RESULTS & DISCUSSION

4.1 Scorch appearance

Scorch appearance was illustrated in Figures 4.1(a) and 4.1(b). The physical properties of PVC/nitrile rubber(NBR) blends at 20:80 ratio having carbon black or carbon black/silica fillers can not be measured because of their scorch. However, at other ratios, the scorch may occur but it did not appear on the surface of the samples because the rubber amount is not high.

4.2 ODR measurements

Figure 4.2 shows the oscillating disk rheograph of unfilled and filled compounded rubbers for different types of fillers. The scorch time and cure time of the compounded rubbers were presented in Table 4.1.

(a)   (b)
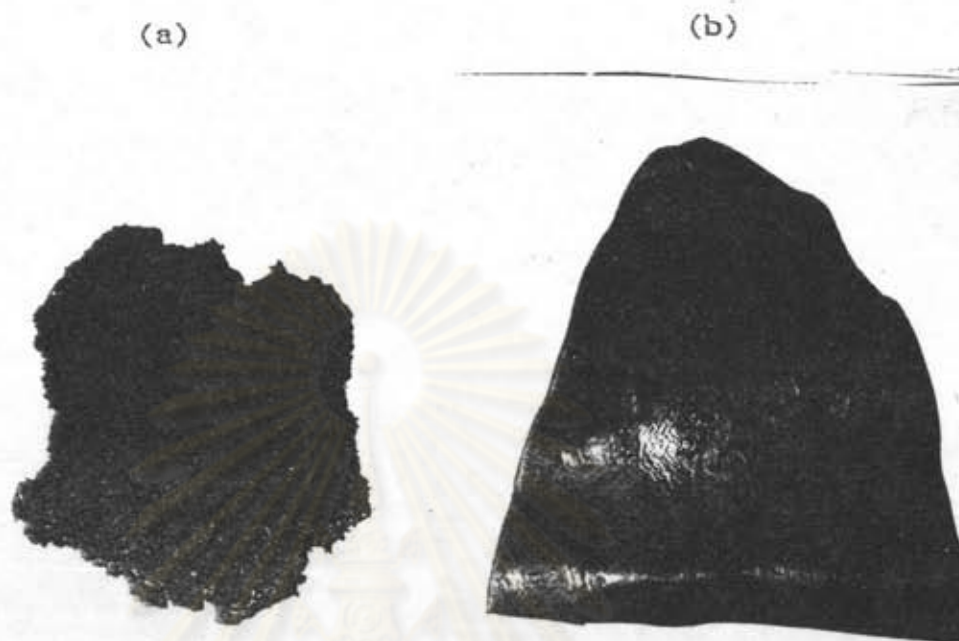

Figure 4.1 (a) The scorch of PVC/vulcanized nitrile rubber
                blend at 20:80 ratio which has carbon black
                filler.
          (b) No scorch of PVC/vulcanized nitrile rubber
                blend at 60:40 ratio which has carbon black
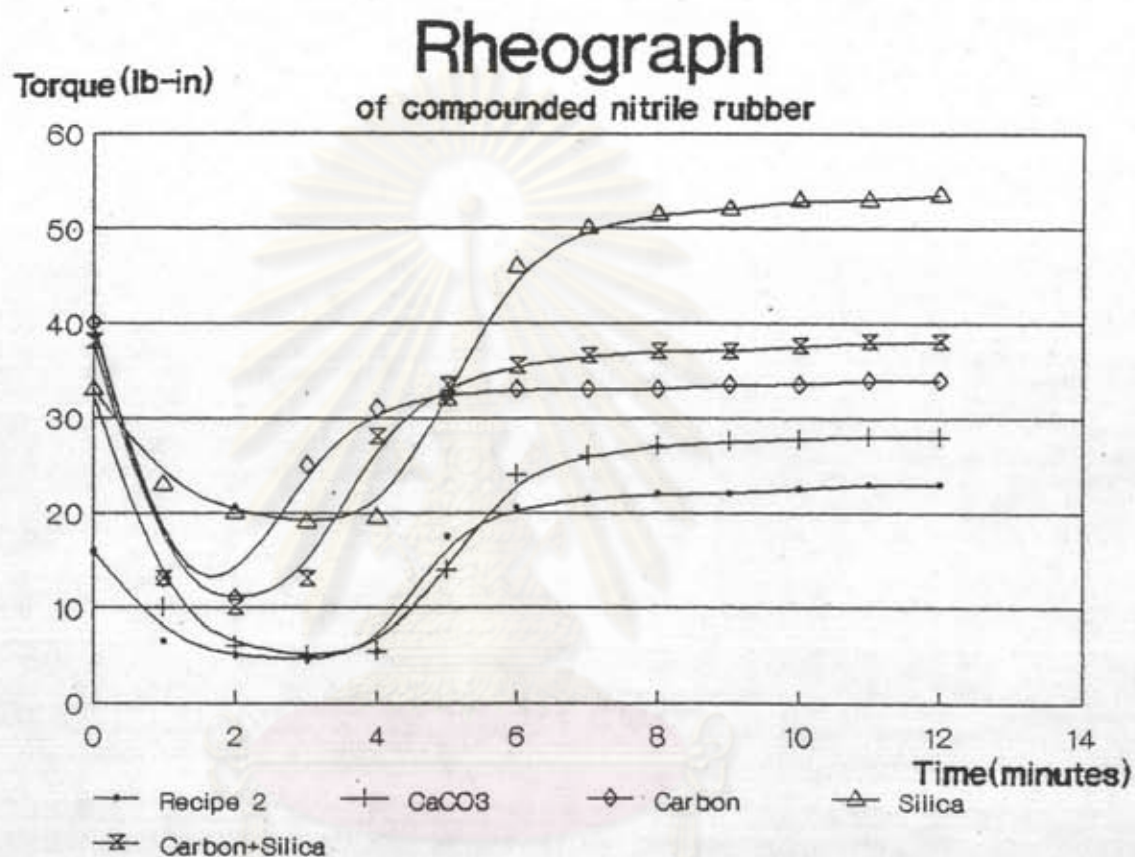   filler.

Figure 4.2 The rheograph of unfilled compounded rubbers
and filled compounded rubbers for different
types of fillers.

Table 4.1 The scorch time and cure time of compounded
rubbers.

Compounded rubber	scorch time(t_{s2}) (minutes)	cure time(t_{g0}) (minutes)
Recipe 1	5.90	8.95
Recipe 2	3.90	7.56
CaCO$_3$ filler in Recipe 2	4.00	6.75
Silica filler in Recipe 2	4.00	7.13
Carbon black filler in Recipe 2	2.10	4.20
Carbon black+silica filler in Recipe 2	2.90	5.75

From this table, carbon black filler reduces the scorch time.

4.3 Hardness measurements

Hardness of unfilled and filled PVC/NBR blends are shown in
Figures 4.3, 4.4 and in Tables C.1, C.2. From Figure 4.3 for
unfilled PVC/NBR blends (so called unfilled compounds), the hardness
values decreased with increasing amount of rubber. In addition, the
hardness values of PVC/NBR blends at 20:80 ratio of recipe 1 and
recipe 2 compounds were close to the hardness values at 40:60 ratio.
It can be seen that PVC compounds and vulcanized rubber can enhance

the hardness property because PVC compounds are stiffer than unvulcanized rubbers despite adding 40 % DOP plasticizer into PVC compounds (88 Shore A hardness for PVC compounds). Since vulcanized rubbers have more elastic property than unvulcanized rubbers, consequently vulcanized rubbers have force to resist the indentation of hardness Shore A indentor (the indentation hardness is dependent on the viscoelastic behavior of the material). The hardness of unfilled PVC/NBR blends in Recipe1 and in Recipe2 are the same tendency.

Powdered nitrile rubber(grade P83) has PVC as partitioning agent (9 phr) for avoiding agglomeration of powder. In addition, P83 is precrosslinking before mixing with PVC. Thus, the hardness values of PVC/P83 blends are higher than conventional PVC/NBR blends.

For filled PVC/NBR blends, the reinforcing fillers, silica and carbon black can increase the hardness values for all range of PVC/NBR blends composition. The inert filler ($CaCO_3$) affect the hardness values not much. There are some reasons to support these results. First, $CaCO_3$ material is soft (Mohs 3 on the hardness scale)[19] while silica is hard (Mohs 6.5-7). Secondly, the interaction between polymer and filler affect the hardness property because high interaction force (good adhesion between carbon black filler and polymer), therefore the hardness of carbon black filled compounds increases.
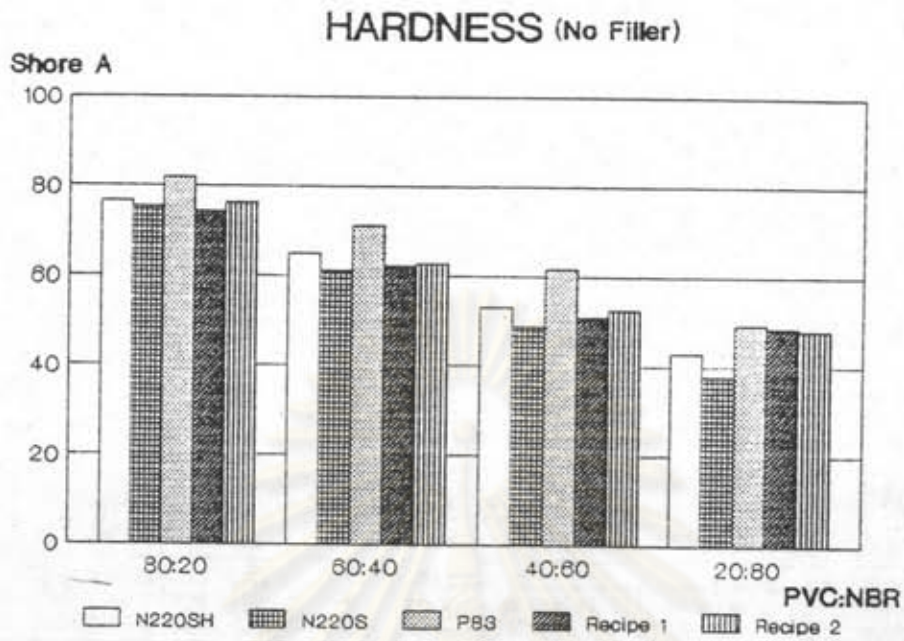
HARDNESS (No Filler)

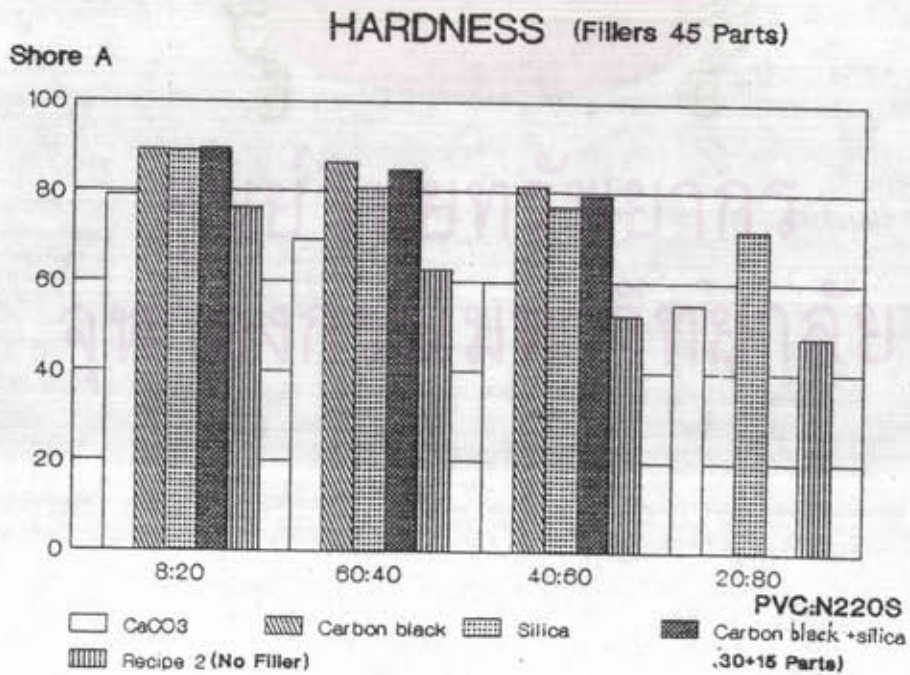Figure 4.3 Hardness of unfilled compounds.

HARDNESS (Fillers 45 Parts)

Figure 4.4 Hardness of filled compounds.

4.4 Tensile measurements

Effects of PVC/NBR blends compositions and fillers upon the mechanical properties were examined. The values of tensile strength, elongation at break and modulus are shown in Figures 4.5-4.12 and in Tables C.3- C.10.

4.4.1 Modulus For unfilled compounds, the modulus at 100 % and 300 % elongation of polymer blends increase with increasing PVC/NBR ratio because PVC compounds are characterized to be self-reinforcing in polymer blends (this behavior is similar to the hardness values). Modulus at 100 % and 300% elongation of PVC/P83 blends are higher than that of conventional PVC/NBR blends. Modulus at 100% and 300% elongation of PVC/NBR blends in Recipe1 and in Recipe2 are the same tendency.

For filled compounds, modulus at 100% elongation of carbon black filled compounds presented the highest level of reinforcement while silica and $CaCO_3$ filled compounds show lower level of reinforcement. For carbon black/silica mixed filled compounds, the modulus values are between those of carbon black filled and silica filled compounds. At 300% elongation, there are some interesting results, the modulus of carbon black and carbon black/silica filled compounds at high rubber content of 40:60 ratio of PVC/NBR blends are higher than that of 60:40 ratio. This can be explained that the compounded rubber and carbon black filler have high interaction which may occur from bound rubber between rubber and carbon black filler while this effect is very small for silica filler and do not occur for $CaCO_3$ filler.

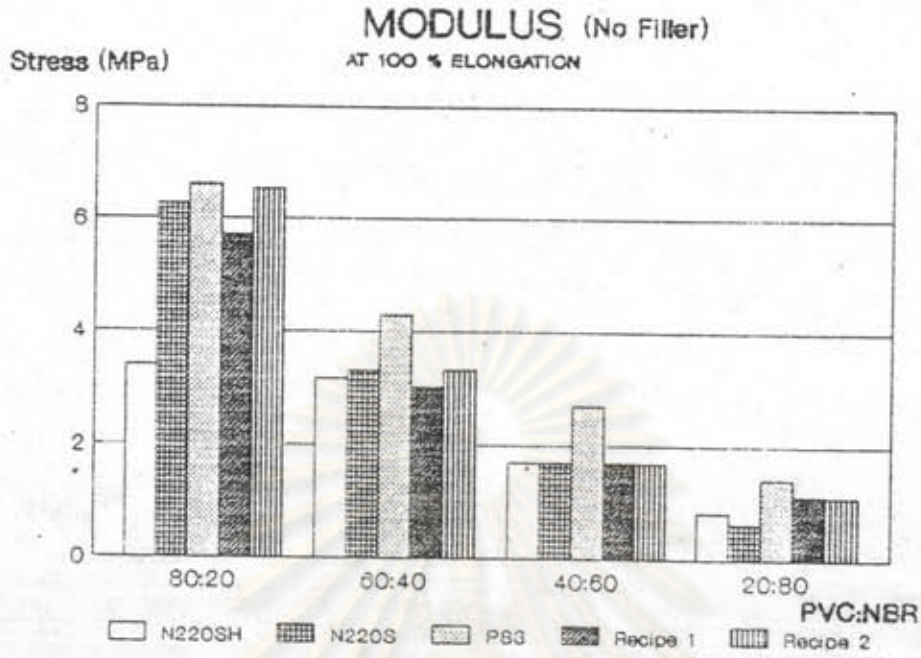## MODULUS (No Filler)
AT 100 % ELONGATION

Stress (MPa)

Figure 4.5 Modulus at 100 % elongation of unfilled compounds.

MODULUS (Fillers 45 Parts)
AT 100 % ELONGATION

Stress (MPa)
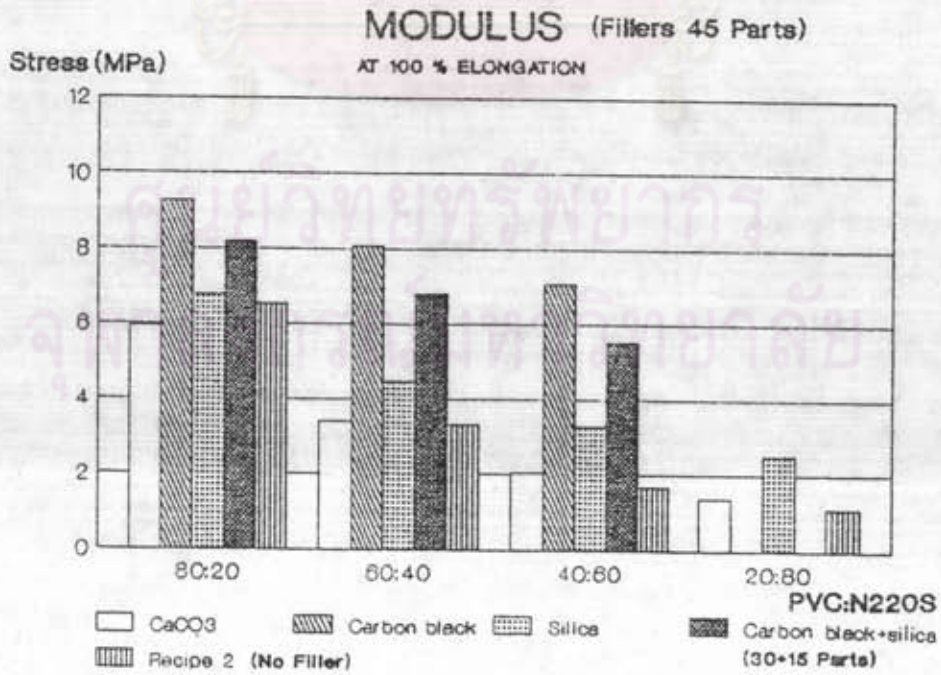
Figure 4.6 Modulus at 100 % elongation of filled compounds.

MODULUS (No Filler)
AT 300 % ELONGATION

STRESS(MPa)
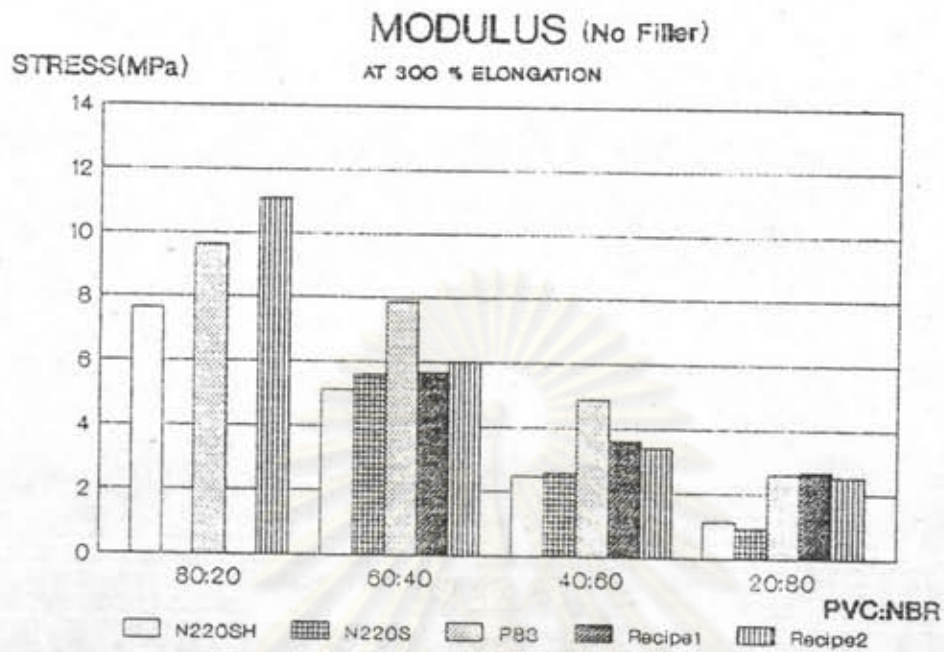
Figure 4.7 Modulus at 300 % elongation of unfilled compounds.

MODULUS (Fillers 45 Parts)
AT 300 % ELONGATION

Stress (MPa)
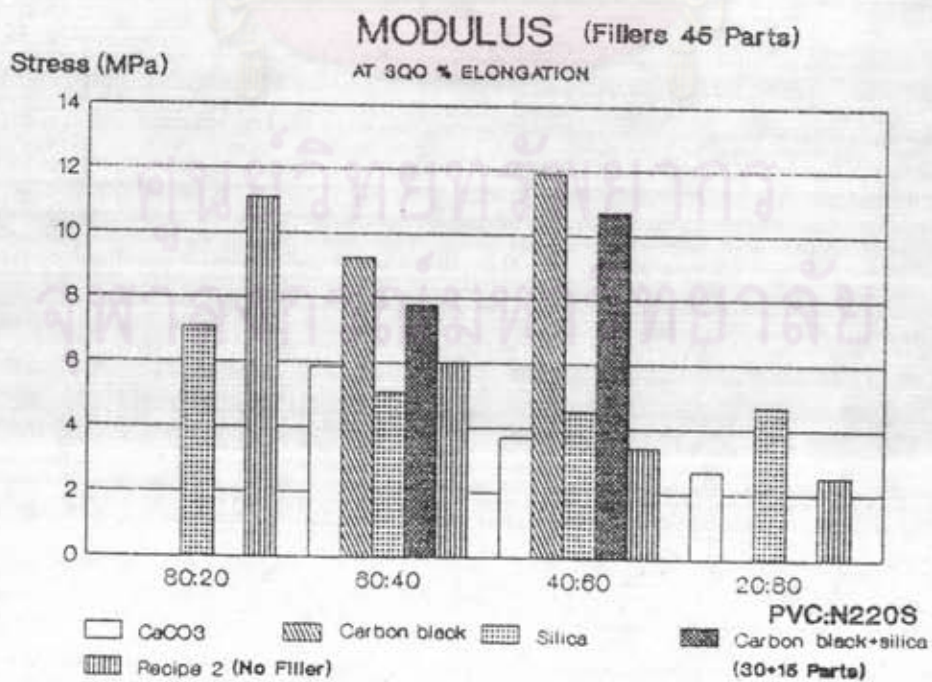
Figure 4.8 Modulus at 300 % elongation of filled compounds.

4.4.2 Tensile strength and elongation at break

For unfilled PVC/NBR(unvulcanized rubber) blends at high rubber content, tensile strength is low and elongation at break is high compared with unfilled PVC/NBR(vulcanized rubber) blends. From these results, unvulcanized rubbers improve elongation at break of polymer blends but deteriorate the tensile strength of material because unvulcanized rubbers are soft and have higher plasticity than vulcanized rubbers. Therefore, unvulcanized rubbers can flow and extend more easily than vulcanized rubbers.

For unfilled compounds, PVC/NBR blends of vulcanized rubber (Recipe1, Recipe2), tensile strength and elongation at break increase with increasing rubber content up to 40:60 PVC/NBR ratio. But at 20:80 ratio, the tensile strength and elongation at break decrease. This can be explained that there is good adhesion between PVC and vulcanized rubber at low rubber content but poor adhesion at high rubber content. Because the vulcanized rubber particles disperse in PVC matrix phase (plastic phase) due to dynamic vulcanization, consequently, at high rubber content, the reverse phase can occur, thus PVC phase disperses in vulcanized rubber matrix phase and interaction force between rubber and plastic phases is low.

In study of the tensile strength and elongation at break of filled PVC/NBR blends, two cases are considered. The first case is PVC/NBR blends at high PVC content (80:20 ratio of PVC:NBR blend). Nielsen (1966)[6] had sought to include stress-strain behavior as a function of filler concentration in the plastic material for the cases of (a) perfect adhesion between polymer and filler (b)no
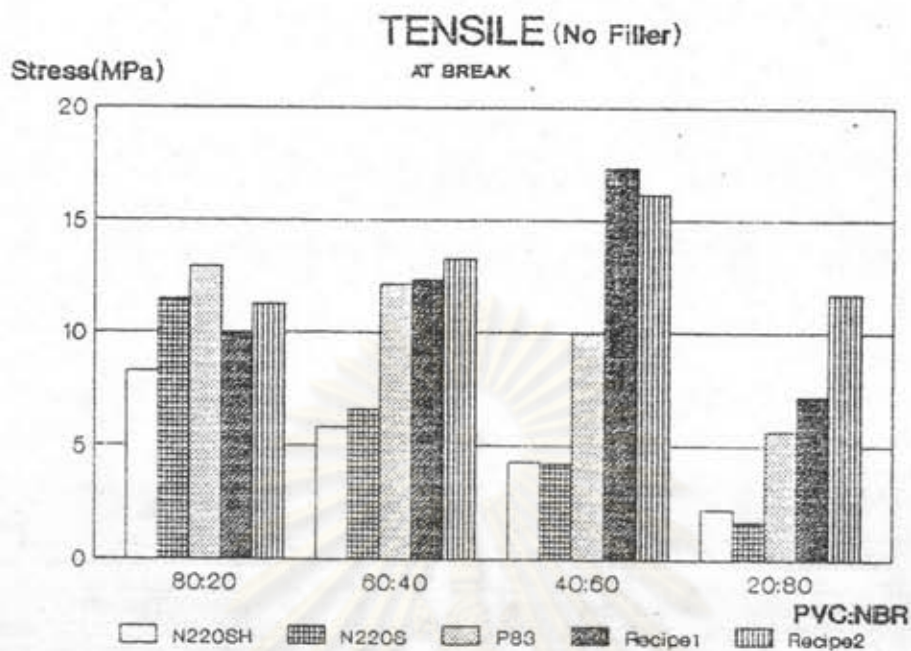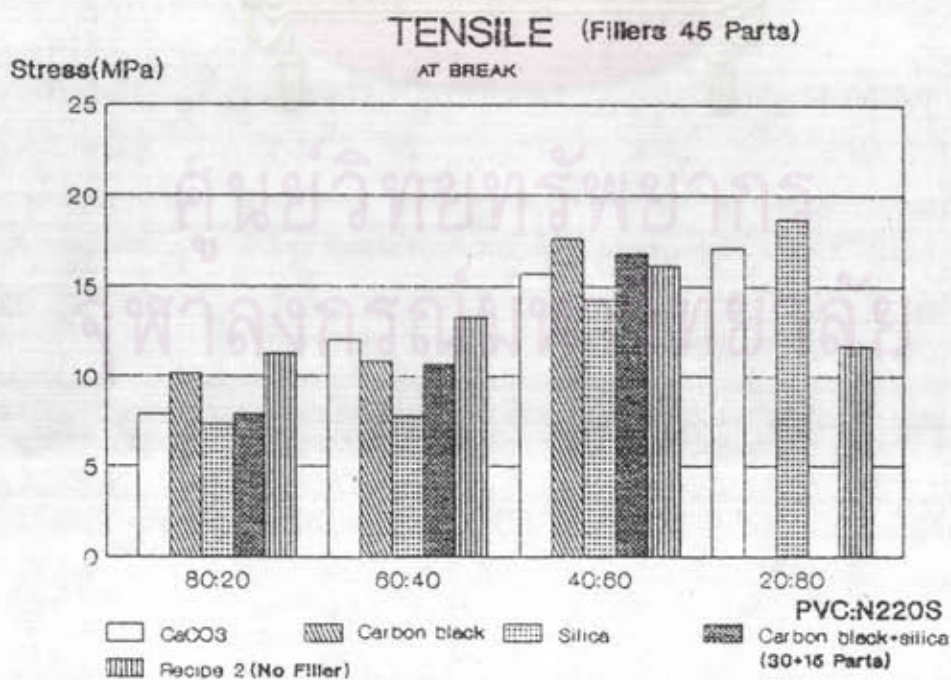
TENSILE (No Filler)

Stress(MPa) AT BREAK

Figure 4.9 Tensile strength of unfilled compounds.

TENSILE (Fillers 45 Parts)

Stress(MPa) AT BREAK

Figure 4.10 Tensile strength of filled compounds.

Elongation (No Filler)

Elongation(%)

AT BREAK

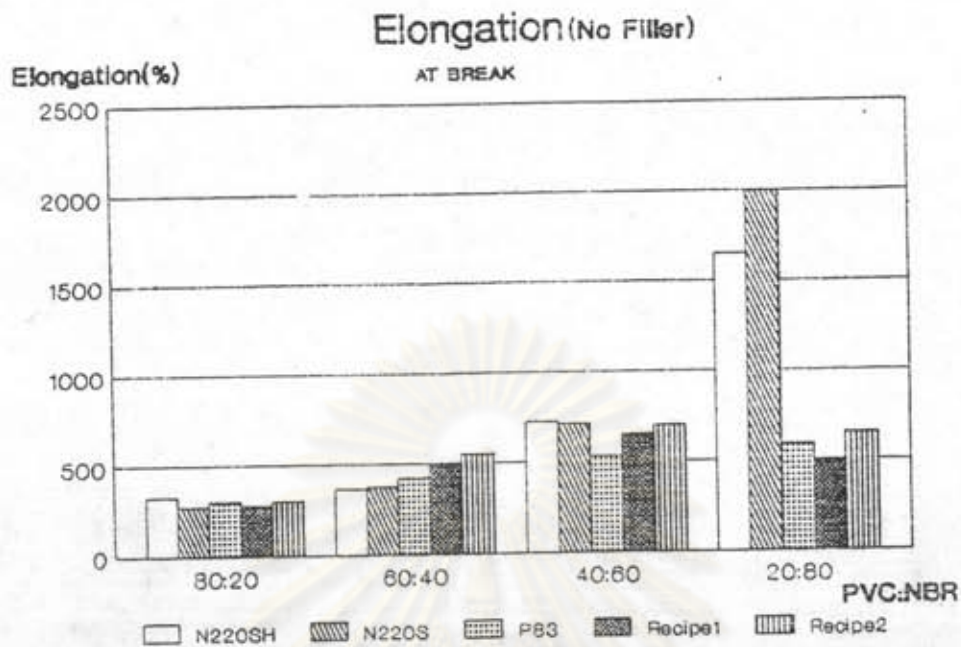Figure 4.11 Elongation at break of unfilled compounds.

Elongation (Fillers 45 Parts)

Elongation(%)
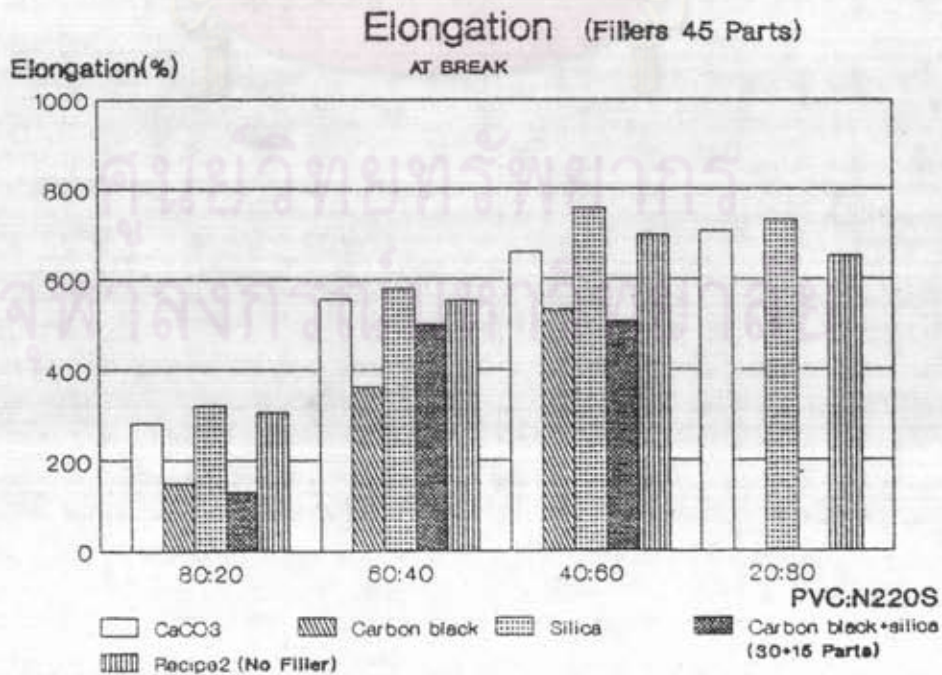
AT BREAK

Figure 4.12 Elongation at break of filled compounds.

adhesion between them. Assuming perfect adhesion, Nielsen calculated the elongation at break of the plastic (in the composite) relative to the overall elongation at break of the filled specimen to be

$$\varepsilon_{B(filled)}/\varepsilon_{B(unfilled)} \quad = \quad 1 - v_f^{1/3} \quad \text{for perfect adhesion}$$

where v_f = volume fraction of filler

The curve of this function was plotted in Figure A.1 (lower curve). For tensile strength, the curves of adhesion are given by Kerner's equation(1956)[6] or Eilers' equation(1941) and the curve of no adhesion is given by Nielsen's equation as illustrated in Figure A.2.

The tensile strength of carbon black filled compounds at 80:20 ratio is high but the elongation at break is low compared with silica and $CaCO_3$ filled compounds. It can be concluded that carbon black compounds have good adhesion between the carbon black filler and the polymer blends while low adhesion occurs between the silica or $CaCO_3$ fillers and the polymer blends.

The second case is PVC/NBR blend at high NBR content(40:60 ratio of PVC/NBR blend). The tensile strength of carbon black filled compounds are higher than $CaCO_3$ and silica filled compounds but the elongation at break of carbon black filled compounds is less. Because in general, highly reinforced elastomers are less extensible, but have a higher stress to break than less reinforced elastomers[6]. These results are the similar manner in PVC/NBR blends at 80:20

ratio.

However, the tensile strength and elongation at break of filled compounds increased with increasing rubber content for all range of PVC/NBR blends (except carbon black filled and carbon black/silica filled compounds at 20:80 ratio of PVC/NBR blends because of no data). The evidents which support these results are electron micrographs from Figure 4.24 to Figure 4.29. Although these fracture surfaces were taken from the tear test, the fracture surfaces from tension test should be in the similar manner. From Figure 4.24, Figure 4.26 and Figure 4.28 , at high PVC content, the fracture surfaces occur due to brittleness while at low PVC content, from Figure 4.25, Figure 4.27 and Figure 4.29, the fracture surfaces occur as ductile material. The force-extension curves of filled compounds of 80:20 and 40:60 PVC/NBR for different fillers are shown in Figures B.1 and B.2, respectively.

4.5 Tear measurements

Effects of PVC/NBR blends compositions and fillers on tear strength are illustrated in Figures 4.13, 4.14 and in Tables C.11, C.12. For unfilled compounds, the tear strengths of PVC/NBR blends decrease with decreasing PVC content. The explanations of tear strength are the same as mentioned earlier for modulus at 100 % elongation of unfilled compounds. For filled compounds, the tear strengths of carbon black filled compounds are the highest values. The explanations are the same as mentioned earlier for modulus at 100 % and 300 % elongation of filled compounds.
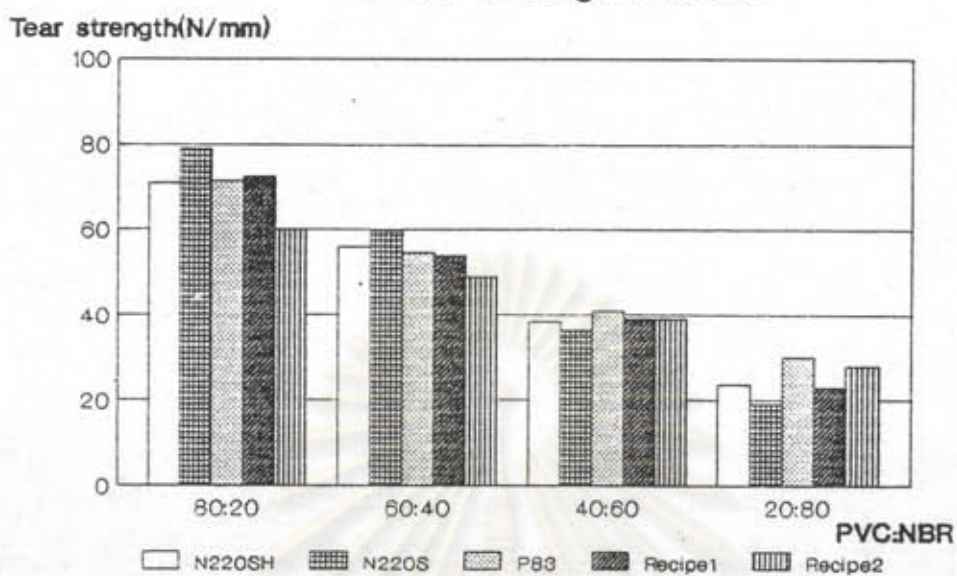
Tear Strength (No Filler)

Tear strength(N/mm)

Figure 4.13 Tear strength of unfilled compounds.

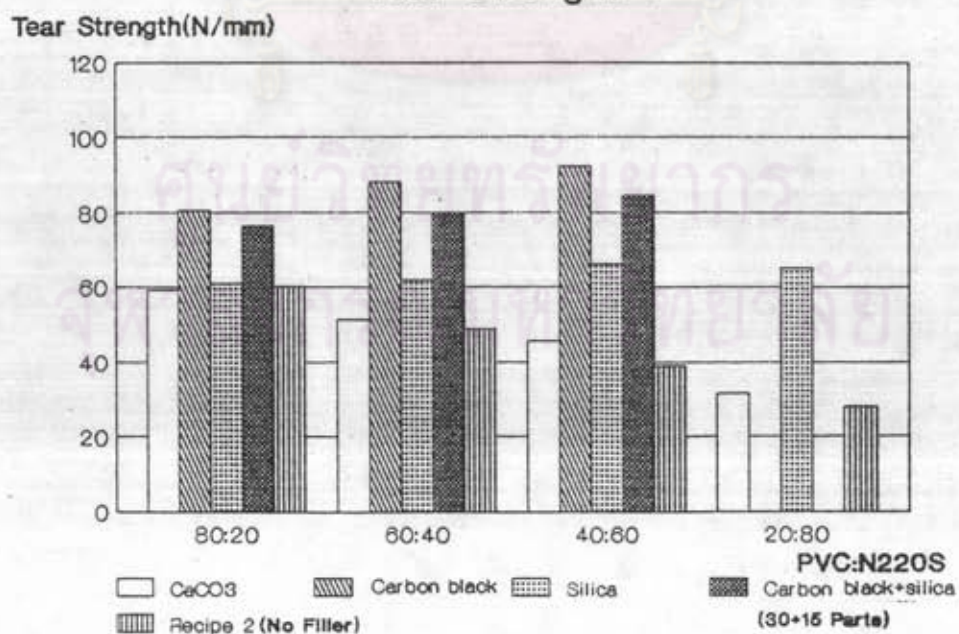## Tear Strength (Fillers 45 Parts)

Tear Strength(N/mm)

Figure 4.14 Tear strength of filled compounds.

4.6 Liquid resistance measurements

The changes in mass (%) from liquid resistance measurements for filled and unfilled PVC/NBR blends are shown in Figures 4.15, 4.16 and in Tables C.13, C.14. For unfilled compounds, the oil resistance can be measured by oil swell(%), the lower values of oil swell, the higher oil resistance. At high PVC content, the PVC can enhance the oil resistance of PVC/NBR blends although NBR is used in oil resistance application. This result confirms one of the advantages of PVC in PVC/NBR blends. In addition, the vulcanized rubber compounds improve the oil resistance. The reason is that for specific solvent, higher the crosslink density of the rubber gives lower the swelling property. This relationship is quantitatively expressed by the Flory-Rehner equation[3].

For filled compounds, carbon black and silica filled compounds exhibits higher oil resistance than $CaCO_3$ filled compounds. It can be seen that the reinforcing filler can improve the oil resistance of polymer blends because of the restriction of the swelling of the polymer matrix due to the presence of reinforcing filler[3]. For inert filler, $CaCO_3$ do not have interaction with polymer, thus, its compound has more void fraction than the carbon black or silica filled compounds, finally, oil can penetrate through the surface of specimens. The oil resistances of silica filled compounds are higher than carbon black filled compounds. It can be explained that carbon black filler is organic filler which is compatible with organic solvent while silica filler is inorganic filler, thus, the carbon black filled compounds give higher oil swell than silica filled compounds. However, the carbon black is
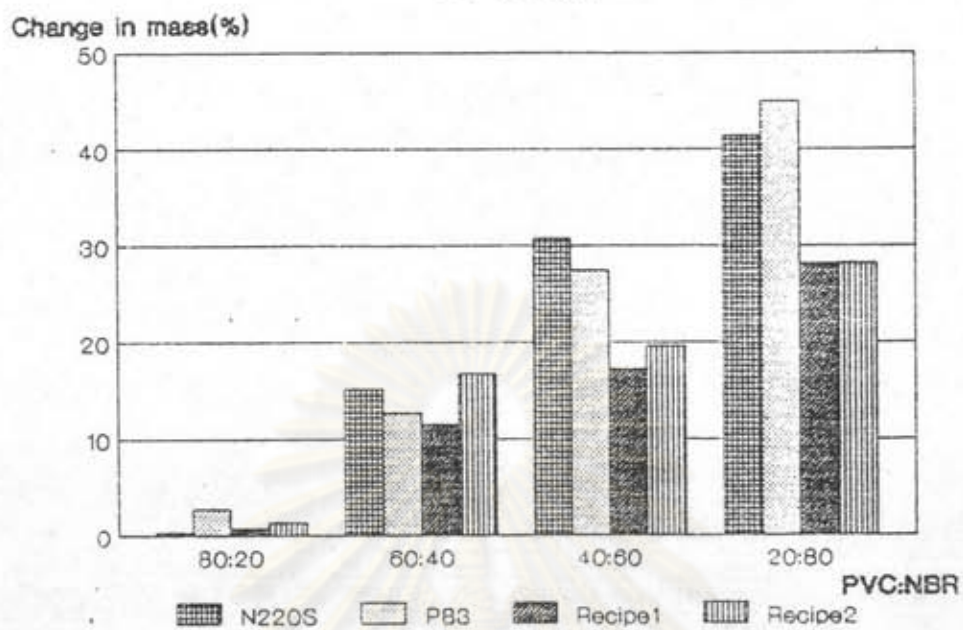
Oil Swell (No Filler)

Change in mass(%)

Figure 4.15 Oil resistance of unfilled compounds.

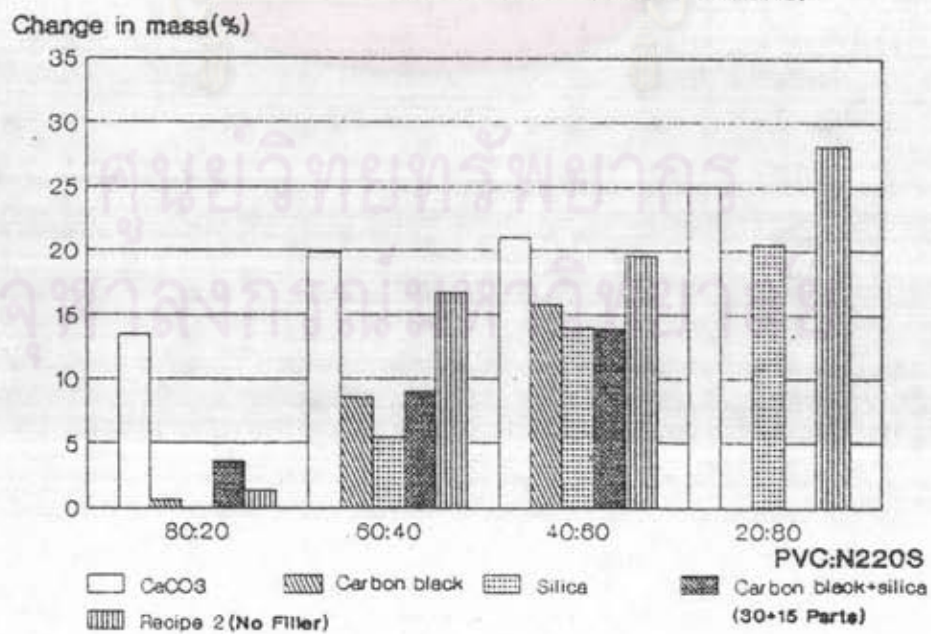## Oil Swell (Fillers 45 Parts)

Change in mass(%)

Figure 4.16 Oil resistance of filled compounds.

reinforcing filler and has interaction with rubber as bound rubber. From these results, the oil resistance of carbon black filled compounds is higher than that of CaCO3 filled compounds and unfilled compounds.

4.7 Abrasion resistance measurements

The abrasion resistances expressed as volume loss of filled and unfilled compounds are shown in Figures 4.17, 4.18 and Tables C.15,C.16. For unfilled compounds, the abrasion resistances of unvulcanized rubber compounds are very low (high volume loss), particularly, at high rubber content while the abrasion resistances of vulcanized rubber compounds are approximately constant. It can be explained that the unvulcanized rubber has more plasticity property and can be deformed more easily than vulcanized rubber, consequently, the mass on the surface of specimens can be lost by abrasive surface more easily.

For filled compounds, the abrasion resistances of carbon black filled compounds are higher than silica and $CaCO_3$ filled compounds, respectively because carbon black and silica fillers are reinforcing fillers. In addition, the carbon black and rubber have high interaction force and form bound rubber, thus, the carbon black filled compounds can resist to the abrasive surface better than the silica filled compounds. However, the unfilled compounds have the best abrasion resistances in all range of compounds. These results may be described that unfilled compounds are more resilient and more elastic than filled compounds, thus, unfilled compounds did not lose mass due to the abrasive surface.
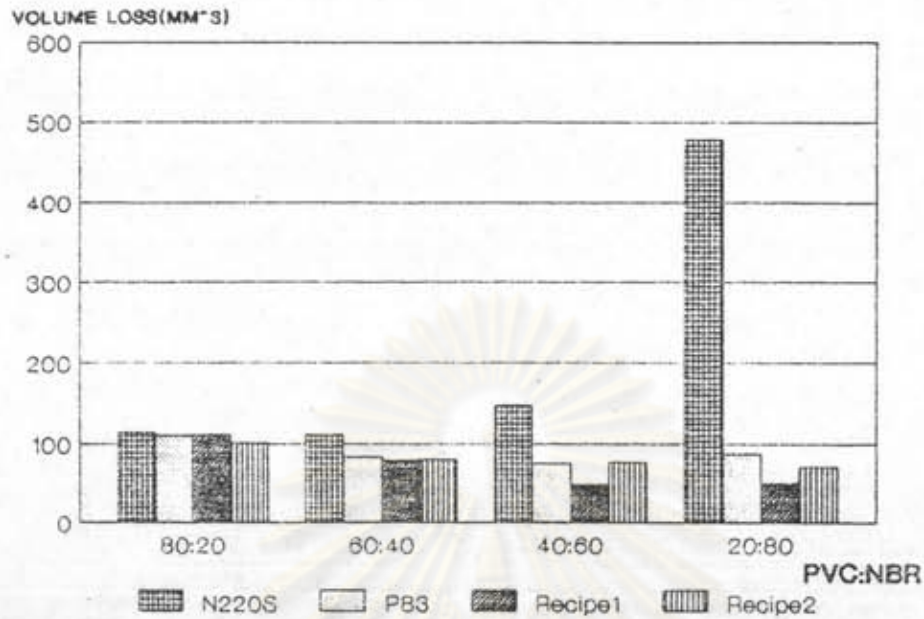
ABRASION RESISTANCE (No Filler)

VOLUME LOSS(MM^3)

Figure 4.17   Abrasion resistance of unfilled compounds.

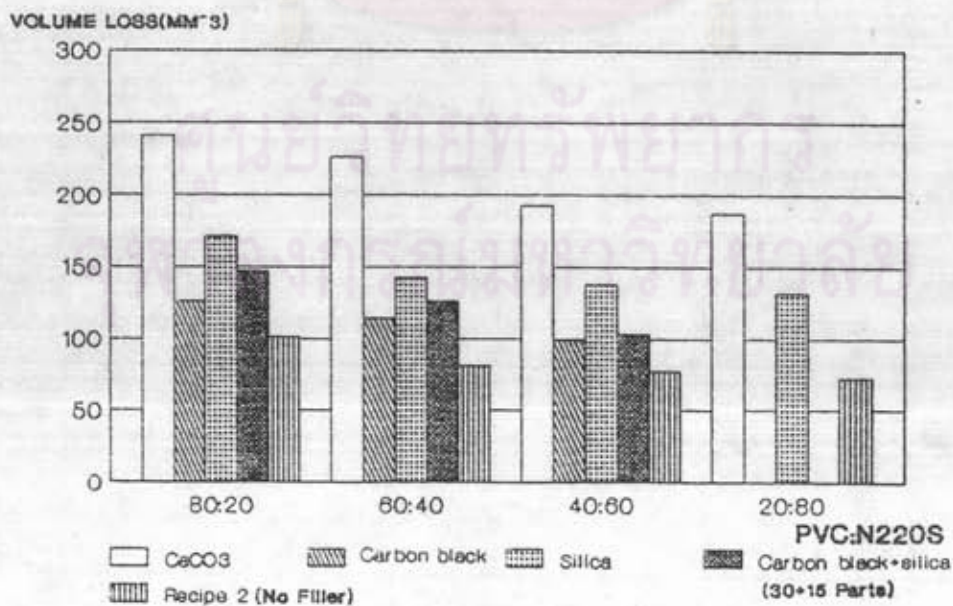## ABRASION RESISTANCE (Fillers 45 Parts)

VOLUME LOSS(MM^3)

Figure 4.18   Abrasion resistance of filled compounds.

4.8 Electron microscopic study

The electron micrograph (Figures 4.19 and 4.20) show that the rubber phase disperses in plastic phase(matrix phase) and particle sizes of unvulcanized rubber and vulcanized rubber are approximately $0.3 - 0.9\mu$m. and rubber particles look like eliptical shape.

From Figure 4.21 (a),(b) show the large particle sizes of $CaCO_3$ filler and the sizes are different. From Figure 4.22 (a),(b) and Figure 4.23 (a),(b), carbon black and silica fillers show the same characteristic which are the aggregation of the small particles (0.03μm for carbon black filler and 0.02μm for silica filler). From Figure 4.24, 4.26 and 4.28, the fracture surfaces of tear specimen of PVC/NBR blends at high PVC content (80:20, PVC/NBR ratio) indicate the brittle fracture and show less elongation than blends at low PVC content or high rubber content. From Figure 4.25, 4.27, 4.29, the fracture of PVC/NBR blend at 40:60 is in a ductile fashion.

4.9 Polarized microscopic study

The polarized microscope was used to observe the dispersion of $CaCO_3$ and silica filler in polymer phase. From Figure 4.30 to Figure 4.33, show that $CaCO_3$ filler can disperse in PVC and nitrile rubber homogenously both at high and low PVC content while silica filler can not disperse homogenously. At high rubber content, agglomeration of silica filler in rubber phase may occur but not appear in plastic phase, consequently, the color of rubber phase is clear.

4.10 Differential scanning calorimetry measurements

Figures 4.34 and 4.35 show the DSC curves of PVC/NBR blends. These figures show two glass transition temperatures(T_g) (T_g of PVC approximately 80 ± 10 $^{\circ}$C, T_g of NBR approximately -20 ± 10 $^{\circ}$C) which mean that the PVC/nitrile rubber blends can not be complete miscible. The peak of nitrile rubber is not deep compared with the peak of PVC despite high rubber content. These results can not be explained clearly. Two peaks occured from the difference of their thermal conductivities and heat capacities. However, T_g of PVC is observed clearly while T_g of nitrile rubber is hardly seen.
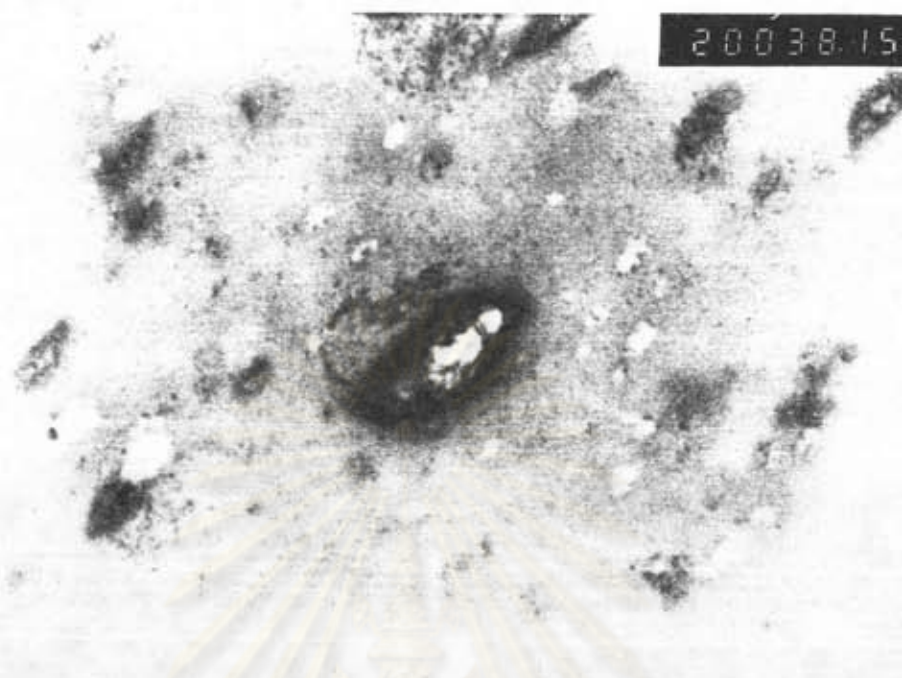
Figure 4.19 Transmission electron micrograph of an ultrathin
section of PVC/unvulcanized nitrile rubber blends
at 60:40 ratio.(x 30,000)
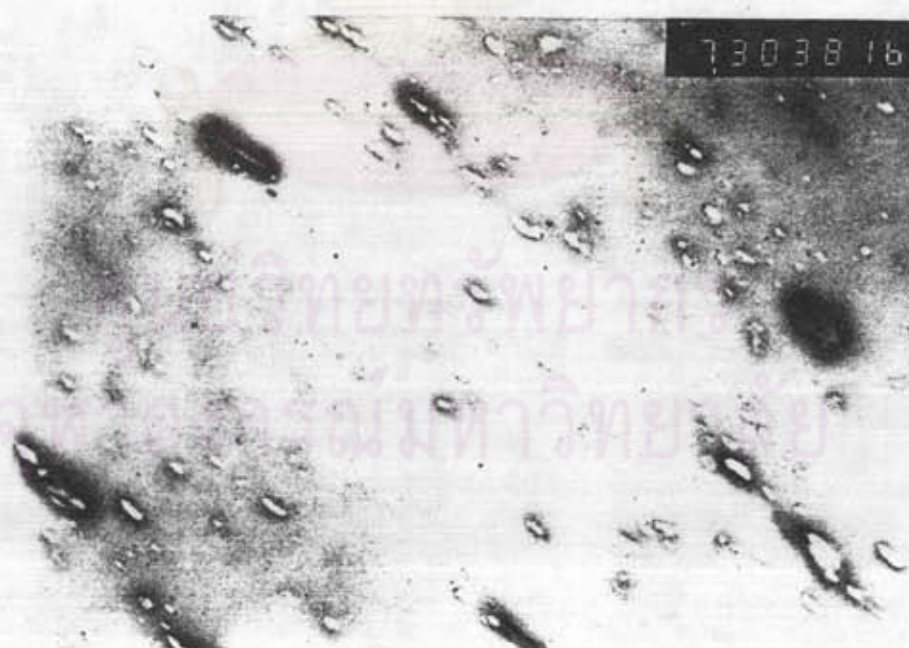
Figure 4.20 Transmission electron micrograph of an ultrathin
section of PVC/vulcanized nitrile rubber blends
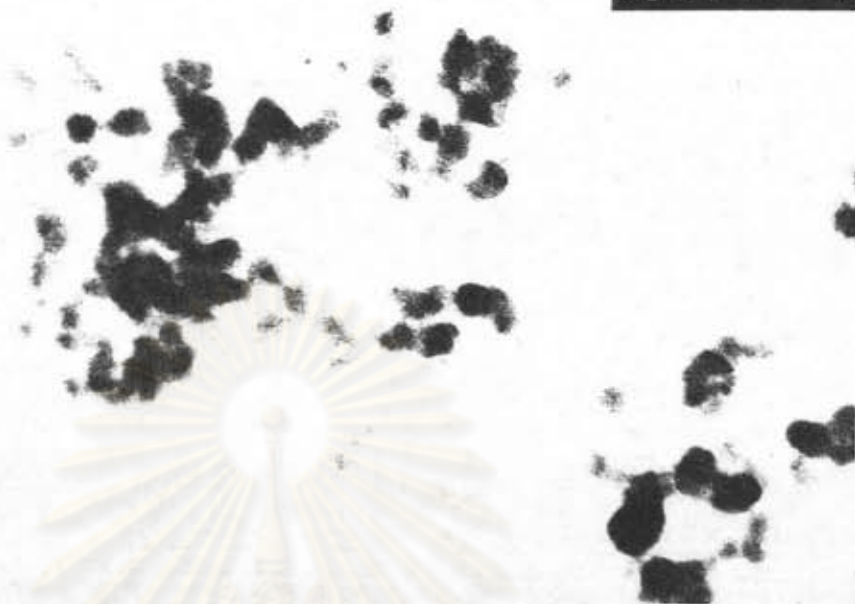at 60:40 ratio.(x 10,950)

10003885
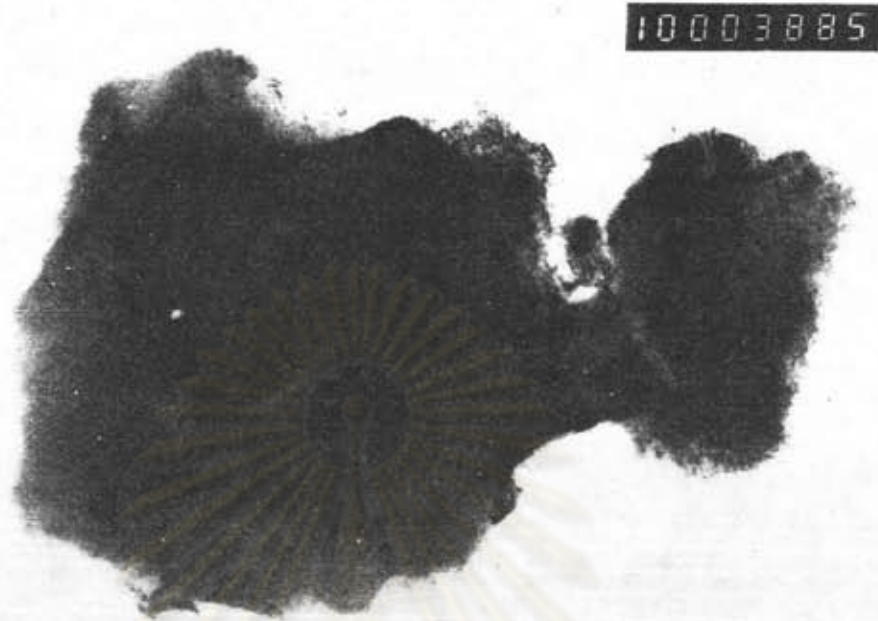
Figure 4.21(a) Transmission electron micrograph of CaCO₃ filler.
(x 150,000)

6003883

Figure 4.21(b) Transmission electron micrograph of CaCO₃ filler.
(x 9,000)

Figure 4.22(a)   Transmission electron micrograph of carbon black
filler.(x 150,000)

Figure 4.22(b)   Transmission electron micrograph of carbon black
filler.(x 55,500)

Figure 4.23(a) Transmission electron micrograph of silica filler.

(x 150,000)

Figure 4.23(b) Transmission electron micrograph of silica filler.
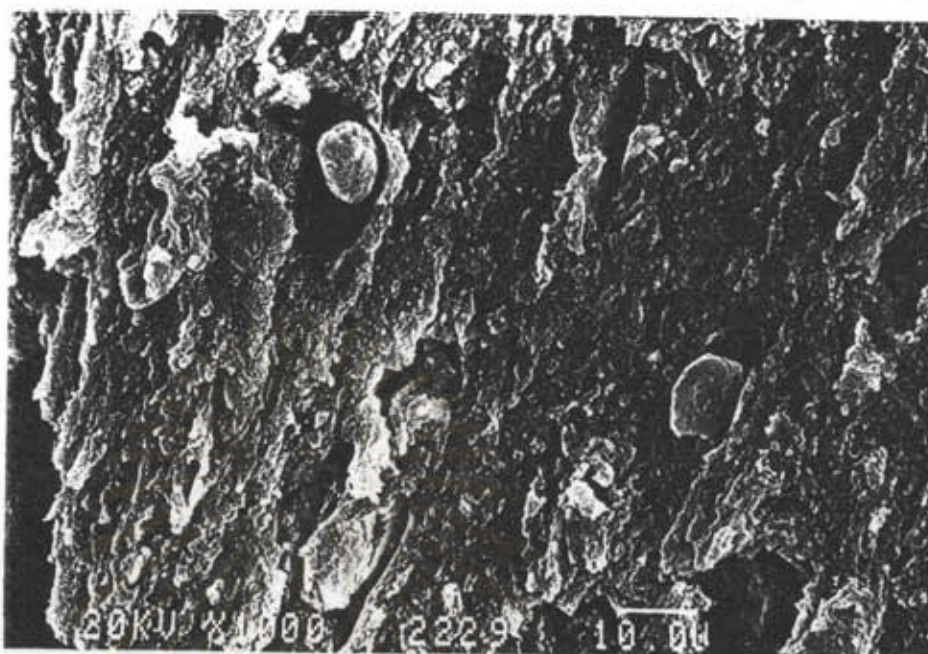
(x 45,000)

Figure 4.24 Scanning electron micrograph of fracture surface in tear
test of CaCO$_3$ filled compound at 80:20 ratio of PVC/NBR
blends.
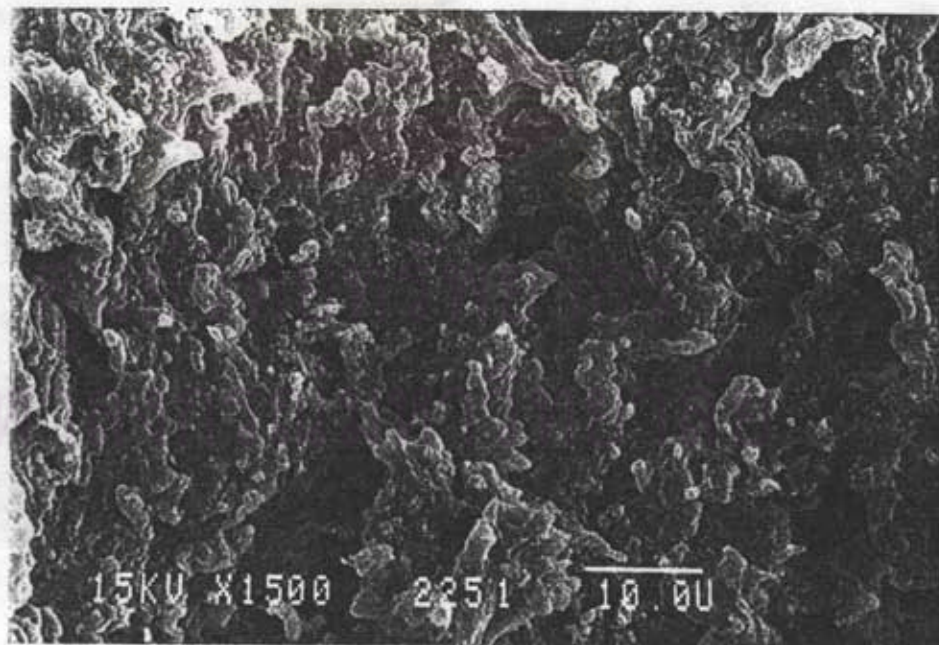
Figure 4.25 Scanning electron micrograph of fracture surface in tear
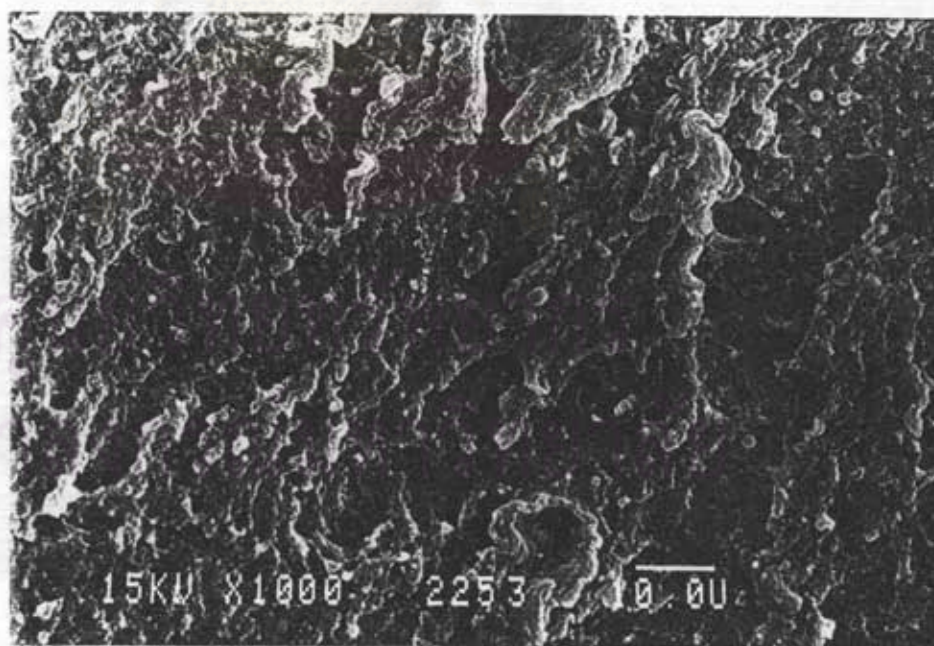test of CaCO$_3$ filled compound at 40:60 ratio of PVC/NBR
blends.
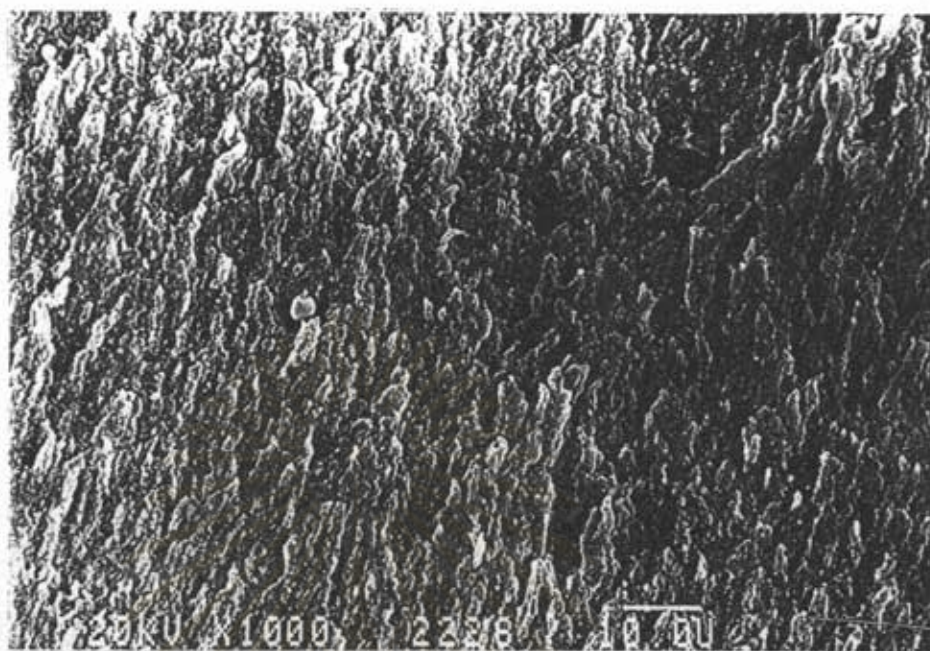
Figure 4.26 Scanning electron micrograph of fracture surface in tear
test of carbon black filled compound at 80:20 ratio of
PVC/NBR blends.
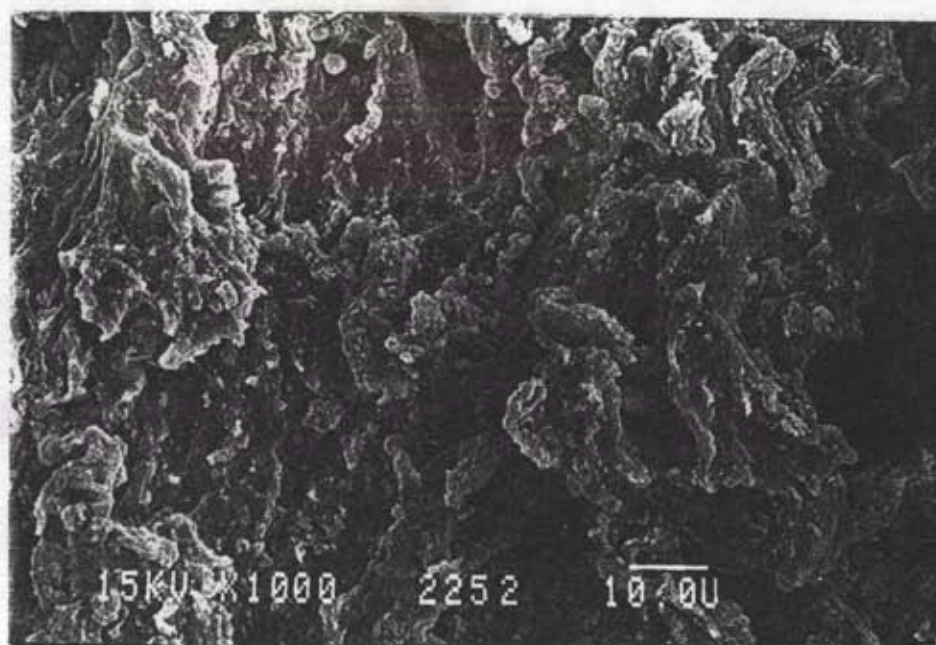
Figure 4.27 Scanning electron micrograph of fracture surface in tear
test of carbon black filled compound at 40:60 ratio of
PVC/NBR blends.

Figure 4.28 Scanning electron micrograph of fracture surface in tear
test of silica filled compound at 80:20 ratio of PVC/NBR
blends.

Figure 4.29 Scanning electron micrograph of fracture surface in tear
test of silica filled compound at 40:60 ratio of PVC/NBR
blends.
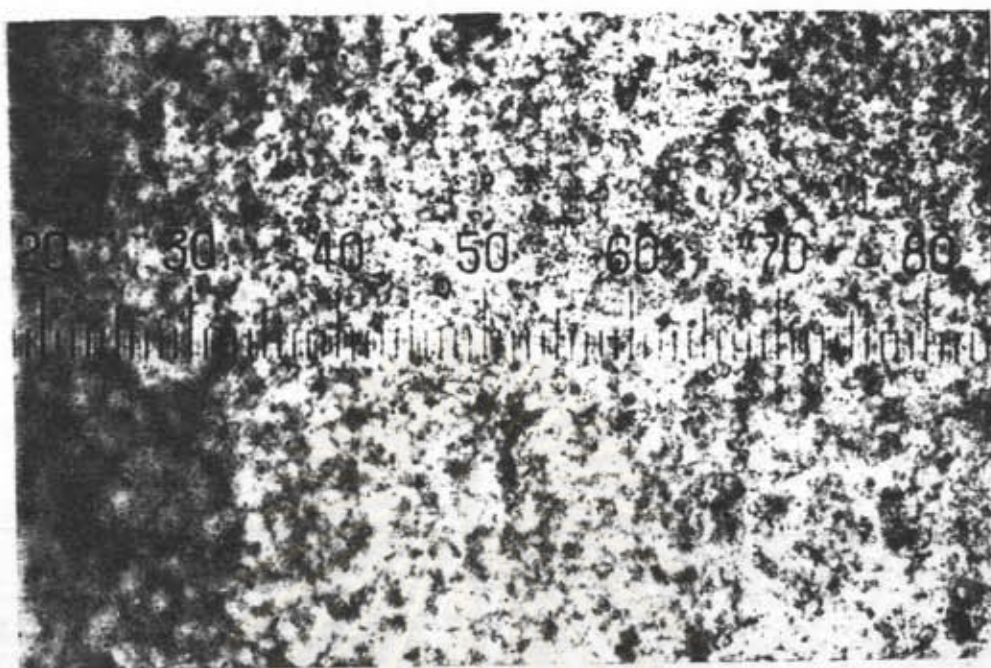
Figure 4.30 Polarized micrograph of thin layer of CaCO$_3$ filled
PVC/vulcanized NBR blends at 80:20 ratio.
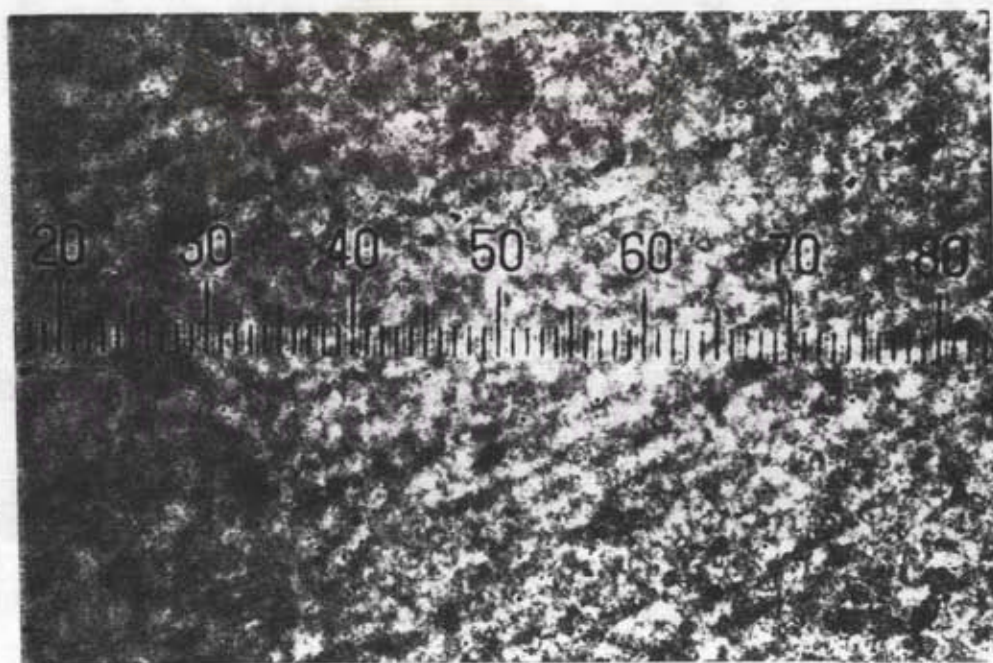(Magnification x 100, at the 10th degree of analyzer)

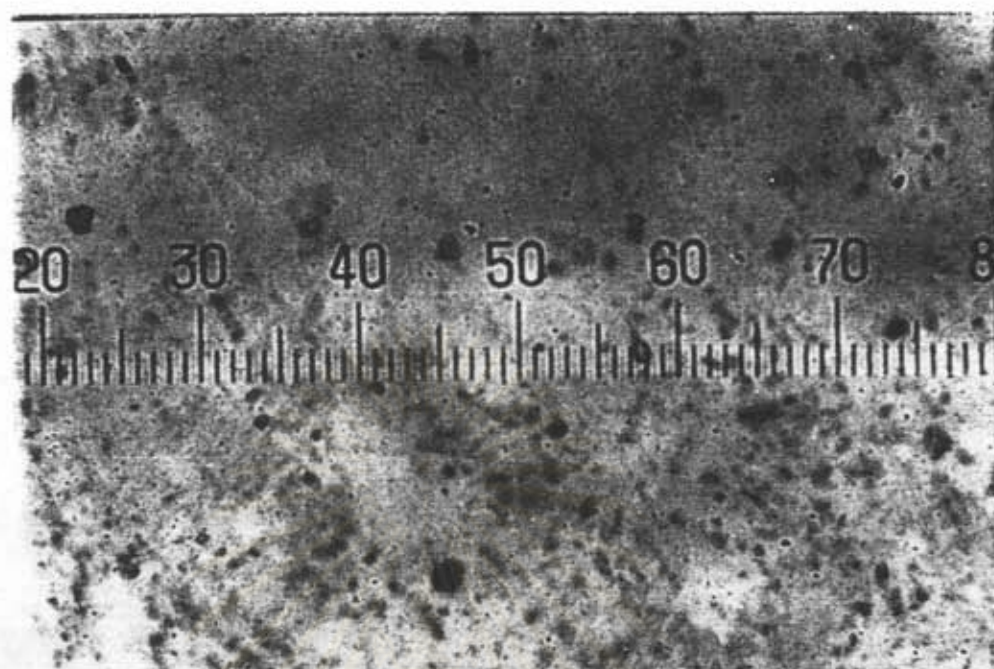Figure 4.31 Polarized micrograph of thin layer of CaCO$_3$ filled
PVC/vulcanized NBR blends at 20:80 ratio.
(Magnification x 100, at the 10th degree of analyzer)

Figure 4.32   Polarized micrograph of thin layer of silca filled
              PVC/vulcanized NBR blends at 80:20 ratio.
              (Magnification x 100, at the 10th degree of analyzer)
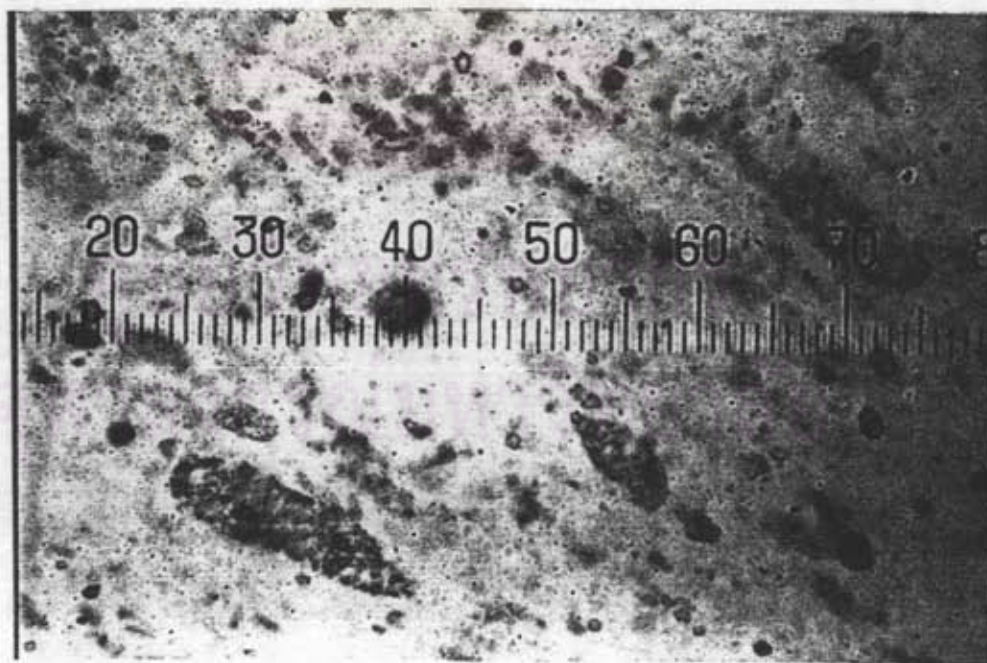

Figure 4.33   Polarized micrograph of thin layer of silica filled
              PVC/vulcanized NBR blends at 20:80 ratio.
              (Magnification x 100, at the 10th degree of analyzer)
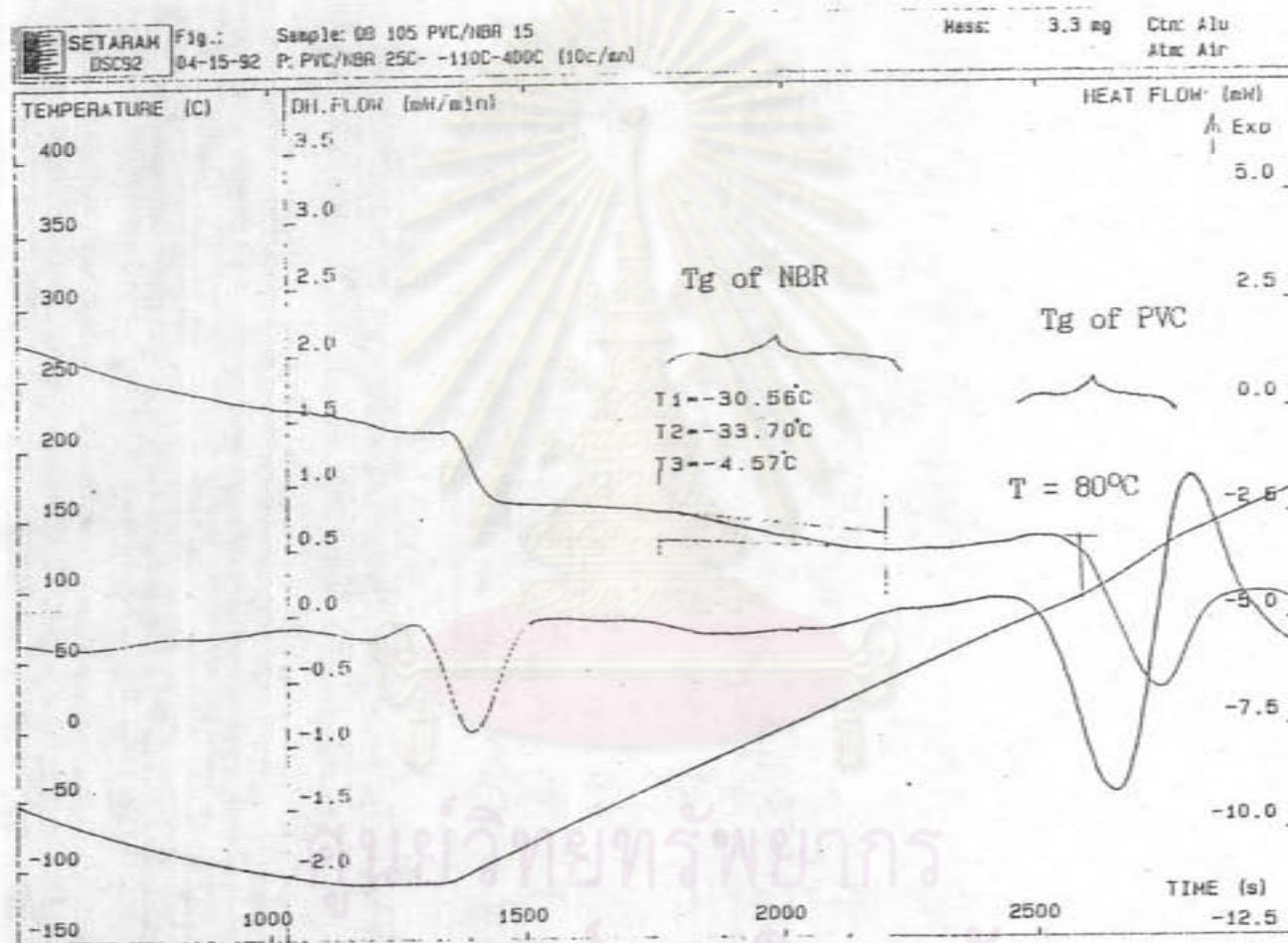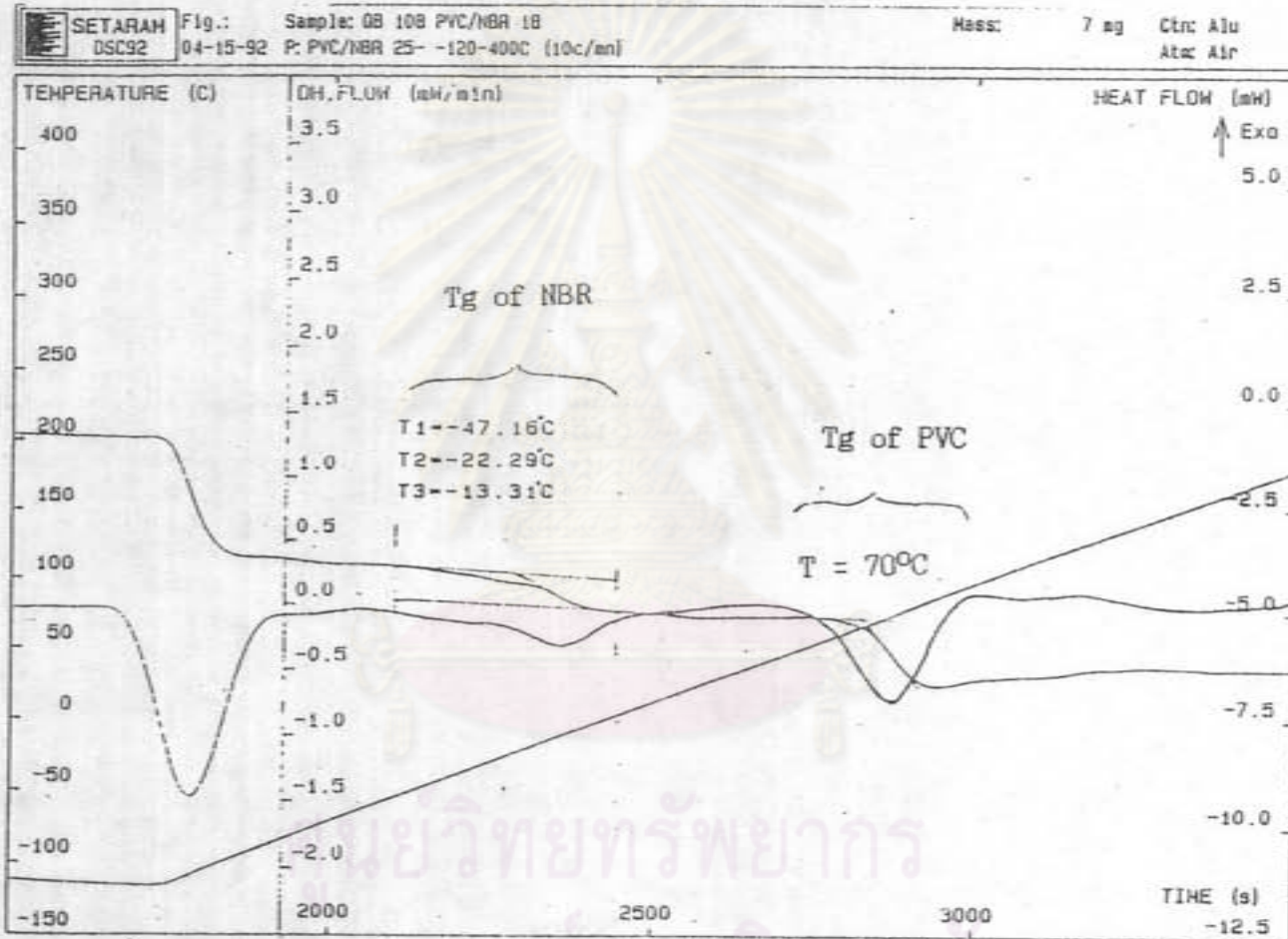
Figure 4.34 DSC curve of PVC/NBR blends at 80:20 ratio.

Figure 4.35 DSC curve of PVC/NBR blends at 20:80 ratio.