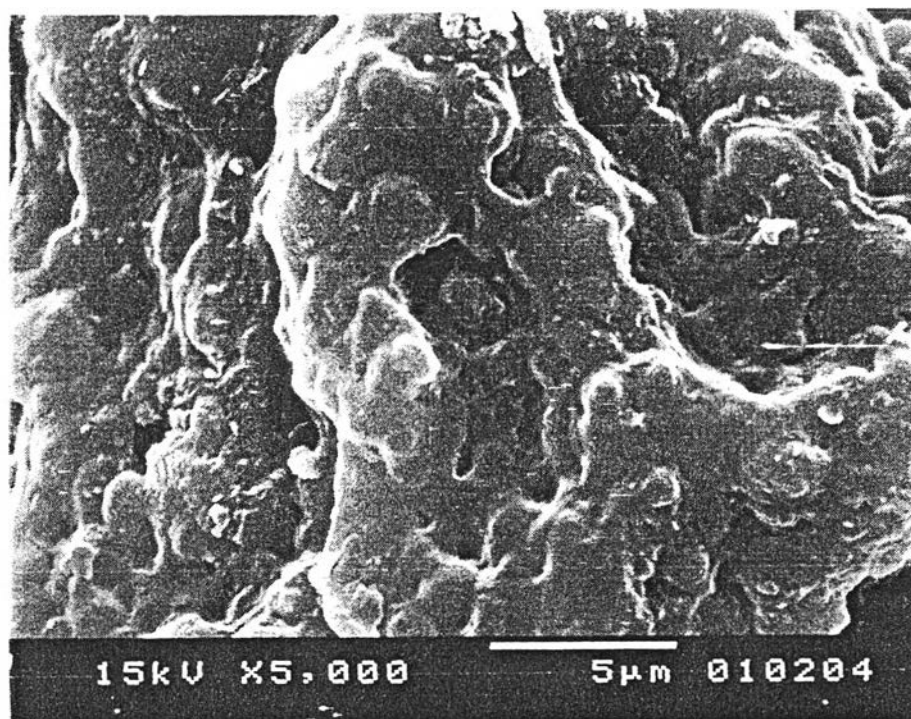


Figure 4.13 SEM photomicrograph of NR/PMMA semi-IPNs = 60/40.

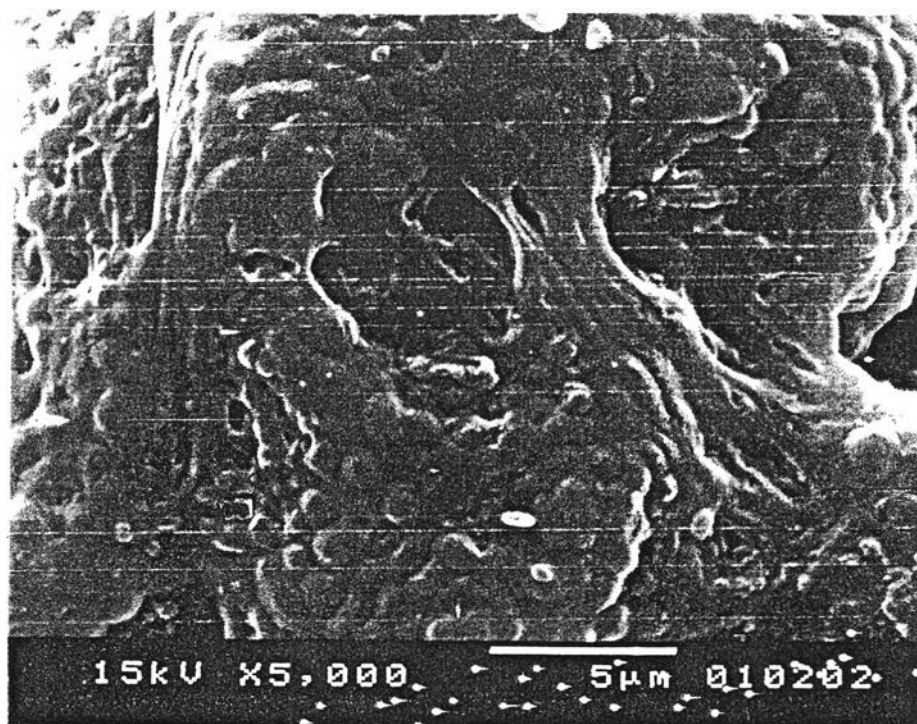
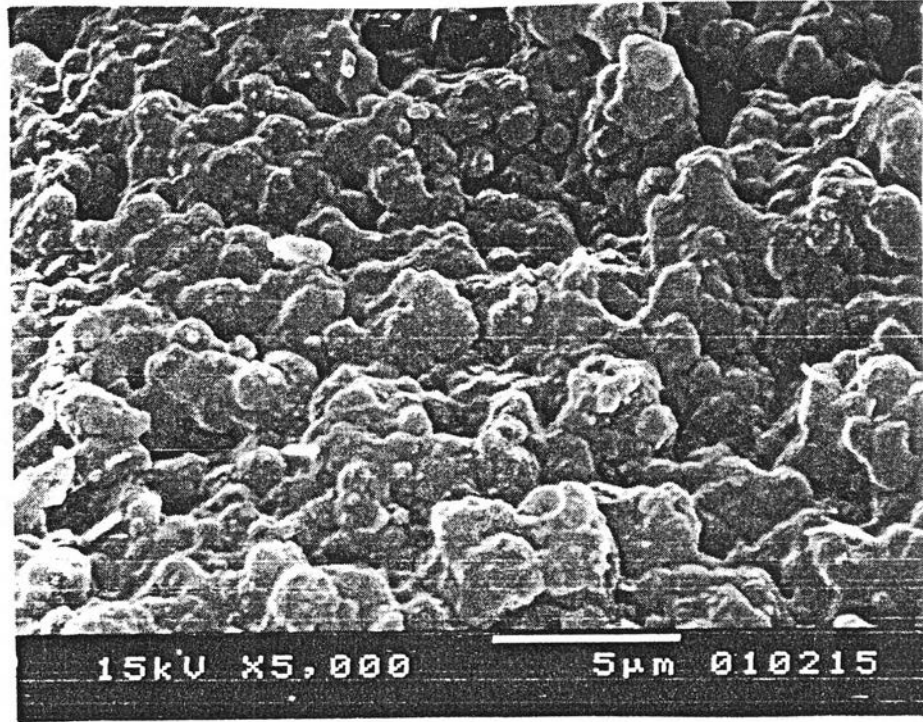


Figure 4.14 SEM photomicrograph of NR/PMMA semi-IPNs = 70/30.





**Figure 4.15** SEM photomicrograph of NR/PMMA semi-IPNs = 80/20.



### 4.3 Thermal Properties of IPNs Product

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) analyzed thermal properties of synthetic products. DSC was used to obtain the glass transition temperature ( $T_g$ )  $^{\circ}\text{C}$  and the evaluation of the miscibility between components of polymer blends. TGA was used to determine thermal stability of IPNs products.

**Table 4.5** Glass transition temperature ( $T_g$ ) of composite NR/PMMA

Component NR/PMMA	$T_g$ ( $^{\circ}\text{C}$ ) of PMMA
IPNs 60:40	114.8
IPNs 60:40	114.6
IPNs 60:40	114.1
Semi-IPNs 60:40	113.1

From DSC thermogram, increasing the amount of the secondary polymers in the latex particles improved the resolution of the DSC measurements. The value of glass transition temperatures of PMMA ( $114^{\circ}\text{C}$ ) closely coincided with pure PMMA. The literature reported  $105^{\circ}\text{C}$  for the  $T_g$  of PMMA. The higher value  $T_g$  of the PMMA phase can be explained by a relatively high molecular weight of the PMMA chains. The limiting glass transition temperature for PMMA is  $114^{\circ}\text{C}$  at very high molecular weights.

#### 4.3.1 Thermogravimetric Analysis

Thermogravimetric analysis was used to determine the thermal stability and the decomposition curves. These composite products are used to improve their

impact resistance. They must be stable at processing temperatures of 200 or 270 °C for about 3-5 min depending on the toughened polymer matrix. Assuming the worst possible case, dried prevulcanized natural latex particles were exposed to a flow of ordinary air and heated at a constant rate (20 °C/min) until 800 °C to analyze their degradation behavior at elevated temperatures.

#### 4.4 Mechanical Properties of IPNs Product

Mechanical properties of composite NR/PMMA were investigated to evaluate the values of tensile properties, hardness and tear strength.

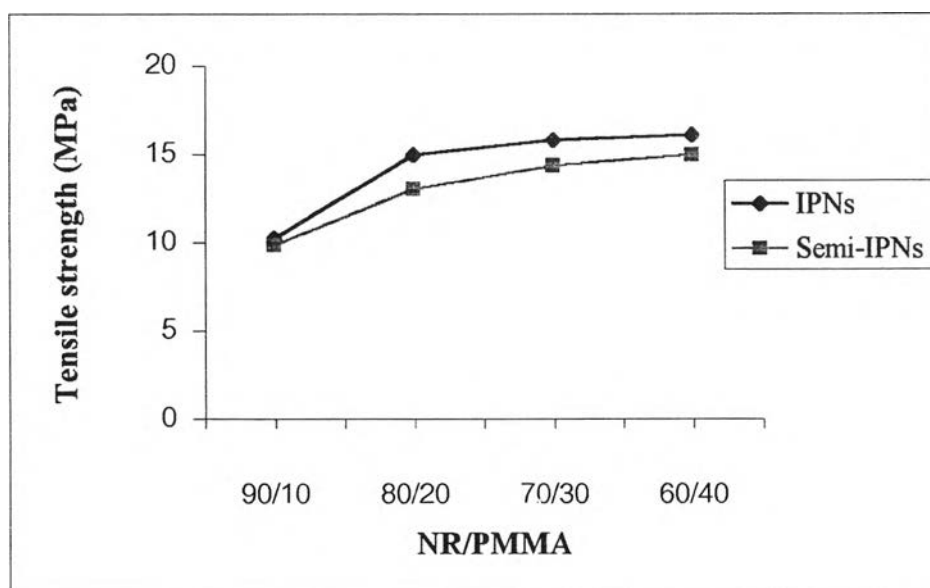
**Table 4.6** Effect of PMMA content on the mechanical properties of IPNs and semi-IPNs products.

Properties	60/40		70/30		80/20		90/10	
	IPNs	Semi-	IPNs	Semi-	IPNs	Semi-	IPNs	Semi-
Tensile strength (MPa)	17.30	16.40	16.01	15.40	14.60	13.85	10.23	9.13
Elongation at Break(%)	531.0	588.9	751.2	798.8	779.5	859.0	824.9	860.5
Modulus (MPa)	6.95	6.64	5.72	5.54	4.98	4.75	3.96	3.80
Hardness (Shore D)	80.94	80.52	77.70	75.50	70.80	69.30	52.60	52.30
Flexural strength (Kg/cm <sup>2</sup> )	210.5	205.0	197.0	194.1	169.4	166.4	148.7	145.7

### 4.4.1 Tensile Properties

The effect of PMMA content on tensile properties of IPNs product is shown in Figures 4.16, 4.17 and 4.18. The tensile strength (TS) and modulus increase with increasing of PMMA content. Properties, like TS and modulus for both semi-IPNs and IPNs, exhibited increasing trends because PMMA that has high mechanical strength and elastomer can reinforce rubber phase.

In Figure 4.17, the elongation at break decreases with increasing PMMA contents. Due to the fact that the PMMA is a naturally rigid, glassy thermoplastic (low percent strain), therefore the rubber component in NR/PMMA composite improves the elongation property of the product.



**Figure 4.16** The tensile strength of semi-IPNs and IPNs of NR/PMMA composite.

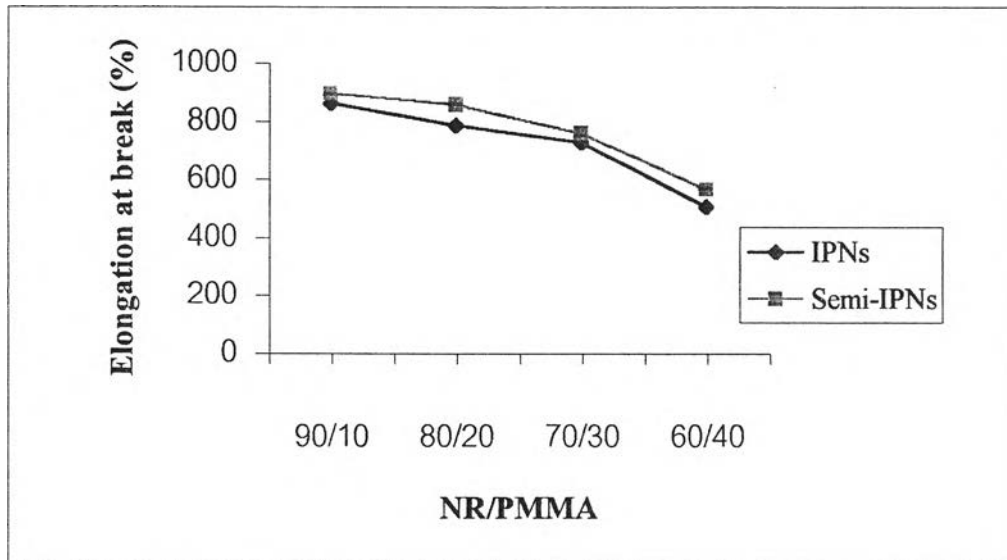


Figure 4.17 The elongation at break of semi-IPNs and IPNs of NR/PMMA composite.

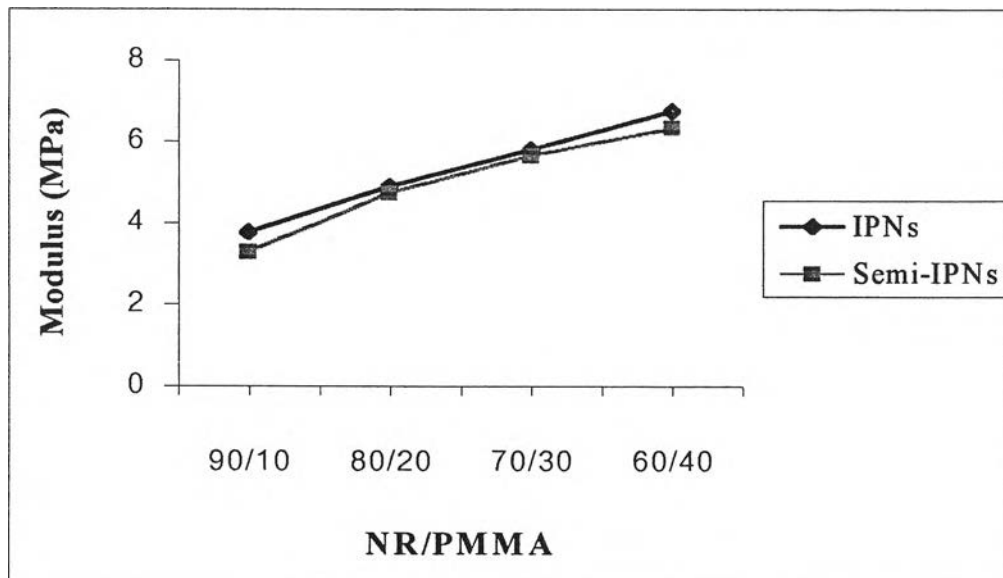
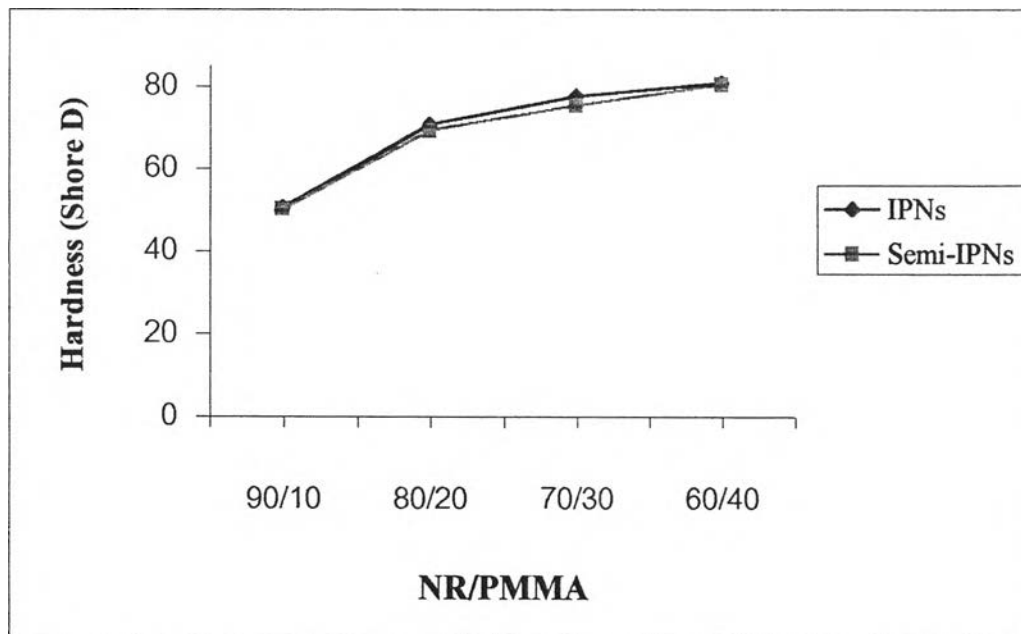


Figure 4.18 The modulus of semi-IPNs and IPNs of NR/PMMA composite.

### 4.2.2 Hardness

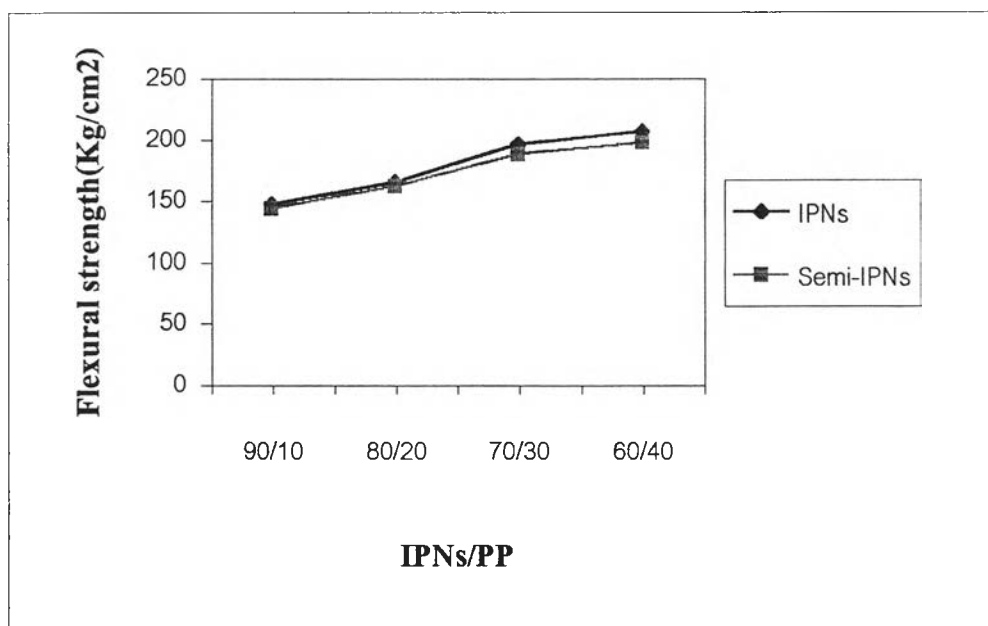
The hardness of NR/PMMA composite products is shown in Figure 4.19. The hardness of composites increased with increasing PMMA content. This can be explained by the PMMA component in NR/PMMA composite which had more plastic property, consequently, the blends were more rigid.



**Figure 4.19** The hardness of semi-IPNs and IPNs of NR/PMMA composite.

### 4.3.3 Flexural strength

The effect of PMMA content on flexural strength of NR/PMMA composite is presented in Figure 4.20. Analysis of flexural strength suggested that the incorporation of PMMA resulted in improvement of the composite property. As the PMMA content increased, the flexural strength also increased, indicating that the PMMA is capable of imparting substantial flexibility in property.



**Figure 4.20** The flexural strength of semi-IPNs and IPNs of NR/PMMA composite.

### 4.4.4 Comparison of the Mechanical Property with EPDM and Engage

NR/PMMA composite products of this research are used as impact modifier for PP. At present, a popular impact modifier used for PP is EPDM and Engage 8100. The comparison of all products, including semi-IPNs and IPNs NR/PMMA

= 60/40, 70/30, 80/20 and 90/10, indicated that the IPNs products have better mechanical properties than semi-IPNs. The mechanical property comparisons of selected IPNs products with EPDM and Engage 8100 are shown in Table 4.7.

**Table 4.7** The mechanical properties comparisons of selected-IPNs products between EPDM and Engage

Mechanical Properties	EPDM	Engage 8100	IPNs 50:50	IPNs 60:40	IPNs 70:30
Tensile strength	10.8	22.06	17.30	16.40	14.60
Elongation	280	345.20	531.0	751.2	779.5
Modulus 200%	6.6-9.5	7.95	6.95	5.72	4.98

## 4.5 Blending of IPNs products and PP

### 4.5.1 Properties of PP and IPNs products

An isotactic homopolymer of PP (2500TC) was used. Thai Petrochemical Industry Public Co., Ltd. (TPI) supplied it. Typical data of PP (2500TC) is shown in Table 4.8.



**Table 4.8** Typical data of PP grade 2500 TC

Typical Data	Unit	Value	Test Method
MFI 2.16 kg/230°C	g/10 min	45	ASTM D1238
Tensile Strength at Yield	N/mm <sup>2</sup>	21	ASTM D638
Charpy Impact Strength At-20°C	mJ/mm <sup>2</sup>	5.5	DIN 53453
Shear Modulus	N/mm <sup>2</sup>	430	DIN 53457
Ball Indentation Hardness	N/mm <sup>2</sup>	53	DIN 53456
Heat Distortion Temp. at 0.45 N/mm <sup>2</sup>	°C	90	ASTM D648

Source : Thai Petrochemical Industry Public Co., Ltd.

IPNs products were prepared by emulsion polymerization for 6 hours at 60 °C. The basic formulation was as follows:

- Initiator/activator (1/1) concentration : 1.5 phr
- Crosslinking agent concentration : 0.25% wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- NR/PMMA content : 60/40, 70/30, 80/20

The properties of NR/PMMA composite are shown in Table 4.7. The PP and 10, 15, 20, and 25 phr of IPNs products (60/40, 70/30, 80/20) were prepared. The mechanical properties were investigated.

#### 4.5.2 Mechanical Properties of PP Blended with IPNs products

The effects of the composition of PP/IPNs product blends and PP/EPDM blends on the mechanical properties were investigated. The values of tensile properties, hardness, impact strength and flexural strength are shown in Tables 4.9, 4.10, 4.11, and 4.12, respectively.

**Table 4.9** Effect of EPDM and Engage 8100 compare with IPNs products content on the tensile strength (MPa) of PP/rubber blends.

PP/Rubber	EPDM	Engage8100	80/20	70/30	60/40
100/0	15.00	15.00	15.00	15.00	15.00
90/10	14.00	21.75	14.16	18.03	18.85
85/15	12.61	20.59	12.98	13.36	15.74
80/20	11.12	19.92	12.54	11.72	13.48
75/25	10.25	19.10	10.33	10.68	12.25

**Table 4.10** Effect of EPDM and engage 8100 compare with IPNs products content on the hardness (Shore D) of PP/rubber blends.

PP/Rubber	EPDM	Engage8100	80/20	70/30	60/40
100/0	60.8	60.9	60.9	60.9	60.9
90/10	54.0	51.5	49.0	52.1	58.1
85/15	49.3	46.4	45.1	45.6	57.1
80/20	46.0	44.2	44.3	48.2	54.4
75/25	45.4	43.1	43.8	48.0	53.6

**Table 4.11** Effect of EPDM and engage 8100 compare with IPNs products content on the impact strength ( $\text{kJ/m}^2$ ) of PP/rubber blends.

PP/ Rubber	EPDM	Engage8100	80/20	70/30	60/40
100/0	207.0	207.0	207.0	207.0	207.0
90/10	630.4	750.1	583.4	528.8	495.8
85/15	664.0	801.8	609.6	636.4	617.0
80/20	711.2	898.7	619.6	644.0	629.8
75/25	715.6	959.5	638.6	672.4	650.2

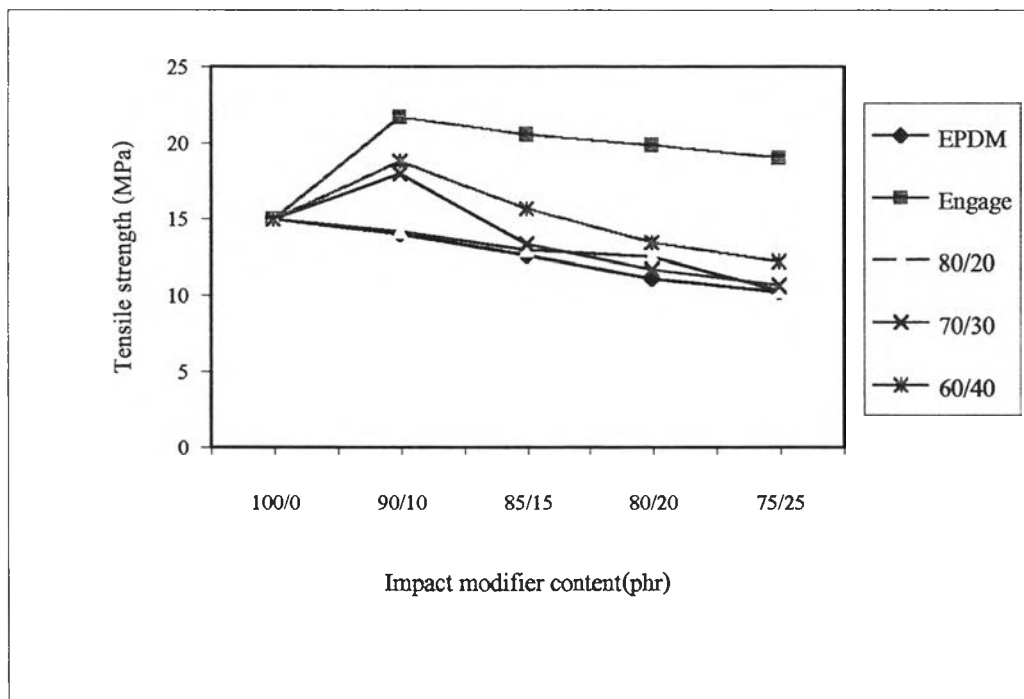
**Table 4.12** Effect of EPDM and engage 8100 compare with IPNs products content on the flexural strength ( $\text{kJ/cm}^2$ ) of PP/rubber blends.

PP/ Rubber	EPDM	Engage8100	80/20	70/30	60/40
100/0	205.8	205.8	205.8	205.8	205.8
90/10	630.3	635.0	495.8	528.7	483.5
85/15	664.5	668.9	517.0	536.4	509.6
80/20	711.2	735.3	529.8	544.0	519.5
75/25	715.6	738.2	550.2	572.4	538.6



## 1. Tensile Strength

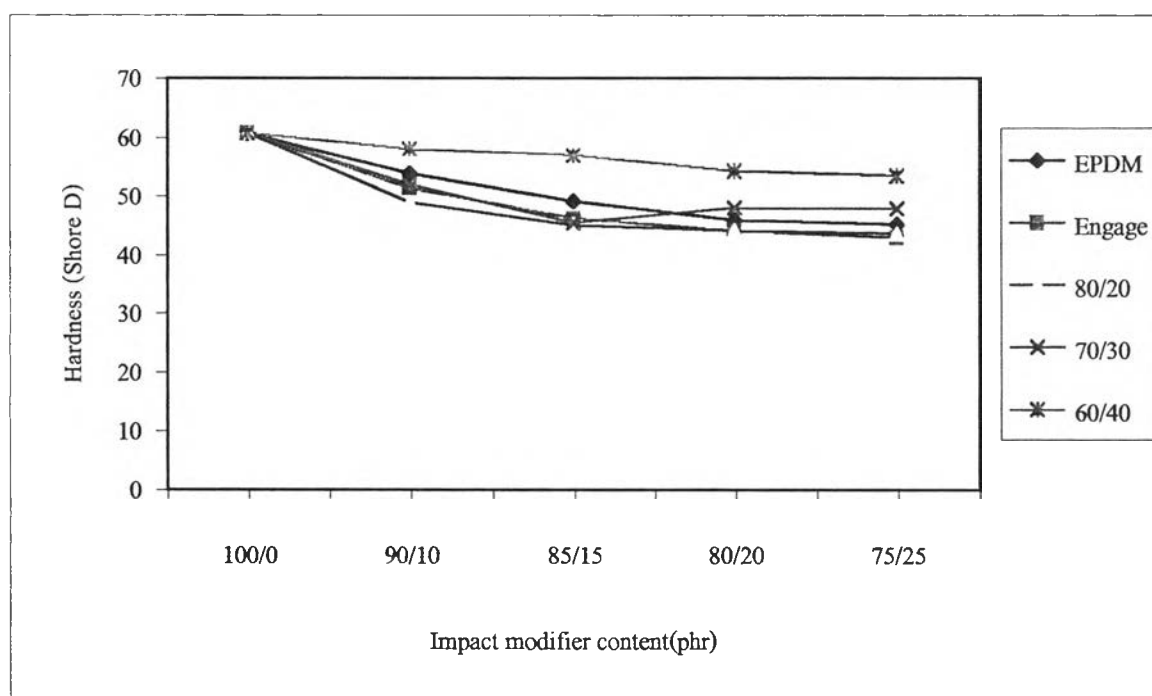
The effect of impact modifier contents, IPNs products with EPDM and Engage 8100 on the tensile strength of PP blends are shown in Figure 4.21. In Figure 4.21, the tensile strength slightly decreases with increasing impact modifier content. This can be explained by the high toughness that is obtained by the addition of an amorphous rubber, but the stiffness and strength of PP are degraded. The tensile strength increases with increasing PMMA in IPNs products due to the fact that PMMA has high tensile strength. Thus, the polymer blends have higher tensile strength.



**Figure 4.21** The tensile strength of PP/IPNs blends.

## 2. Hardness

The hardness of PP/rubber blends is presented in Figure 4.22. The hardness of blend decreased only slightly with increasing rubber content. This can be explained by the fact that the rubber components in blend products are more elastic, consequently, the blends deformed easily.



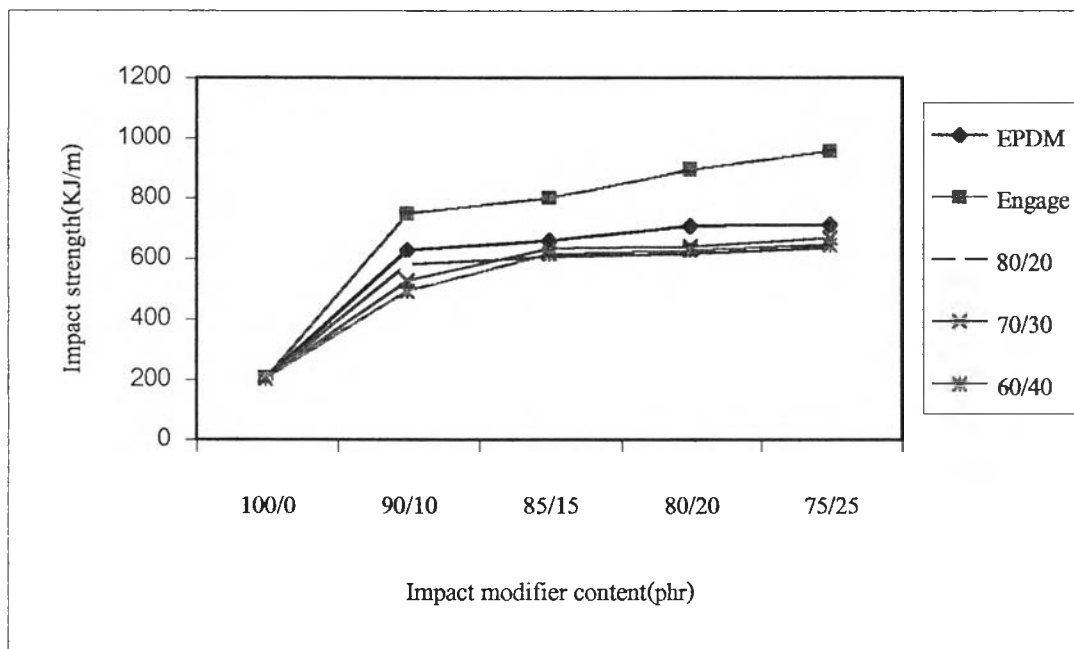
**Figure 4.22** The hardness of PP/IPNs blends.

## 3. Impact Strength

Figure 4.23 shows the effect of impact modifier content on the impact strength of PP/rubber blends. The impact strength increases with increasing rubber phase. At 25 phr impact modifier (EPDM, and IPNs 60/40), the impact

resistance of glassy plastics is increased by the addition of small quantities of rubber in the form of a polymer blend. The rubber promotes crazing in the material, which absorbs the energy locally. The effect of a large number of impact modifiers content is the capability of dissipating a large amount of energy. This makes crack propagation more difficult, leading to the increased impact strength.

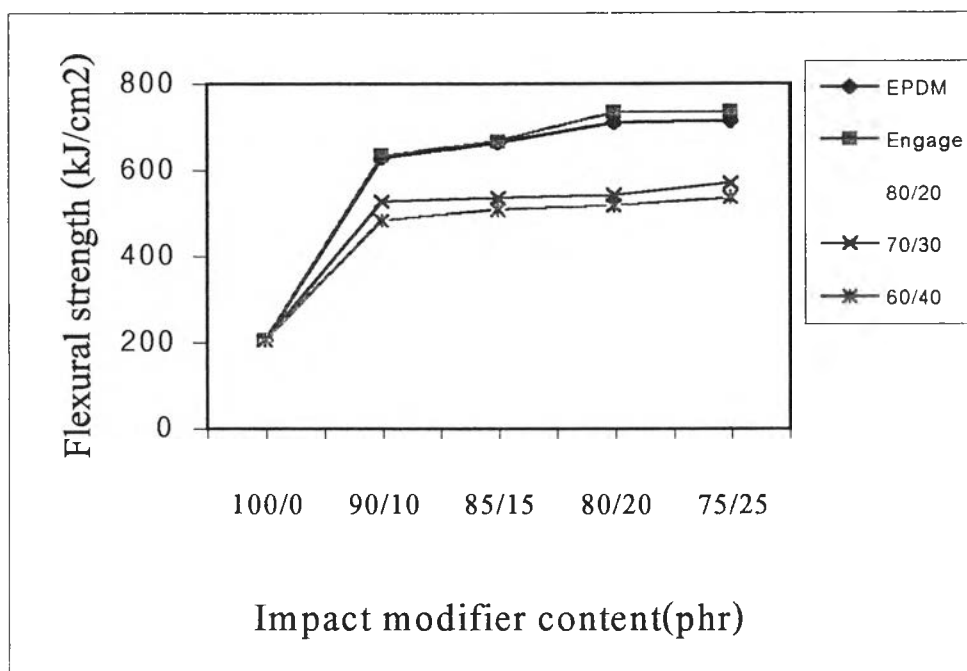
The impact strength is considered from IPNs product, increases with increasing of PMMA content to 30-40%, but at 50% PMMA content, the impact strength decreases. At low PMMA content, it can be mixed well with PP. However, at high PMMA content, the impact strength decreases because PMMA is a brittle plastic. When PMMA content is more than 40%, the impact strength decreases. Impact modifier from IPNs products which is appropriate for PP blends is NR/PMMA = 60/40. The appropriate impact modifier contents used are in the range of 10-15 phr.



**Figure 4.23** The impact strength of PP/IPNs blends.

#### 4.4 Flexural strength

Analysis of flexural strength revealed that incorporation of PMMA resulted in improvement of the composite. As the PMMA content increased, the flexural strength also increased, indicating that the PMMA is capable of imparting substantial flexibility in the property. Flexural properties were measured using a Universal Testing Machine Model LR 30K. For a 3-point bending flexural testing, the length of the support span depends upon the thickness. Specimen was loaded at a 10.05-mm diameter of crosshead loading nose using the rate of crosshead motion at 1.7 mm/min.



**Figure 4.24** The Flexural strength of PP/IPNs blends.

### 4.5.3 Scanning Electron Microscopy (SEM)

The scanning electron microscopy was used to analyze the distribution of polymer blend on surface of the specimen.

In Figure 4.25, at 5,000-x magnification, the SEM micrograph of the PP/EPDM blends at 15 phr EPDM reveals the distribution of EPDM particle in PP matrix. The EPDM particle distribution of PP/EPDM blend can be clearly seen.

In Figure 4.26, at 5000-x magnification, the SEM micrograph of the PP/IPNs product blend shows the distribution of IPNs in the PP matrix. It can be seen that the smooth surface of PP/IPNs product blend seems to be a bulk IPNs product distribution in the PP matrix.



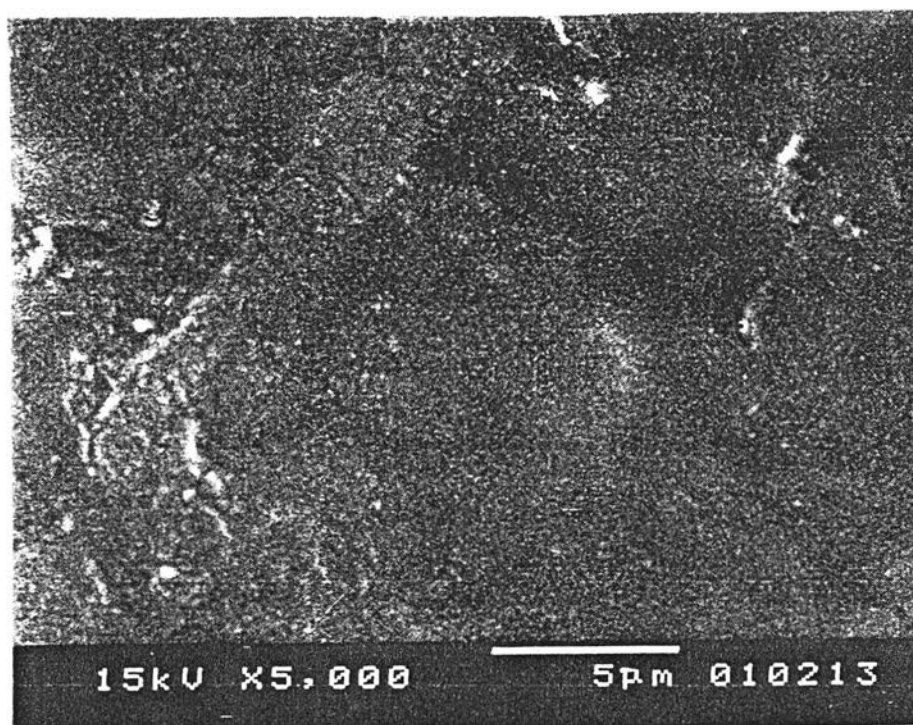


Figure 4.25 SEM photomicrograph of surface of PP/EPDM blend.

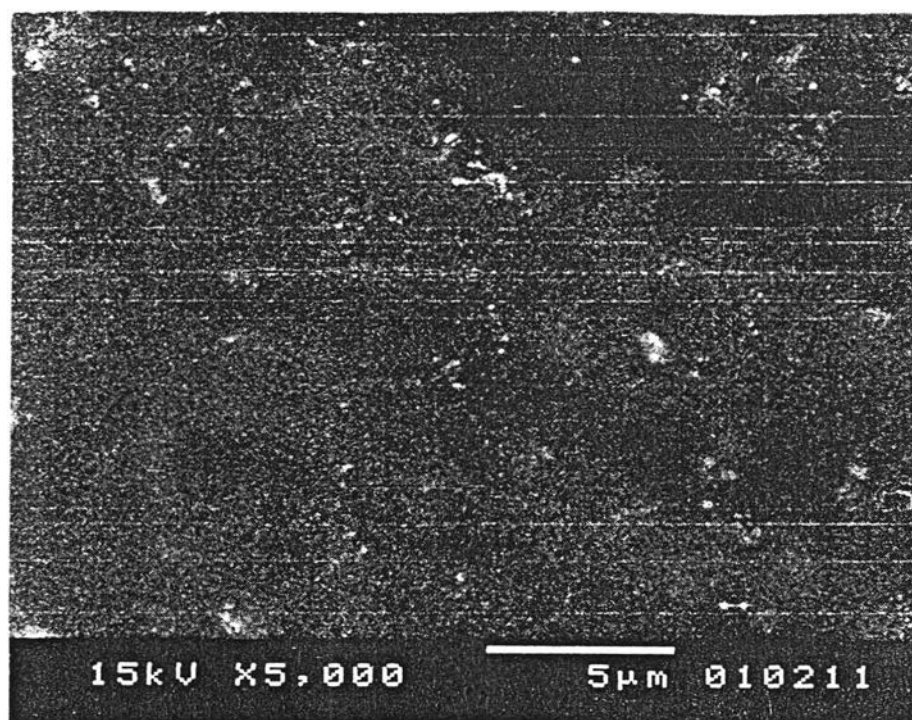


Figure 4.26 SEM photomicrograph of surface of PP/IPNs blend.

#### 4.6 Economic consideration

From the result of this research, the best composition is PP/IPNs at 85/15, which its mechanical properties approach to commercial resin. The cost of this blend is based on the cost of PP, prevulcanized NR latex, MMA and antioxidant. The costs of PP, Pre vulcanized NR latex, MMA and antioxidant in September 2001 are 30, 37, 25 and 500 baht/kg, respectively. Table 4.13 indicated the cost analysis of the blends. It can be seen that the cost of the blends per kilogram is relatively low. Therefore, the price of the synthetic composite will be attractive as an alternative to the reduction of import commercial resin. However, it is noteworthy that this cost of composite does not include the cost of mixing and other management costs.

**Table 4.13** Cost analysis of PP/IPNs blends

PP/IPNs composite	Materials Cost in Sep, 2001 (Baht/kg)				Cost of composite (Baht/kg)
	PP	Pre vulcanized NR latex	MMA	Antioxidant	
85/15/0.2	30	37	25	500	40.20