

CHAPTER IV

RESULTS AND DISCUSSION

4.1 CTAB adsorption on clay and surface characterization

The CTAB adsorption isotherm on clay is shown in figure 4.1. The isotherm presented the characteristics of region 2, 3 and 4. The slope of isotherm is greater than 1 from a concentration of CTAB in the aqueous solution of 600 μmolar to a concentration of 1,500 μmolar . This suggest that the surfactant bilayer occur. From the plateau region data, the maximum adsorption of CTAB on clay is approximately 85 $\mu\text{moles/g}$.

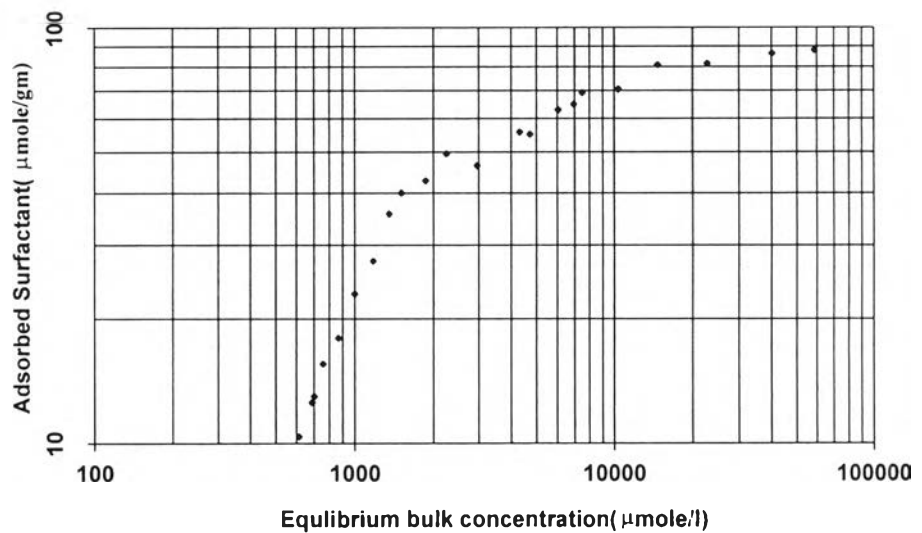


Figure 4.1 Adsorption Isotherm of CTAB on Clay.

The surface modification has an effect on clay physical properties, including BET N_2 surface area, pore volume and mean agglomerate particle

size as shown in table 4.1. The in-situ polymerization of styrene-isoprene onto the clay surface reduces nitrogen BET surface area and increases the mean agglomerate particle size. The increment of mean agglomerate particle size may be resulted from the polymer forming on the surface or the aggregates being joined by polymer bridges. Another reason may be attributed to the reprocessing of modified clay such as washing, drying and regrinding steps. The changing in pore volume is not followed the anticipation which the pore volume should be reduced after modification process. This may be due to the characteristic of clay which has low surface area and pore volume. There is no appearance simple explanation for this trend.

Table 4.1 Characteristics of Unmodified and Modified Clays

CLAY	BET Surface area(m ² /g)	Mean agglomerate particle size(μm)	Pore volume (cm ³ /g)	% Carbon
CONTROL	4.10	4.36	0.0003	0.03
SIC # 1	3.44	4.43	0.0010	0.53
SIC # 2	3.69	5.01	0.0003	0.44
SIC # 3	3.27	5.02	0.0003	0.48
SIC # 4	3.80	4.86	0.0004	0.34
SIC # 5	3.60	4.55	0.0008	0.45

The effect of the modification process on the clay surface is also presented from the scanning electron micrograph in figure 4.2-4.7 for unmodified clay and all five modified clay. The SEM micrographs showed an increase in particle agglomeration. However, they are no other obvious changes in clay surfaces.

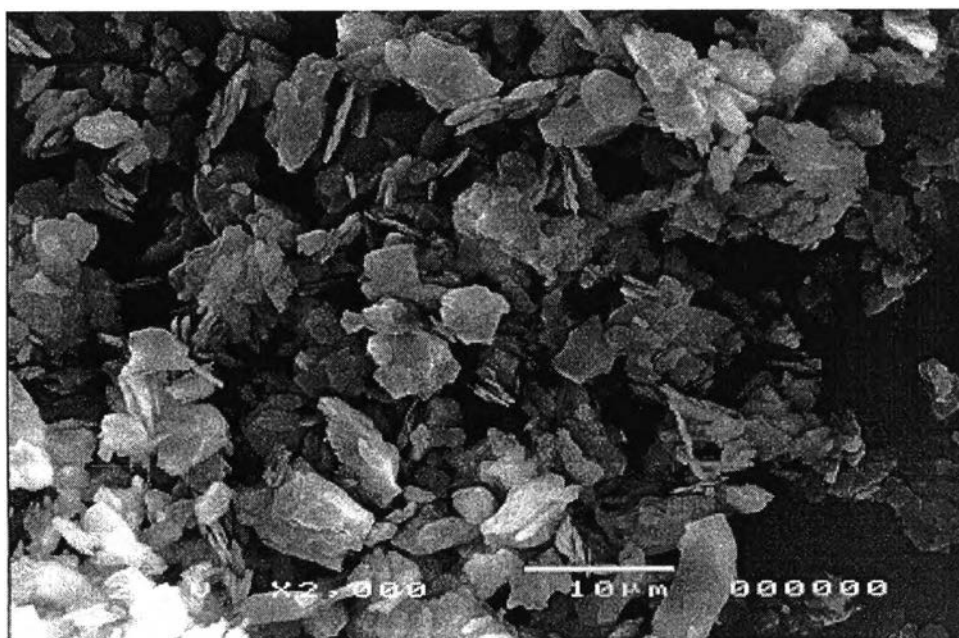


Figure 4.2 Scanning Electron Micrograph of Unmodified Clay at 2000X Magnification.

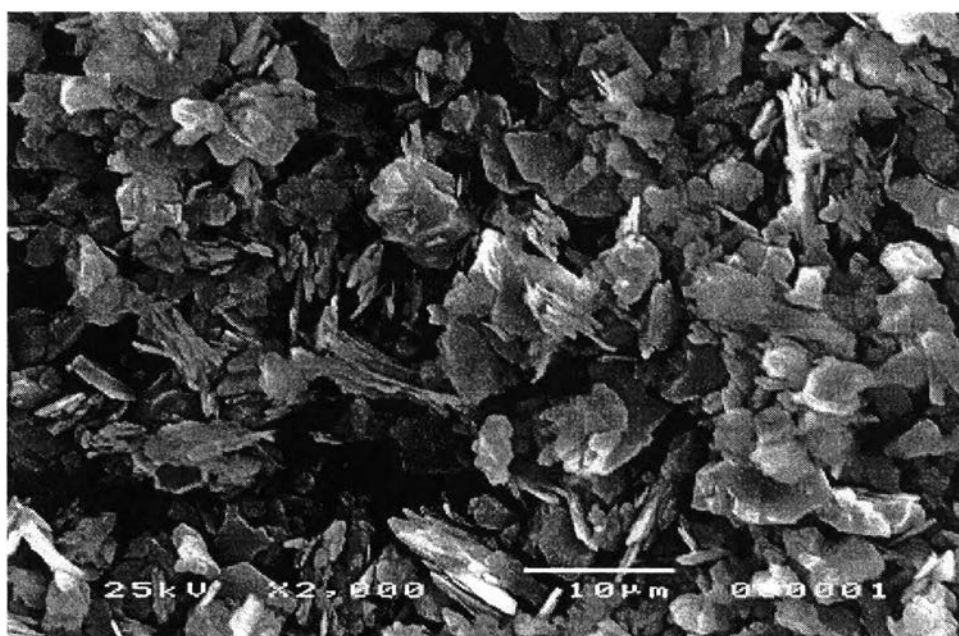


Figure 4.3 Scanning Electron Micrograph of Modified Clay, SIC # 1 at 2000X Magnification.

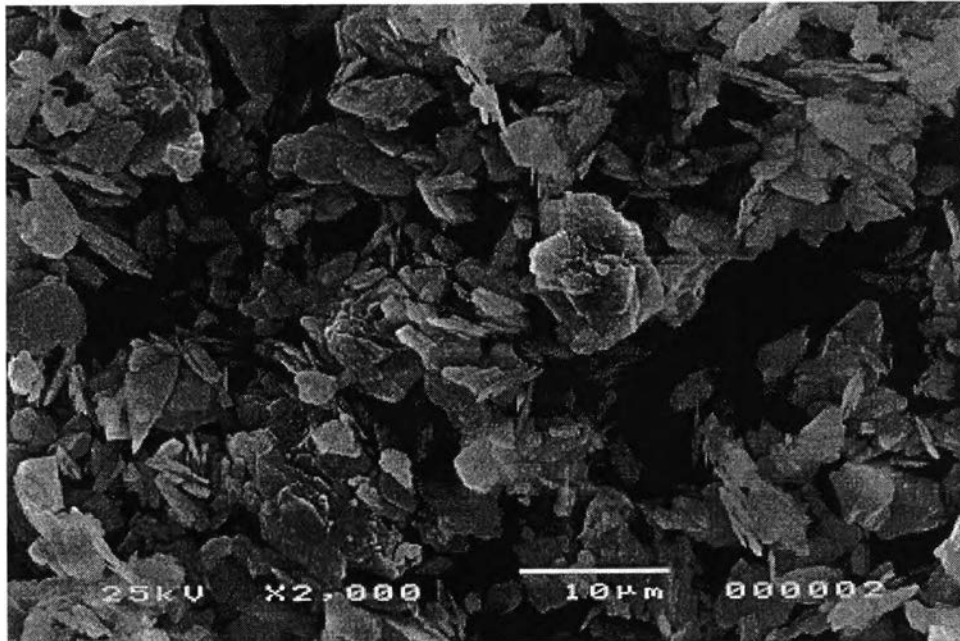


Figure 4.4 Scanning Electron Micrograph of Modified Clay, SIC # 2 at 2000X Magnification.

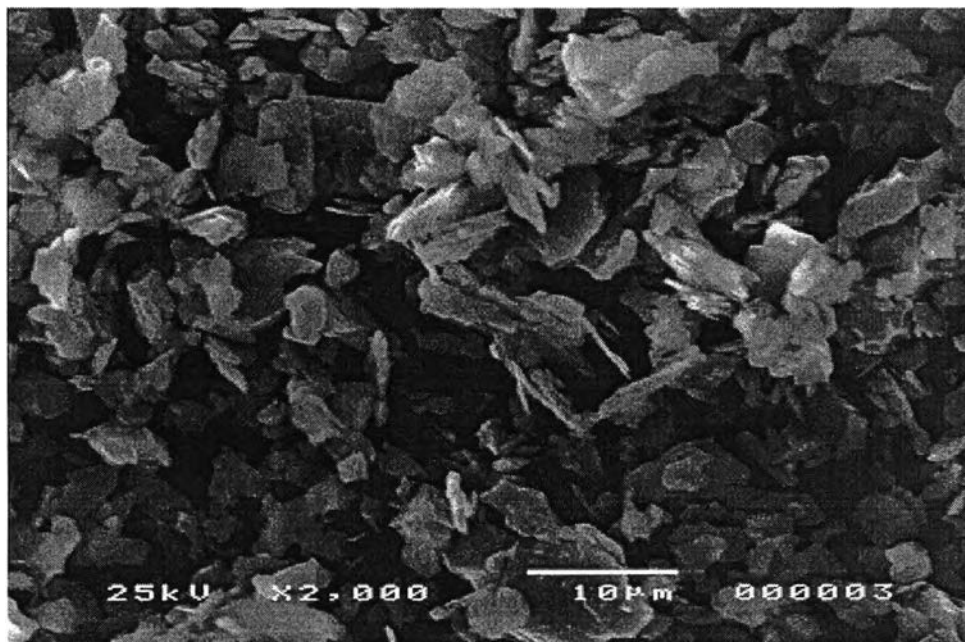


Figure 4.5 Scanning Electron Micrograph of Modified Clay, SIC #3 at 2000X Magnification.

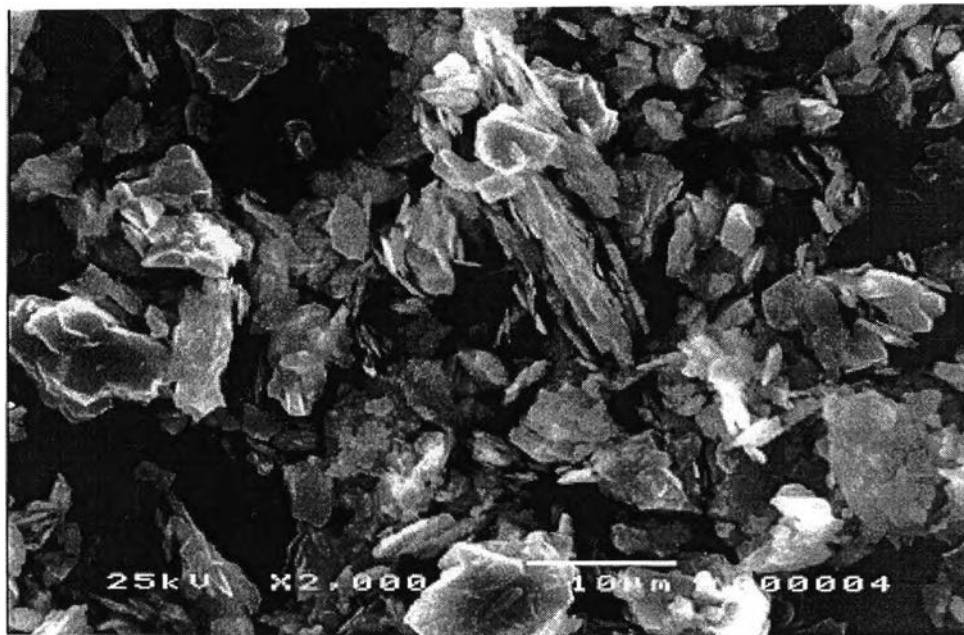


Figure 4.6 Scanning Electron Micrograph of Modified Clay, SIC # 4 at 2000X Magnification.

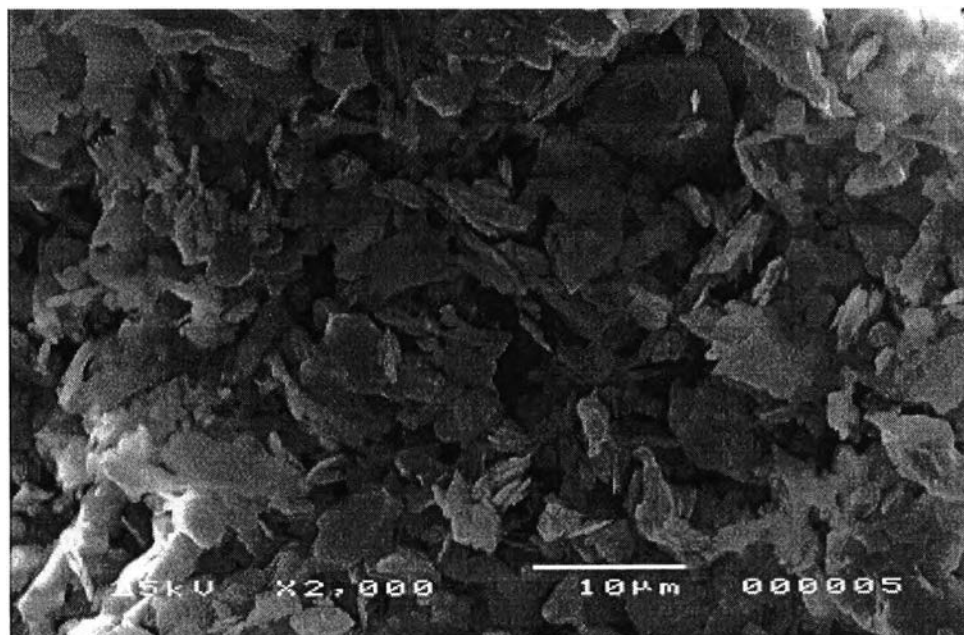


Figure 4.7 Scanning Electron Micrograph of Modified Clay, SIC# 5 at 2000X Magnification.

The carbon content analysis supported the idea that most of the polymer and the monolayer of surfactant below it remained on the clay surface after the washing step. The data shown in table 4.2 are based on the assumption that all of the monomer and half of the absorbed surfactant remain after washing.

Table 4.2 Carbon Content between Measured and Predicted Value

CLAY	Measure % carbon	Predicted % carbon
CONTROL	0.03	0
SIC # 1	0.53	0.52
SIC # 2	0.44	0.27
SIC # 3	0.48	0.44
SIC # 4	0.34	0.36
SIC # 5	0.45	0.40

The presence of polystyrene-isoprene copolymer on clay was tested qualitatively by observing the hydrophobic property of coated clay. All modified clay float on the surface of water, while unmodified clay sink. This phenomena occurs because, after the outer layer of surfactant was removed by washing, the hydrophobic tails part of the surfactant and co-polymer remained on the clay surface, making the pore more hydrophobic and prevents water getting back into the pore.

4.2 Rubber compound testing

The physical properties of rubber compound using various surface modification were investigated. The complete performance data of all clays studied in the rubber compound formulation (table 3.3) is summarized in table 4.3. The data shown that all modified clay decreases the cure time and scorch time. This phenomena may be occurred from the formation of co-polymer on

clay surface, covering some of surface silanol groups which has acidity property while the accelerator and activator have basicity property. Therefore, the activity between silanol groups and the additives used in rubber vulcanization, namely the accelerator and zinc oxide activator decreased. The increasing in Mooney viscosity may be due to the copolymer on surface of modified clay increased the interaction between elastomer and fillers.

Table 4.3 Physical Properties of Vulcanisates Using Unmodified and Various Modified Clays

PROPERTIES	CONTROL	SIC # 1	SIC # 2	SIC # 3	SIC # 4	SIC # 5
Cure time(min:sec)	7.22	4.19	4.88	4.29	4.70	4.47
Mooney viscosity(ML 1+4 @ 100 °C)	34.40	33.43	35.08	37.79	39.15	38.33
Scorch Time(s ₅), min:sec	11.70	4.28	5.09	4.67	4.94	4.71
Unaged Tensile(MPa)	16.04	15.04	13.82	14.58	16.39	18.20
Aged Tensile(MPa)	8.31	7.09	6.44	4.86	5.38	4.13
Unaged Elongation(%)	610.72	582.33	370.15	561.41	595.22	540.30
Aged Elongation(%)	357.36	361.50	250.36	265.98	352.73	315.15
Unaged Tear(N/mm)	29.58	31.26	28.06	27.45	28.43	29.30
Aged Tear(N/mm)	27.51	26.50	25.13	23.27	26.79	27.04
Unaged Modulus @ 300% (MPa)	3.25	3.42	3.70	3.49	3.53	3.79
Aged Modulus @ 300%(MPa)	3.15	3.61	3.53	3.88	3.40	4.09
Unaged Hardness(Shore A)	45.34	46.82	47.38	50.03	50.43	50.85
Aged Hardness(shore A)	47.90	51.04	50.78	54.90	53.53	55.00
Resilience(%)	79.93	82.56	83.35	88.12	86.40	86.20
Abrasion loss(ml/kilocycles)	1.79	1.77	1.83	1.94	2.00	2.01
Flex Cracking resistance(kilocycles)	5.32	5.55	5.14	4.05	3.92	3.66
Resistance to fatigue(kilocycles)	89.98	113.13	51.18	71.85	81.42	86.32
Compression Set(%)	45.46	56.60	55.09	64.99	58.40	56.42

A comparative study of physical properties showed that all polymer-modified clays improved the tensile strength, tear, modulus and hardness except abrasion loss, flex cracking resistance, compression set and resistance to fatigue.

The resilience property of cured rubber compounds, which shown in figure 4.8, were slightly increased upon the in situ polymerization of comonomers compared to the unmodified clay. However, unmodified clay gave high resilience in general. So that, the modified clay did not improve resilience significantly.

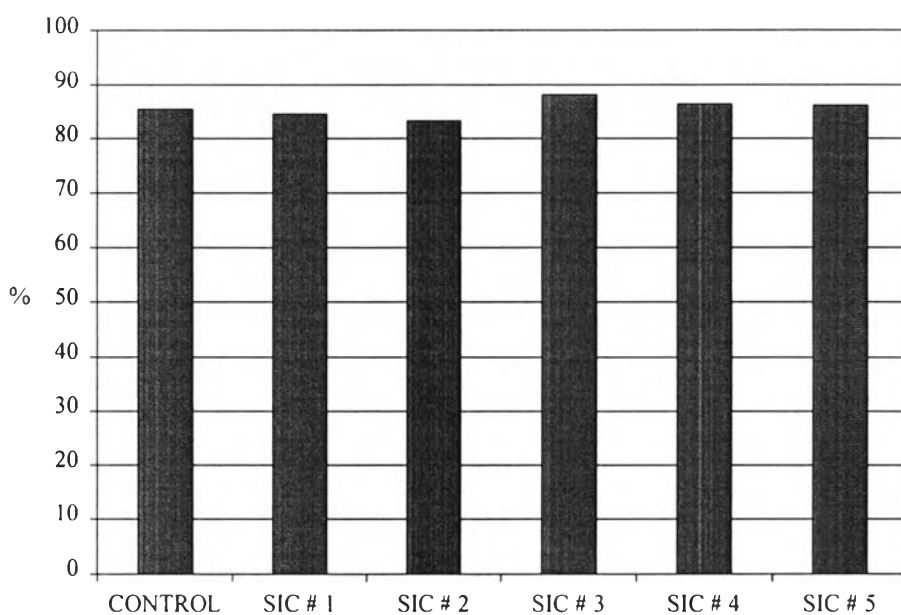


Figure 4.8 Resilience of Unmodified and Modified Clay.

From figure 4.9, all conditions of modified clay improved the hardness when compared to unmodified clay. The increasing in this property may be due to the styrene and isoprene co-polymer film and remaining surfactant that coated on clay surface which increases the interaction between elastomer and filler. All conditions of modified clay almost gave the same value when compared among conditions.

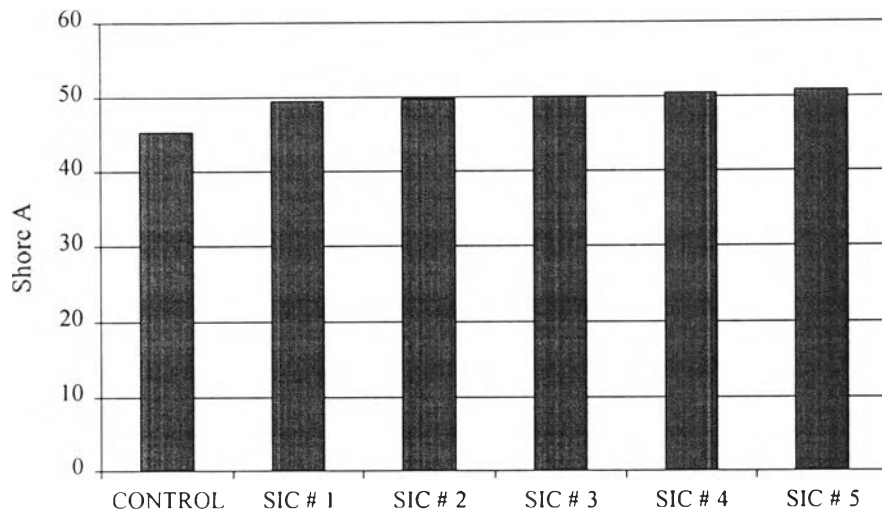


Figure 4.9 Hardness of Unmodified and Modified Clay.

The abrasion loss, compression set, flex cracking resistance, fatigue to failure properties are shown in figure 4.10, 4.11, 4.12 and 4.13 respectively. All conditions of modified clay did not improve abrasion loss and compression set.

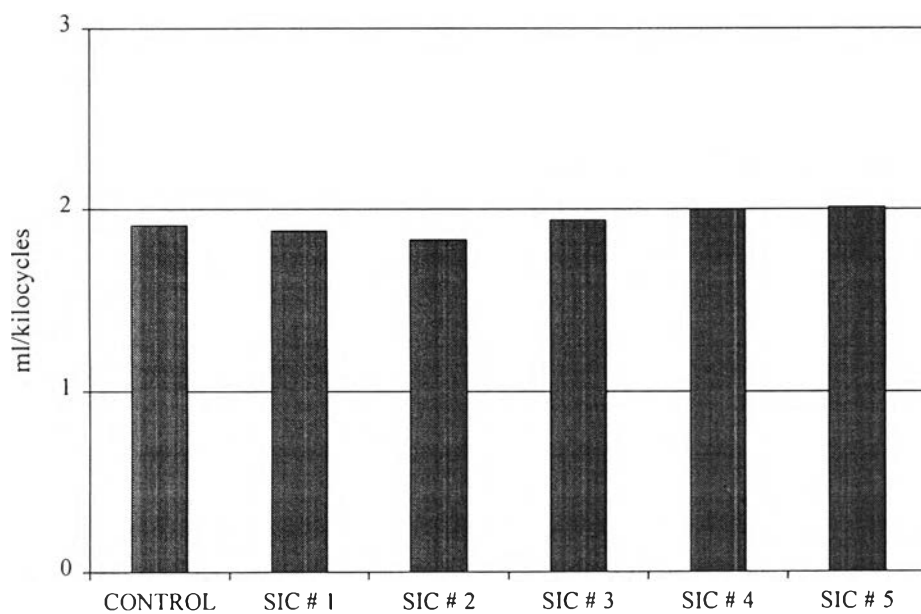


Figure 4.10 Abrasion loss of Unmodified and Modified Clay.

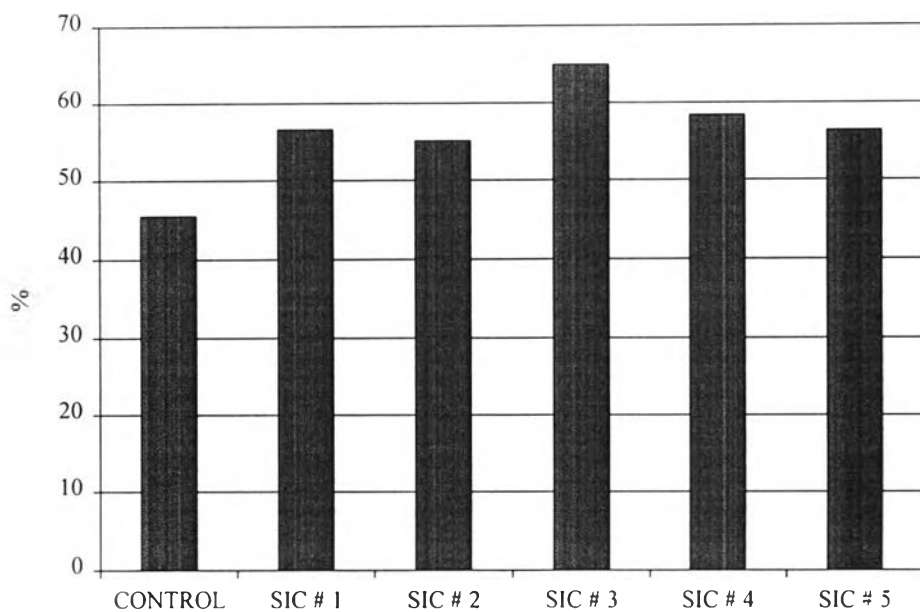


Figure 4.11 Compression Set of Unmodified and Modified Clay.

Some conditions of modified clay improve the flex cracking resistance and fatigue to failure property.

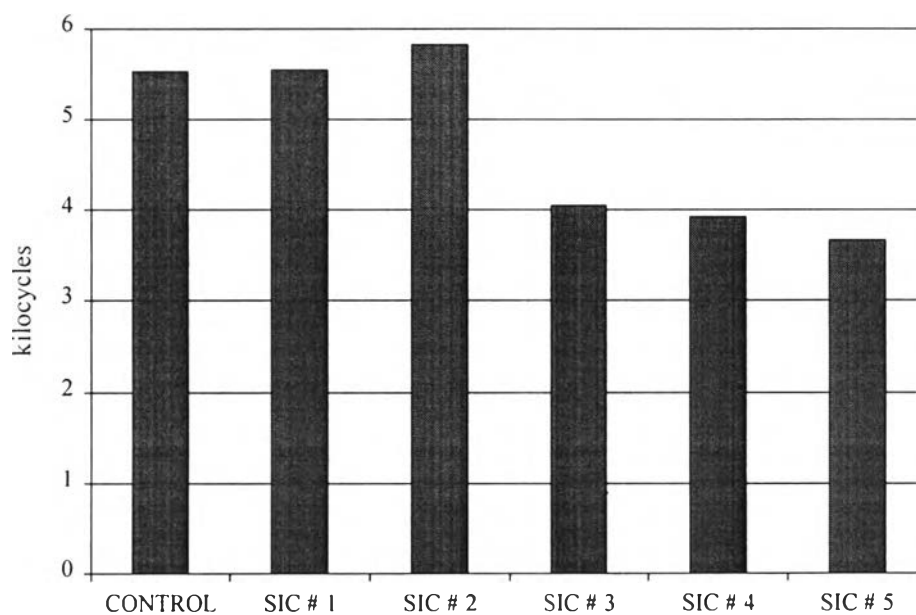


Figure 4.12 Flex Cracking Resistance of Unmodified and Modified Clay.

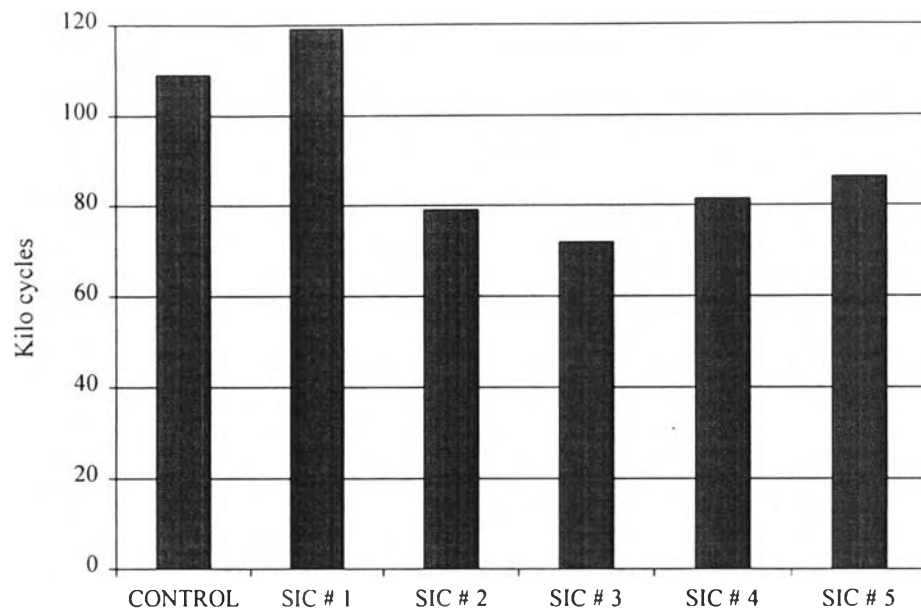


Figure 4.13 Fatigue to Failure of Unmodified and Modified Clay.

It is seen that, the SIC # 2 (low surfactant, low co-monomer) increases flex cracking resistance while SIC # 1 (high surfactant, high co-monomer) increases fatigue to failure. This can infer that SIC # 2 and SIC # 1 are the optimum condition for flex cracking resistance and fatigue to failure respectively.

The effect of amount of surfactant and co-monomers on physical properties, shown in the table 3.1 and figure 3.1 , was studied. Figure 4.14 revealed the effect of the amount of surfactant and co-monomer on tensile property.

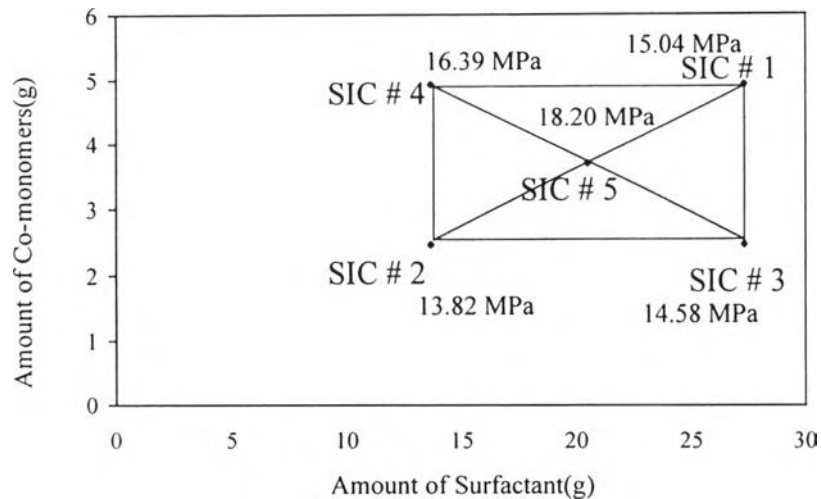


Figure 4.14 The Effect of Amount of Surfactant and Co-monomer on Tensile Strength.

As the increasing in the amount of surfactant, tensile strength increases when using low co-monomer content, but decreases when using high co-monomer.

The SIC # 5(intermediate condition) is the optimum condition for tensile property.

The effect of amount surfactant and co-monomer on elongation at break present in figure 4.15.

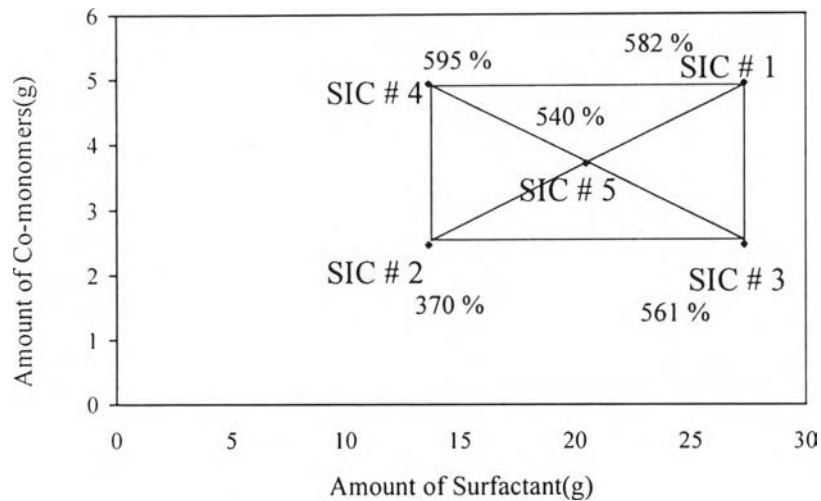


Figure 4.15 The Effect of Amount of Surfactant and Co-monomer on Elongation at Break.

The SIC # 4 provides the maximum on the elongation at break property when using low surfactant and high co-monomer content. However, tensile strength property is the major concerning in rubber industry except specific work that emphasize on elongation at break.

The effect of amount surfactant and co-monomer on the tear strength that shown in figures 4.16.

The tear strength decreases when amount of surfactant increasing at low content of co-monomer. On the other hand, tear strength increases when increasing in surfactant and co-monomer content.

The SIC # 1 (high surfactant, high co-monomer) is the optimum condition for this property.

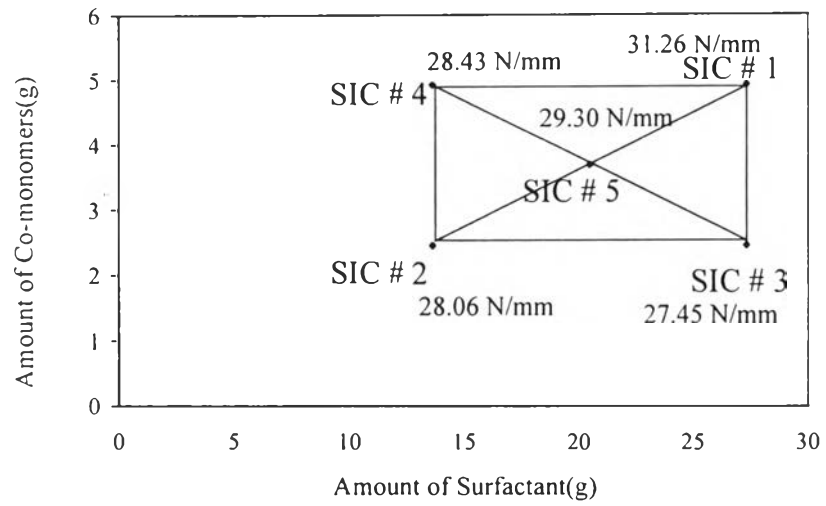


Figure 4.16 The Effect of Amount of Surfactant and Co-monomer on Tear Strength.