

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Organically Modified Montmorillonites

4.1.1 AAS

The amount of Na^+ that was replaced by alkylammonium ion, the protonated form of alkylamine, was determined by employing atomic absorption spectroscopy. The ion-exchange percentage was calculated by multiplying 100 with the ratio between replaced Na^+ determined by AAS and the total amount of Na^+ at the beginning. The calculated results were shown in Table 4.1.

Table 4.1 Na^+ exchanged percentage using different modifying agents

Modifying agent	Na^+ exchanged percentage
DO	92.4
TET	90.5
HEX	87.3
OC	85.8
HEXT	72.6
OCT	70.1

For primary-alkylamine modifying agents, the amount of Na^+ -exchanged percentage was quite high, ranging from 85-93%. The amount of exchanged Na^+ was decreased by the increase in the length of hydrocarbon part in the structure of alkylamine. Similarly, the same trend was obtained by using quaternary-ammonium-salts as modifying agents. By increasing

hydrocarbon part of modifying agents, the affinity between the alkylammonium ion and the negative charge on the silicate layer was decreased leading to the lower ion-exchange percentage. Additionally, in the case of quaternary ammonium salts, the low ion exchange percentage may be resulted from bulky methyl groups that generate steric effect on the molecule of modifying agent.

4.1.2 FTIR

Na-MMT, modifying agents, and organically modified MMTs were characterized by FTIR to verify the incorporation of modifying agent into the structure of clay. FTIR spectra of modifying agents and organically modified MMTs including Na-MMT were separately illustrated in Figures 4.1 and 4.2.

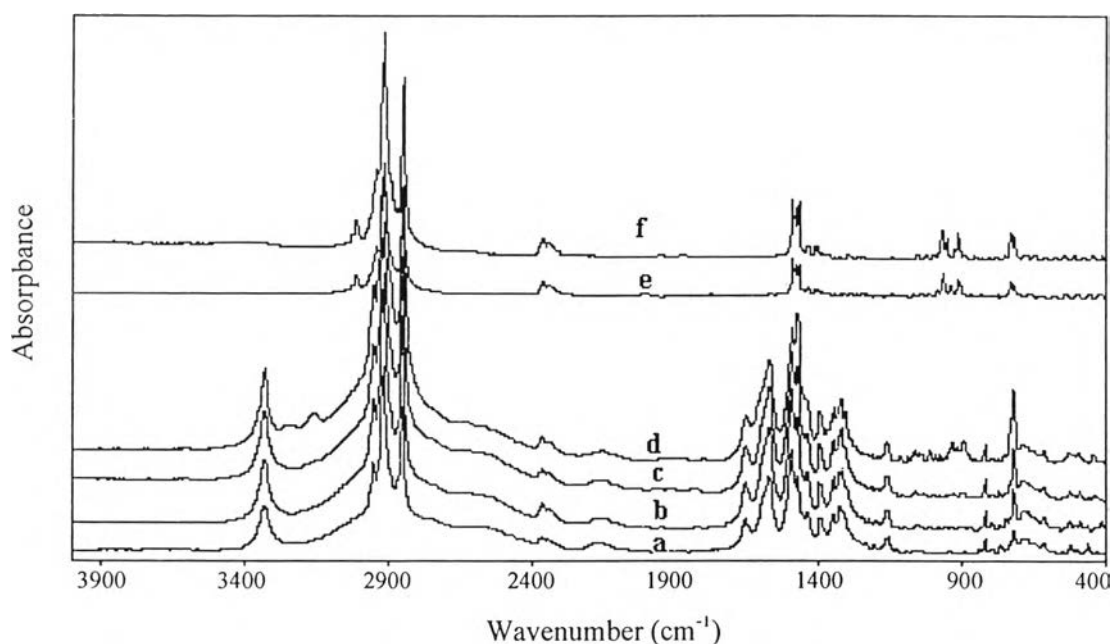


Figure 4.1 FTIR spectra of alkylamines: (a) DO, (b) TET, (c) HEX, (d) OC, (e) HEXT, (f) OCT.

For modifying agents, primary alkylamines (DO, TET, HEX, and OC) showed important absorption peaks of N-H stretching, C-H stretching of

methyl and methylene groups, and C-N stretching at 3300, 2933, 2853, and 1250 cm^{-1} respectively. But, for quaternary-ammonium-salt modifying agents (HEXT and OCT), there is no N-H stretching peak.

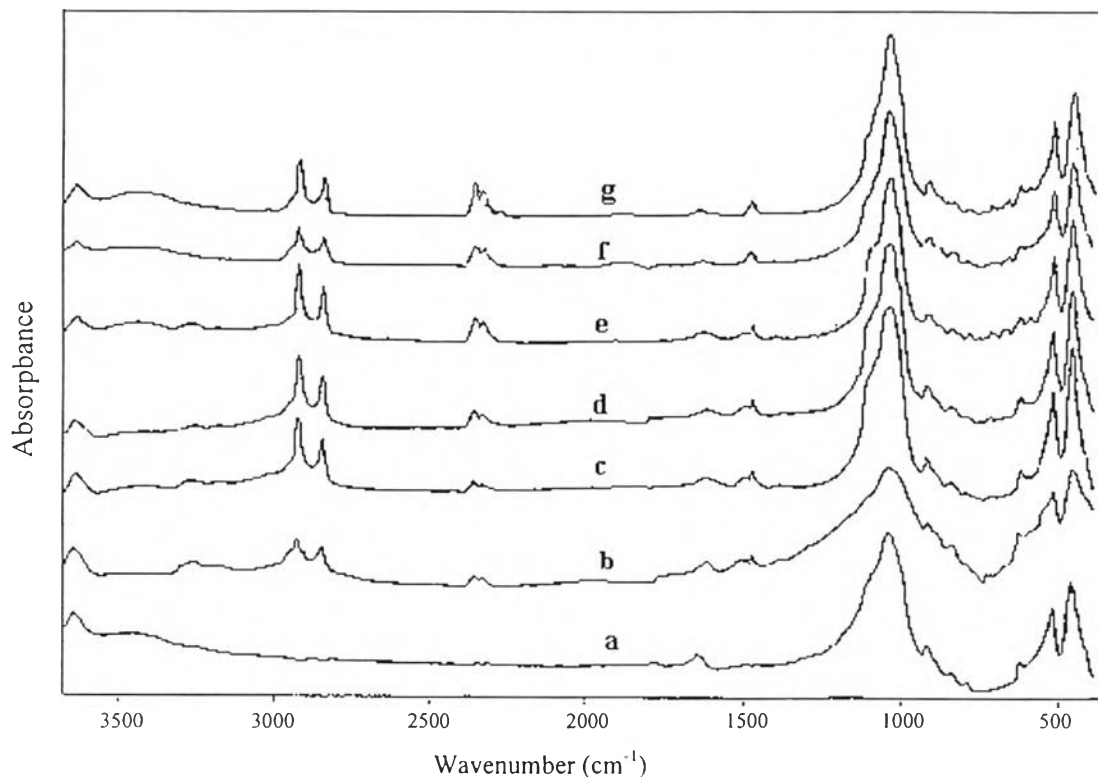


Figure 4.2 FTIR spectra of (a) Na-MMT, (b) DO-MMT, (c) TET-MMT, (d) HEX-MMT, (e) OC-MMT, (f) HEXT-MMT, (g) OCT-MMT.

From Figure 4.2, the pristine clay, Na-MMT, exhibited its unique characteristic peaks at 3630, 1040, 521, and 466 cm^{-1} which can be assigned orderly to O-H stretching, Si-O stretching, Al-O stretching, and Si-O bending. Clearly seen from this Figure, FTIR spectra of organically modified MMTs combined typical peaks of both inorganic Na-MMT and organic modifying agent together. Moreover, the shift of N-H stretching peak to the lower wavenumber could be accounted for the interaction between alkylammonium ion and negative charge on the silicate layer of MMT.

4.1.3 TGA

As well as FTIR, thermogravimetric analysis was applied to confirm the incorporation of modifying agent into MMT structure. Thermograms of representatives, Na-MMT, DO, DO-MMT were shown in Figure 4.3. Thermograms of other modifying agents and organically modified MMTs were shown in Appendix I.

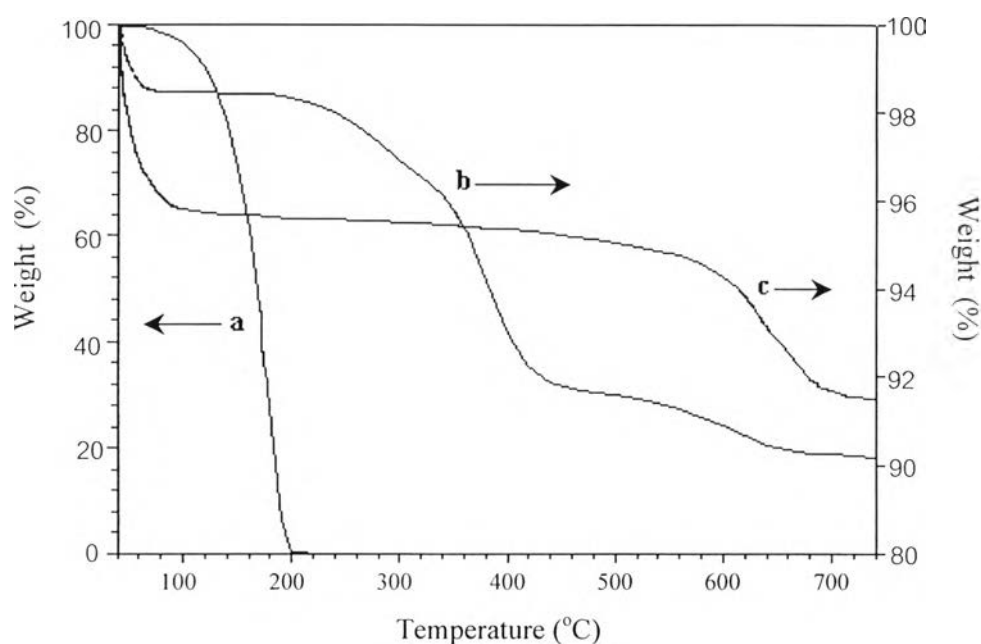


Figure 4.3 TGA thermograms of (a) DO, (b) DO-MMT, (c) Na-MMT.

As evident from Figure 4.3, the decomposition temperature (T_d) of modifying agent, DO, is around 143 °C while that of Na-MMT is approximately 634 °C. The improvement in thermal stability of modifying agent resided between silicate layers could be substantiated by the thermogram of DO-MMT, which showed T_d at 313 °C. Likewise, for other modifying agents, thermal degradation temperatures were shifted to higher temperatures as shown in Table 4.2.

Table 4.2 Thermal degradation temperatures of modifying agents, Na-MMT, and organically modified MMTs.

Modifying agent	T _d of modifying agent (°C)	T _d of organically modified MMT (°C)
DO	143	313
TET	144	315
HEX	164	316
OC	175	319
HEXT	234	329
OCT	237	341

The reason for the improvement in decomposition temperature of modifying agent was probably resulted from the ionic force between alkalammonium ion and negative charge of MMT. Moreover, the heat-insulation effect of the inorganic host, silicate layers, as proposed by Lee et al. (1997), could be partly accounted for the enhancement in thermal degradation temperature of modifying agent.

4.1.4 XRD

The strongly supported evidence for the incorporation of modifying agent into the MMT structure was obtained from XRD. The XRD spectra of Na-MMT and organically modified MMTs synthesized by using primary alkylamines and quaternary ammonium salts as modifying agents were demonstrated in Figures 4.4 and 4.5 respectively.

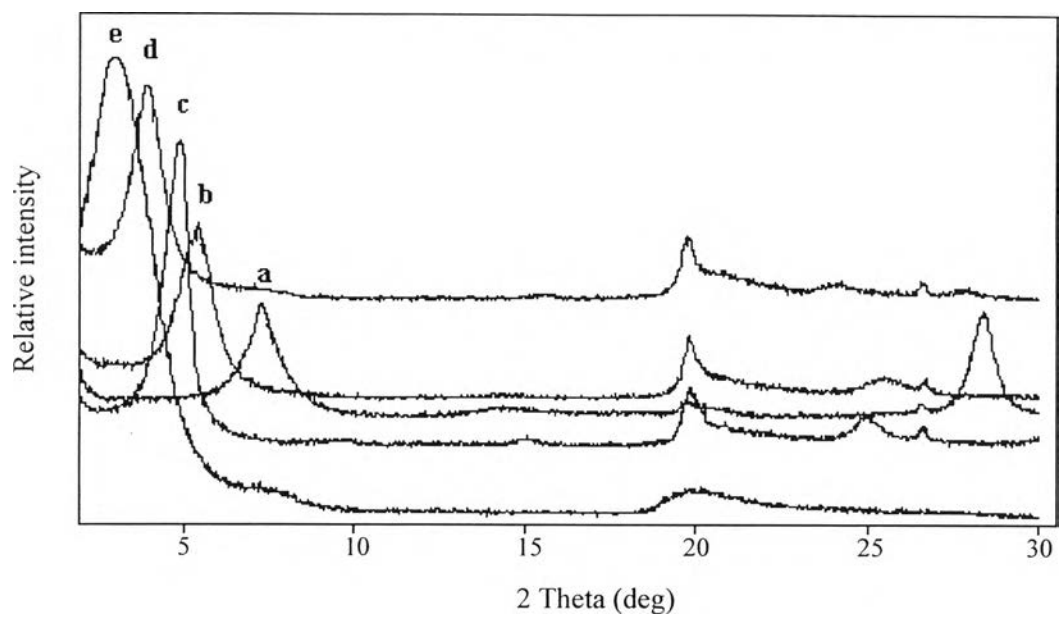


Figure 4.4 XRD spectra of (a) Na-MMT, (b) DO-MMT, (c) TET-MMT, (d) HEX-MMT, (e) OC-MMT.

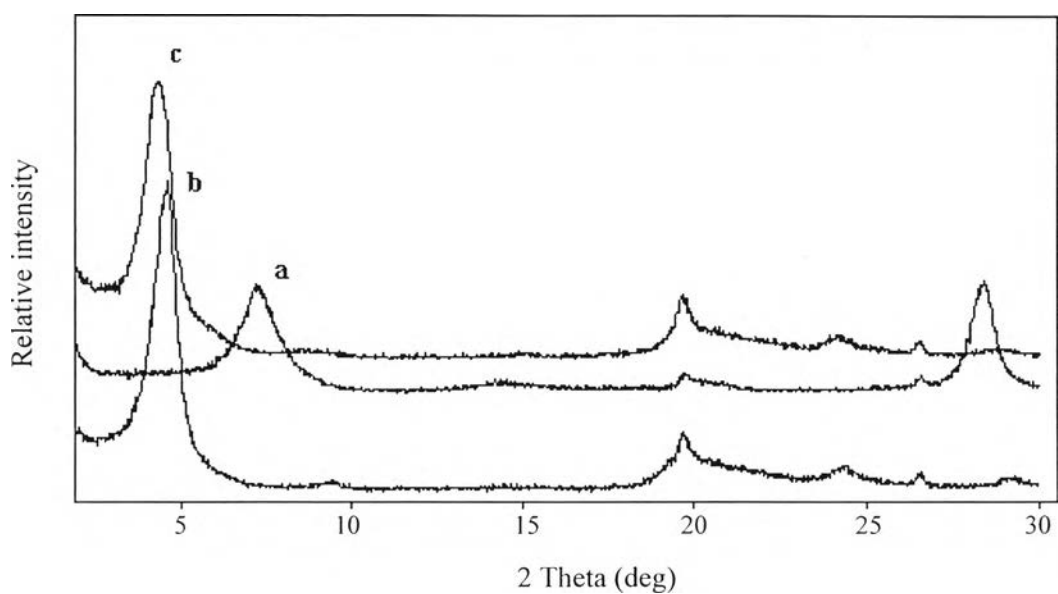


Figure 4.5 XRD spectra of (a) Na-MMT, (b) HEXT-MMT, (c) OCT-MMT.

Clearly seen from both Figures, peak positions of organically modified MMTs were transitioned to lower 2θ angles relative to that of Na-MMT. This was indicated that the distance between silicate layers were expanded significantly because of the incorporation of modifying agents into the MMT structure. The interlayer distances calculated from peak positions of basal spacing reflections were listed in Table 4.3.

Table 4.3 Basal spacings of Na-MMT and organically modified MMTs.

Organically modified MMT	Basal spacing (Å)
Na-MMT	12.13
DO-MMT	16.41
TET-MMT	18.24
HEX-MMT	22.40
OC-MMT	26.91
HEXT-MMT	19.27
OCT-MMT	20.15

The basal spacing of Na-MMT found in this work, 12.31 Å, was closed to that reported by Yang et al. (1999), 12.60 Å, and Giannelis (1996), 11.40 Å. After treatment via ion-exchange reaction, the basal spacing of DO-MMT was measured to be 16.41 Å. This value was consistent with 16.50 Å reported by Phiriyawirat, P. (1999) but it was slightly different from 15.60 Å measured by Pinnavaia et al. (1995). For other primary-alkylamine modified MMTs, the original basal spacings of the pristine clay were enlarged to 18.24-26.91 Å. For quaternary-ammonium-salt modified MMTs, the basal spacing of HEXT-MMT, 19.27 Å, was slightly higher than that, 18.90 Å, reported by Yang et al. (1999) but the basal spacing of OCT-MMT, 20.15 Å, found in this work was lower than 22.10 Å of Pinnavaia et al.'s work (1995).

Obviously, in the case of primary-alkylamine modified MMTs, the degree of basal spacing expansion was increased with the length of hydrocarbon part in the structure of modifying agents. For quaternary-ammonium-salt modified MMTs, the same trend was obtained but the degree of interlayer expansion was lower than that of primary-alkylamine modified counterparts. In general, the higher degree of basal spacing expansion usually resulted in the higher chance of polymer intercalation, which leads to the more possibility of layered-silicate delamination in the polymer matrix.

4.2 Characterization of NR/Clay Composites

The resulting NR/clay composites prepared by both solution and melt techniques were characterized by XRD.

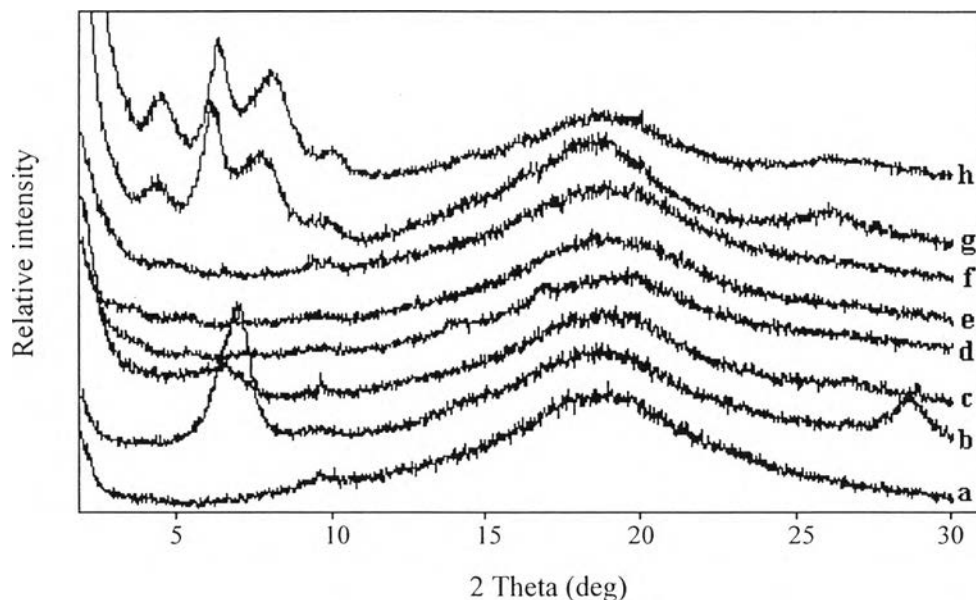


Figure 4.6 XRD spectra of 7 phr NR/Clay composites prepared by solution technique: (a) pure NR, (b) Na-MMT/NR, (c) DO-MMT/NR, (d) TET-MMT/NR, (e) HEX-MMT/NR, (f) OC-MMT/NR, (g) HEXT-MMT/NR, (h) OCT-MMT/NR.

The XRD spectra of organically modified MMTs/NR composites prepared by solution and melt techniques were demonstrated in Figures 4.6 and 4.7. Obviously seen from the Figures, the XRD spectra of Na-MMT/NR composites prepared by both techniques showed a strong characteristic peak of Na-MMT at around 12.5 Å. It could be interpreted that by mixing NR with Na-MMT in the pristine form, the distance between silicate layers was not changed. The original aggregated form of silicate layers still existed, and it was dispersed in the matrix of NR without any change in its structure. In contrast, for primary-amine modified MMT/NR composites, there was no peak presented in 2θ ranged between $2-10^\circ$. It was indicated that silicate layers were separated into individual layer staying away from each other. Consequently, exfoliated nanocomposites of primary-alkylamine modified MMTs and NR could be generated by both solution and melt techniques.

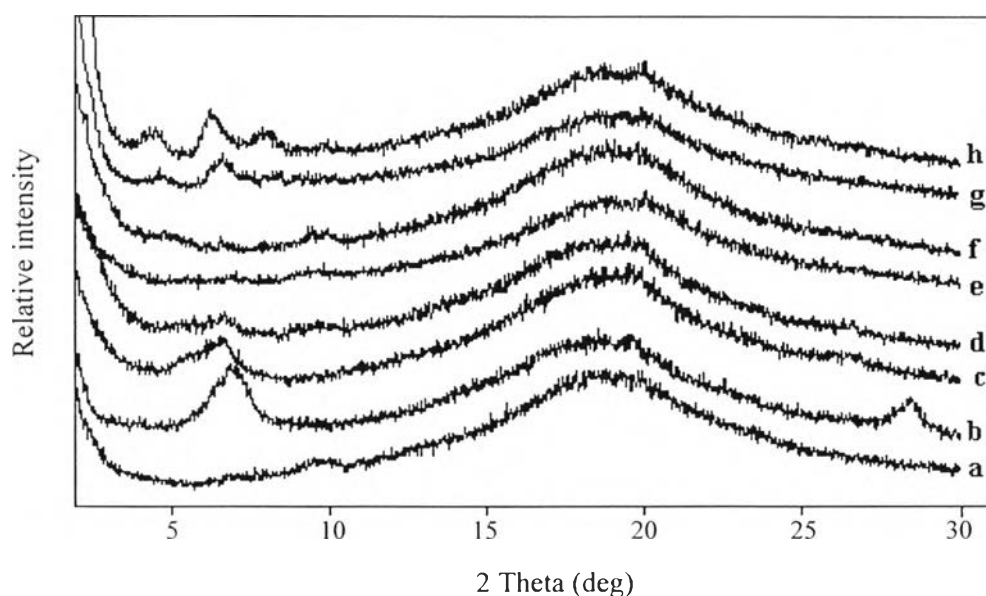


Figure 4.7 XRD spectra of 7 phr NR/clay composites prepared by melt technique: (a) pure NR, (b) Na-MMT/NR, (c) DO-MMT/NR, (d) TET-MMT/NR, (e) HEX-MMT/NR, (f) OC-MMT/NR, (g) HEXT-MMT/NR, (h) OCT-MMT/NR.

The XRD featureless patterns in the low 2θ range found in this work, which resulted from polymer intercalation in melt state, was correspondent with Burnside et al.'s discovery (1995). They reported that the exfoliated nanocomposite between polydimethylsiloxane and organically modified clay could be prepared through the melt technique. However, for DO-MMT/NR composites prepared by both techniques, a broad peak with low intensity at around 6.4° (d-spacing = 13.6 \AA) was observed. This implied that there was a small amount of silicate layers that could not be exfoliated, existing in an aggregated form.

For quaternary-ammonium-salt modified MMT/NR composites prepared by both techniques, the results were different from composites using primary alkylamines as modifying agents. While basal spacings of HEXT-MMT and OCT-MMT were approximately 19.2 and 20.1 \AA , diffraction peaks of composites prepared from such organically modified MMTs were observed at around 4.5° , 6.1° , and 7.7° , corresponding to d-spacings of 19.8 , 14.4 , and 11.4 \AA respectively. This indicated that basal spacings of quaternary-ammonium-salt modified MMTs in composites were not changed significantly compared to their original distances. Therefore, exfoliated dispersion of silicate layers was not generated by using quaternary-ammonium-salts as modifying agents. Furthermore, diffraction peaks at higher 2θ revealed that d-spacings between silicate layers were partly reduced to lower distances. The reduction in the space between silicate layers after forming a composite was also previously reported by Tyan et al.'s work (1999), describing that the polymer molecules outside the silicate layers squeezed the silicate layers during crosslink process of polyimide.

The X-ray diffraction patterns of OC-MMT/NR composites prepared by solution and melt techniques with clay loading of 3, 7, and 10 phr were shown in Figures 4.8 and 4.9 respectively.

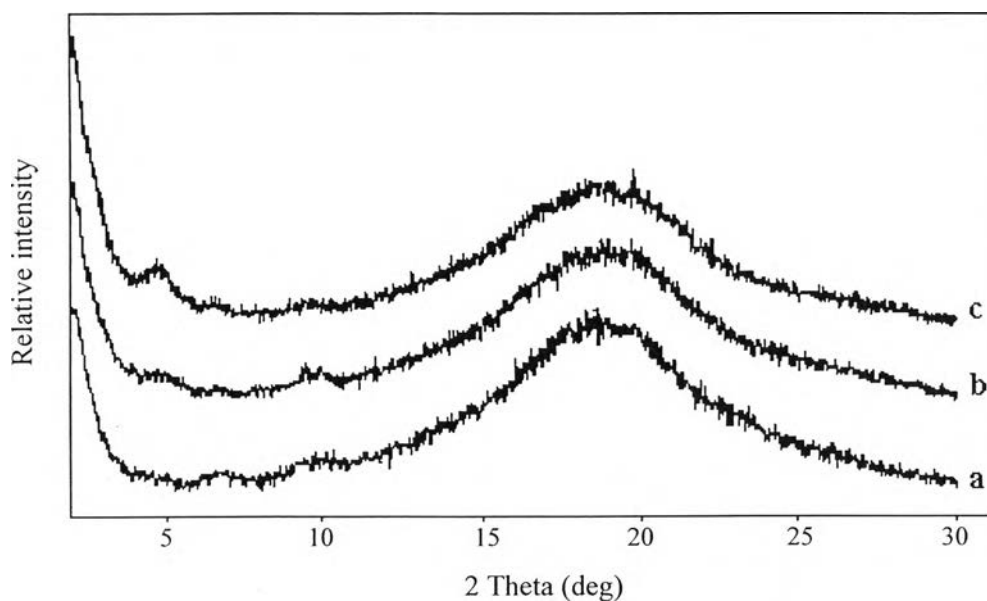


Figure 4.8 XRD spectra of OC-MMT/NR composites prepared by solution technique with clay loading of (a) 3 phr, (b) 7 phr, (c) 10 phr.

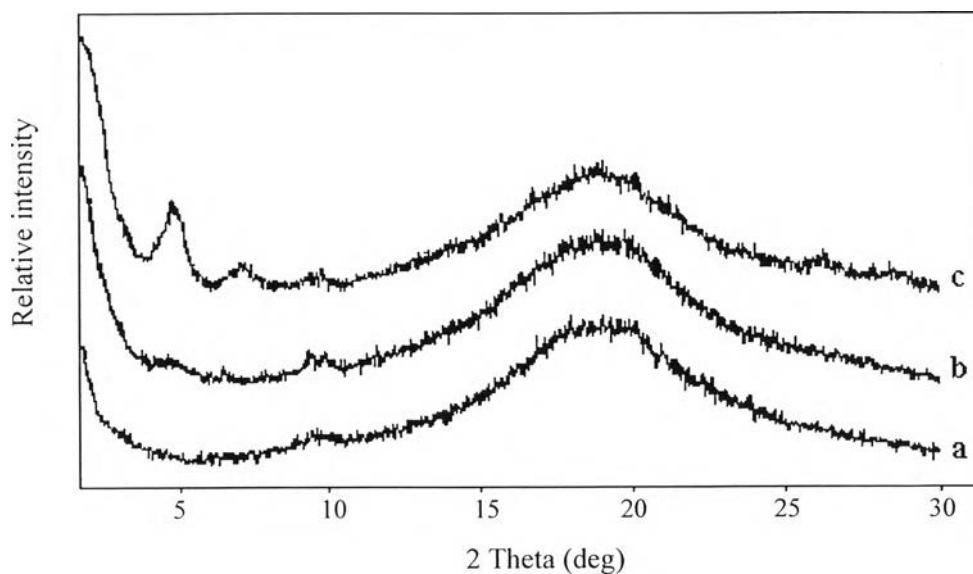


Figure 4.9 XRD spectra of OC-MMT/NR composites prepared by melt technique with clay loading of (a) 3 phr, (b) 7 phr, (c) 10 phr.

The same trend of XRD spectra was observed from both techniques. When clay loading was increased to 10 phr, there was a small peak appearing

at $2\theta = 4.7^\circ$, corresponding with a d-spacing of 18.8 Å. This revealed the presence of silicate layers existed in an intercalated form. In the other words, by increasing clay loading, there was a small amount of silicate layers that could not be exfoliated in the polymer matrix, but dispersed in an intercalated form. This result was consistent with Tyan et al.'s work (1999) that also reported the presence of a small diffraction peak after clay loading was increased to 10%.

4.3 Cure characteristics of NR/Clay Composites

The effect of organically modified MMTs on cure characteristic of NR composites was shown in Table 4.4.

Table 4.4 Cure characteristics of NR/clay (7phr) composites

Cure characteristic	Scorch time (t_{s2}) (min:sec)		Optimum cure time (t_{90})	
	Solution	Melt	Solution	Melt
NR	4.35	4.42	8.31	9.12
Na-MMT	4.06	4.19	6.25	8.15
DO-MMT	3.31	3.49	5.25	6.48
TET-MMT	3.24	3.43	5.15	6.09
HEC-MMT	3.22	3.42	5.10	5.58
OC-MMT	3.28	3.46	5.12	5.54
HEXT-MMT	1.46	1.54	4.10	5.24
OCT-MMT	1.43	1.56	4.08	5.27

From Table 4.4, the data showed that the addition of organically modified MMTs in NR resulted in the accelerated cure characteristics. Scorch times (t_{s2}) and optimum cure times (t_{90}) of NR/clay composites were

decreased significantly compared to the pure NR and the unmodified Na-MMT/NR counterparts, thereby leading to the increase in cure rates. Conspicuously seen from the Table, the effects of primary-alkylamine and quaternary-ammonium-salt modifying agents on cure characteristics of composites were different. The ability of quaternary ammonium salts to reduce cure times was greater than that of primary alkylamines. Similarly, the same trend was observed in the reduction of scorch times. The activity effect of ammonium derivatives on cure characteristics of rubber found in this work was correspondent with the discovery reported by Vladkova et al. (1997).

4.4 Tensile Properties

Tensile properties were measured in order to verify the superior characteristics of nanoscale dispersion of silicate layers in the NR matrix. In this sense, tensile strength, elongation at break, 300% modulus, and hardness of cured NR/clay composites were compared with those of both pure NR and unmodified Na-MMT/NR counterparts.

The effect of types of modifying agents on tensile strength and hardness of composites was illustrated in Figures 4.10 and 4.11. From the Figures, tensile strength and hardness of primary-alkylamine modified MMT/NR composites prepared by solution technique were improved significantly relative to those of pure NR and unmodified Na-MMT/NR counterparts. In this group, tensile strength and hardness was increased with the length of hydrocarbon part in the alkylamine structures. However, tensile strength was slightly decreased by using quaternary ammonium salts as modifying agents. Obviously, the same trends of tensile strength and hardness were obtained from composites prepared by melt technique but the results were inferior to those of solution technique.

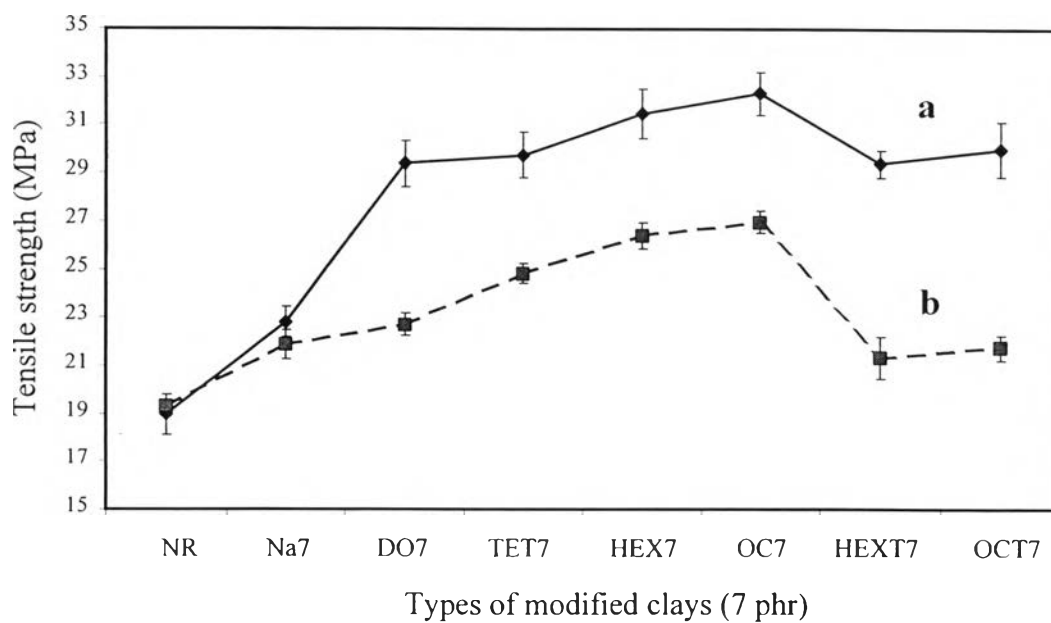


Figure 4.10 Tensile strength of NR/clay composites: (a) solution technique, (b) melt technique.

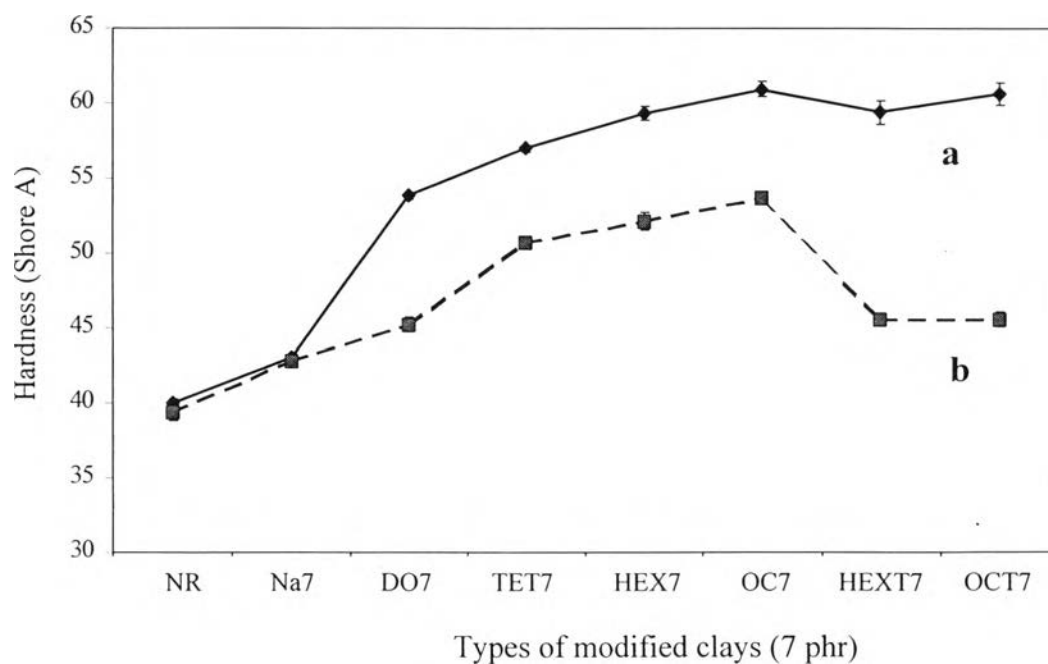


Figure 4.11 Hardness of NR/clay composites: (a) solution technique, (b) melt technique.

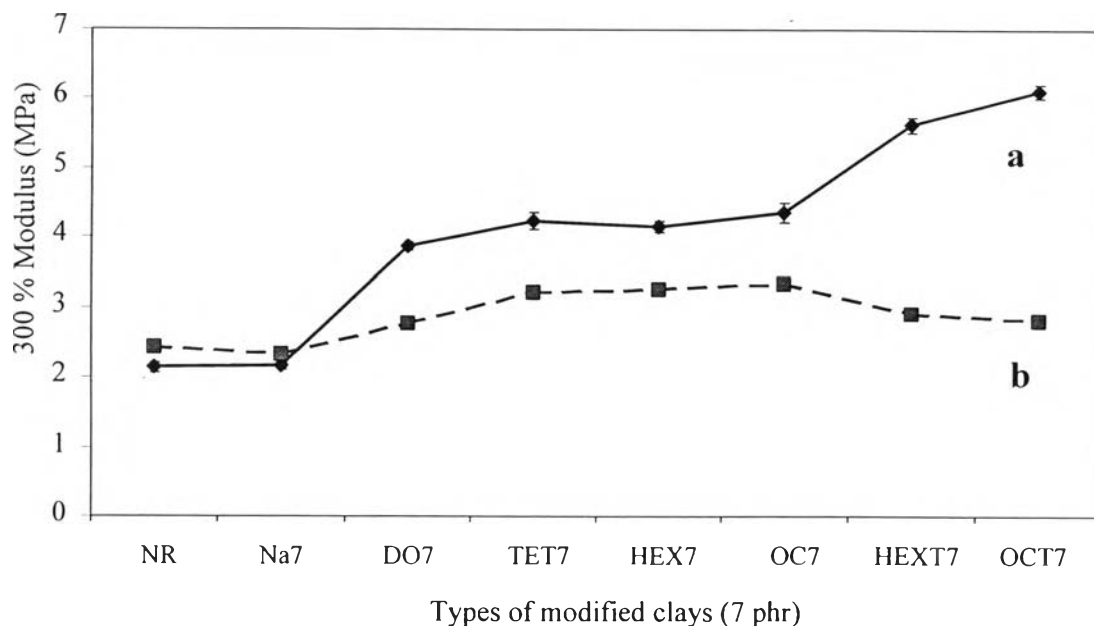


Figure 4.12 300% Modulus of NR/clay composites: (a) solution technique, (b) melt technique.

Like tensile strength and hardness, 300% Modulus of composites prepared by solution technique was considerably increased with the length of hydrocarbon part of modifying agents as shown in Figure 4.12. Interestingly, 300% modulus was increased significantly by using quaternary ammonium salts as modifying agents. However, the abrupt increase in 300% modulus was not presented in the case of composites prepared by melt technique.

Elongation at break of composites prepared by employing different modifying agents were demonstrated in Figure 4.13. Elongation at break of composites using primary alkylamines as modifying agents was decreased slightly relative to that of pure NR. But, it was dropped significantly when quaternary ammonium salts were used. It could be explained that in the primary-alkylamine case, silicate layers were dispersed in an exfoliated form. Therefore, the continuity of NR matrix was not affected by the aggregation of silicate layers. Differently, in the quaternary-ammonium-salt case, the

continuous matrix was interrupted by the aggregation of silicate layers, previously proved by XRD spectra, thereby leading to the ease to be broken.

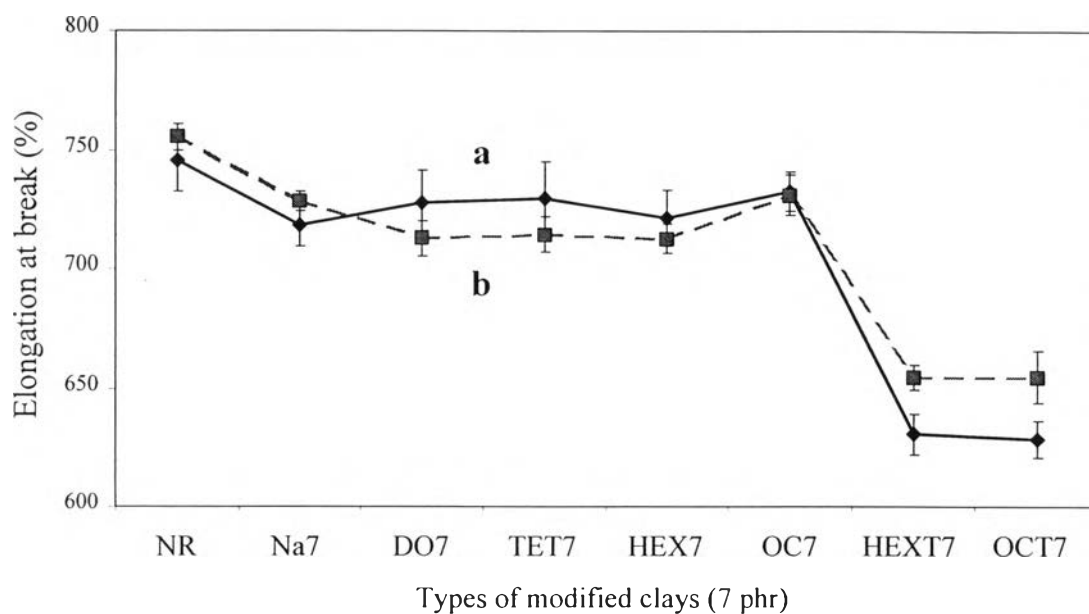


Figure 4.13 Elongation at break of NR/clay composites: (a) solution technique, (b) melt technique.

In general, tensile strength of conventional 50-phr-carbon-black filled NR was typically ranked between 25-30 MPa, and elongation at break was approximately 530% (Hofmann, W., 1989 and Mary, H.G., 1994). Interestingly, not only did tensile strength of NR/clay composites prepared by solution technique with clay loading only 7 phr, 29-32 MPa, showed slightly higher values than that of 50-phr-carbon-black filled NR, but elongation at break, 640-740%, displayed an obviously better property as well.

Effect of clay loading on tensile strength of OC-MMT/NR nanocomposites prepared by both techniques was shown in Figure 4.14. Initially, tensile strength of nanocomposites was gradually increased with the increase of clay loading. After 7 phr of clay loading, tensile strength was dropped toward higher amount of clay loading. The drop in tensile strength

after 7 phr of clay loading was correspondent with the occurring of an aggregated form of silicate layers confirmed by XRD spectra. The presence of silicate layer aggregation resulted in the break of the composite before reaching a fully oriented form, bringing about the drop in tensile strength.

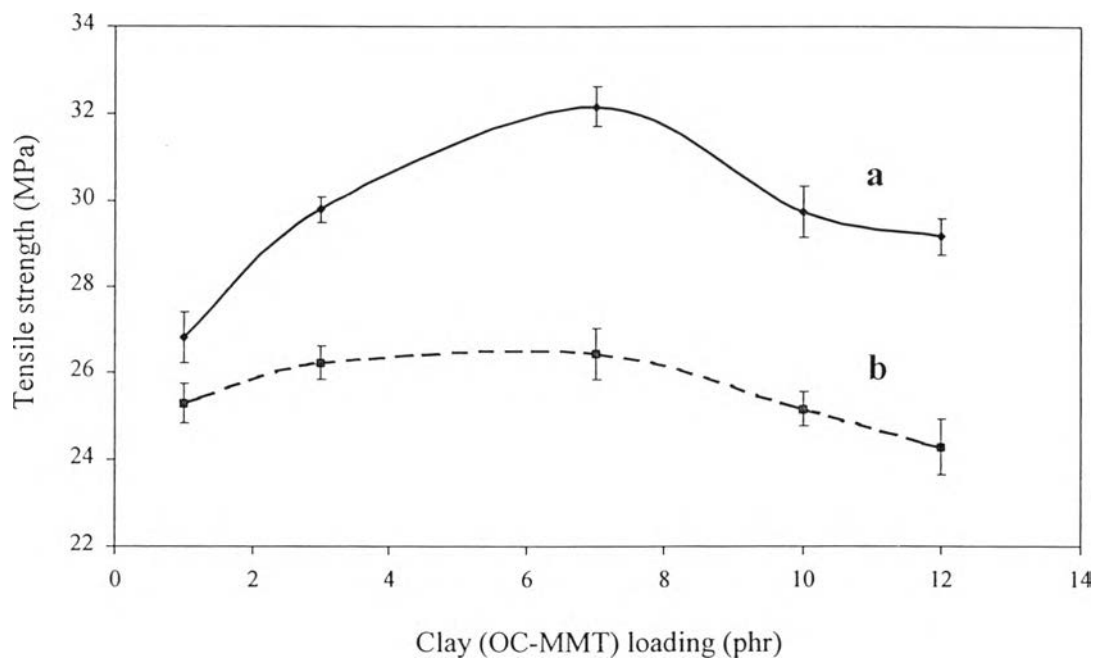


Figure 4.14 Tensile strength of OC-MMT/NR composites as a function of clay loading: (a) solution technique, (b) melt technique.