

CHAPTER IV
MODIFICATION OF CLAY SURFACE FOR RUBBER NANOCOMPOSITE
USING ADMICELLAR POLYMERIZATION SYSTEM

4.1 Abstract

One important consequence of the hydrophilic nature of the surface of clay is incompatibility with a wide range of polymer types. A necessary prerequisite for successful formation of polymer-clay nanocomposites is therefore by alteration of the clay polarity to make the clay organophilic. In order to facilitate interaction between clay layers and a polymer, the clay is modified by a process based on *in situ* polymerization of organic monomers adsorbed in surfactant layers adsorbed onto the surface of the clay. This work aims at developing a method for modifying a clay using a continuous admicellar polymerization system to produce “rubber-ready” nanoscale fillers with improved reinforcing capabilities for rubber nanocomposites and to minimize the use of a cationic surfactant using a continuously-stirring tank reactor (CSTR). Teric X10 was used as a nonionic surfactant for compromising the amount of cationic surfactant (ARQUAD[®]) required. The adsorption isotherms pure and mixed surfactants in various ARQUAD[®] to Teric X10 molar ratios were studied. The effect of ARQUAD[®] to Teric X10 molar ratio on some physico-chemical properties of the modified clay and the resulting rubber compounds was also investigated.

KEYWORDS:

Nanocomposites; clay; admicellar polymerization; natural rubber

4.2 Introduction

Most application of elastomer would be impossible without reinforcement of certain fillers. Polymer-based nanocomposites with clay mineral constitute one of the most promising composite system. Because, by employing minimal addition level (<10wt%), nanoclay is able to enhance mechanical, thermal, dimensional and barrier performance properties significantly. Being non-reinforcing in nature, there are limitations upon its use. If the properties of filler are modified, it will get a high value as a filler. Different methods for synthesizing polymer-layered silicates nanocomposites have been typically described, e.g. *in situ* intercalative polymerization, solution intercalation, and melt intercalation. Several studies have been shown the possibility of preparing intercalated or exfoliated rubber nanocomposites by different methods. It has been reported that the nanolayered silicate dispersed into a rubber matrix provides an effective reinforcement. The modification of clay by a process based on admicellar polymerization of organic monomers solubilized in surfactant layers adsorbed onto the surface of clay in order to enhance clay/elastomer interactions leads to improved rubber product performance. Recently, clay surface modification by admicellar polymerization has been successfully performed only in a batch system which yielded relatively inconsistent properties that would not acceptable for most industrial applications. Thus, a continuous admicellar polymerization process seems to be the best alternative way to produce “rubber-ready” nanoscale fillers with improved reinforcing capabilities for the rubber industry. However, the method requires the use of a cationic surfactant which may prevent further development to a commercial scale because of the cost of the surfactant. A mixture of a nonionic surfactant and a cationic surfactant is an alternative for the clay surface modification by *in situ* polymerization to lessen the operating cost.

The present study focused on optimizing the use of a cationic surfactant in the polymerization on clay, Bentonite H, by a continuously-stirring tank reactor (CSTR). Teric X10 was used as a nonionic surfactant for reducing the amount of cationic surfactant (ARQUAD®). Both surfactants are of commercial grade. The adsorption

isotherms of pure and mixed surfactants in various molar ratios of ARQUAD[®] to Teric X10 were studied. The polymerization of isoprene monomer adsorbed in admicellar layers of the surfactants was then carried out in the CSTR. The effects of surfactant structure and molar ratio of ARQUAD[®] to Teric X10 on the modified clay and the resulting rubber compounds were investigated.

4.3 Experimental

4.3.1 Materials

Tallowtrimethylammonium chloride (ARQUAD[®]) was courteously supplied by Thai Specialty Chemical Co., Ltd. Octyl phenol ethoxylate containing an average of ten moles of ethylene oxide per mole of octyl phenol (Teric X10) was obtained from Huntsman Co., Ltd. Isoprene (98+%) were purchased from Fluka. Azobisisobutyronitrile (AIBN; 98% purity), a water-insoluble initiator, was purchased from Aldrich. Tetrahydrofuran (THF) was purchased from Lab-Scan (Asia) Co., Ltd. Anhydrous ethyl alcohol was purchased from ITALMAR Co., Ltd. Montmorillonite Clay, Bentonite H (BNH), was courteously supplied by Ceramic "R" Us Co., Ltd (Thailand).

4.3.2 Experiment Set-up

The continuously-stirring tank reactor that was used to process the clay in this work consisted mainly of a stirring feed tank, a polymerization reactor, and a product tank. The feed tank made of stainless steel was approximately 17 liters with a lid and baffles. The reactor vessel was a 1 l-borosilicate glass bottle with a screw cap. The product tank was a stainless steel bucket. Mixtures in the reactor and feed tanks were well mixed by way of a magnetic bar and a mechanical stirrer, respectively. Reactor temperature was maintained at $70 \pm 2^\circ\text{C}$ by a circulative temperature-controlled water. Fluid flow rates were controlled using a Masterflex Digital console drive peristaltic pump with easy-load model 7518-60 head.

4.3.3 Adsorption Isotherm of Surfactants onto Bentonite H

Adsorption experiments were conducted in 24-ml capped vials. About 0.2 g of clay was mixed with 20 ml of ARQUAD[®] solution of varying concentration. The samples were allowed to equilibrate at 30°C for 24 hrs and later centrifuged at 6000 rpm for 20 min. The supernatant was taken and its concentration analyzed. The amount of ARQUAD[®] adsorbed was calculated by the difference in the concentration of the initial ARQUAD[®] concentration and the concentration of the supernatant. The same procedure was carried out for Teric X10 and mixed surfactants. The mixed surfactants consist of ARQUAD[®] and Teric X10 at different molar ratios of 1:3, 1:1, and 3:1. From the adsorption isotherm, the critical micelle concentration (CMC) of each surfactant system could be determined as well as the feed concentration that resulted in the concentration of the supernatant that was just below the CMC, which is critical in preventing micelle formation and hence emulsion polymerization.

4.3.4 Surface Modification Procedure

The surface of Bentonite H was modified by isoprene monomers. The molar ratio between the surfactant and the feed monomer was 2:1. The polymerization time was 30 min. The surface modification procedure was performed as follows: (1) weighing 125 g of clay, (2) ARQUAD[®] was weighed, added to 12.5 liter of deionized water and stirred until the surfactant completely dissolved, (3) adding the clay to the surfactant solution in the feed tank, (4) dissolving AIBN and isoprene monomer in 99.7% ethanol at a ratio of 30 ml of isoprene per 0.5 g of AIBN and then slowly adding this mixture to the feed tank, and (5) allowing the system to equilibrate under constant stirring for 24 hrs, forming the feed stock. The reactor was heated to 70°C to initiate the polymerization. By careful adjustment of the flow rate of both the inlet and the outlet to and from the reactor, the resident time of the feed stock (i.e. the polymerization reaction time) was 30 min. The reaction effluent, collected in the product tank, was allowed to settle and the supernatant was decanted. The modified clay was placed in a buchner funnel and washed for five days with daily stirring or until the wash water showed no

persistent foaming upon agitation. The clay was then dried at 110°C for 24 hrs, reground, and sieved through a 180-mesh screen. The same procedure was applied for other surfactant systems (i.e. Teric X10 and the mixed surfactants).

4.3.5 Testing Procedure

The amount of surfactants adsorbed on clay surface was calculated by the difference in the surfactant concentration in the aqueous feed solution and the equilibrium supernatant. The AQUARD[®] concentration was estimated by using a total organic carbon analyzer (TOC-500A, Shimadzu), while the Teric X10 concentration was estimated by using a UV/VIS spectrometer (UV/VIS spectrometer Lamda 10 PERKIN ELMER). Polymer extraction was performed by boiling 7 g of the modified clay in refluxing tetrahydrofuran (THF) for 4 hrs. The extracted slurry was cooled to room temperature, filtered, and rinsed with hot THF. THF was evaporated out by using a rotatory evaporator. Extracted polymer was analyzed by a Fourier Transform Infrared spectrophotometer (FTIR). Thermogravimetric Analyzer (TGA) was used to demonstrate the amount of polymer developed on the modified clay.

4.4 **Results and Discussion**

4.4.1 Surfactant Adsorption Isotherm

Adsorption of mixed-surfactants in various ARQUAD[®] to Teric X10 molar ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 on clay surface at the solid-liquid interface was determined to occur in two steps. In the first step, the cations exchange with protons or other counterions present at the solid-water interface. Once the surface charge has been compensated, the electrostatic driving force for surfactant adsorption is annihilated and the adsorption will only increase if the low affinity of the hydrophobic part of the surfactant for water can promote self-association and consequently further adsorption. The maximum surfactant adsorbed is determined when the surfactant is completely adsorbed on clay surface in a bilayer structure. At the equilibrium concentration of the

surfactant equivalent to the cationic exchange capacity (CEC) of the clay, a monolayer of surfactant is formed, with the alkyl chain of the surfactant pointing towards the solution; the surface of the clay now become hydrophobic and the long-range hydrophobic forces between the alkyl chains on the surface are one of the factors which play important role in aggregation of the particles. Upon subsequent adsorption of the surfactant at the interface, at a high equilibrium concentration but still below the CMC, the adsorption layer generally develops into clusters-like bilayer with the head groups pointing towards the solution. The adsorption isotherms of varies molar ratios of ARQUAD[®] to Teric X10 are presented in Figure 4.1. From the plateau data, the maximum adsorption for the different surfactant systems ranged from about 1400 $\mu\text{mol/g}$ of clay (when the ratio of ARQUAD[®] to Teric X10 ranged between 1:0 to 1:1). With further decreasing ratio of ARQUAD[®] to Teric X10 to 1:3, the maximum adsorption decreased to about 1000 $\mu\text{mol/g}$ of clay or even decreased to about only 150 $\mu\text{mol/g}$ of clay for pure Teric X10.

Furthermore, the total surfactant concentrations before and after adsorption were measured using a TOC analyzer and a UV/VIS spectrometer. Then, the molar ratio of ARQUAD[®] to Teric X10 could be calculated. Interestingly, there is more adsorption of nonionic surfactant on the layered silicate as compared to cationic surfactant in every molar ratios. It was found that the molar ratio of ARQUAD[®] to TericX10 adsorbed on the clay surface was not the same as that of the initial ratio of the mixed surfactants in the solution (see Tables 4.1 to 4.3). These results indicate that the adsorbed layer, which forms on a solid surface, is very rare when the concentration of nonionic surfactant is further increased, it is possible to see the formation of aggregates on solid surface. This may be due to interactions between the polar sites of the adsorbent and the oxyethylene groups of nonionic surfactant molecules with the hydroxyl groups on the clay surface and among oxyethylene groups through hydrogen bondings.

The selected initial surfactant concentrations used to prepare the modified clay in CSTR were 13000, 14400, 9000 and 4800 $\mu\text{mol/l}$ for ratios of various ARQUAD[®] to Teric X10 ratios of 1:0, 3:1, 1:1, and 1:3, respectively.

4.4.2 Surface Characterization of Modified Clays

4.4.2.1 *FTIR*

The material coating on the surface of the modified clays was extracted by refluxing with tetrahydrofuran (THF). The extracted material was analyzed by FTIR in order to verify the existence of polyisoprene. Figures 4.2, 4.3, 4.4 and 4.5 show FTIR spectra of standard Bentonite H, ARQUAD[®], Teric X10 and polyisoprene respectively. Clay is characterized by a broad and strong transmittance at 1150 cm⁻¹ to 900 cm⁻¹. The peak at 3696 cm⁻¹ is due to the O-H stretching of Si-OH. The other peaks at 1568 cm⁻¹ and 1348 cm⁻¹ are characteristic of the OH deformation of H-O-H and Si-OH (Pramanik, 2002). The important peaks that prove the existence of polyisoprene include C-H stretching at 2850-2970 cm⁻¹, 1340-1470 cm⁻¹, alkene C=C stretching at 3010-3095 cm⁻¹, 675-995 cm⁻¹ and aliphatic double bond (C=C) peak at 1600-1680 cm⁻¹, respectively. The spectra of the extracted materials from all of the modified clays are illustrated in Figures 4.6 to 4.9, while Figures 4.10 and 4.11 show the overlay plots of transmission FTIR for the extracted materials obtained from various molar ratios of ARQUAD[®] to Teric X10. It has been observed that with increasing molar ratio of nonionic surfactant, the intensity of the peak in the range of 675-995 cm⁻¹ which due to alkene C-H stretching decreases, suggesting that polyisoprene was less likely to be form when the amount of Teric X10 increased. Possible explanation could be the incompatibility between the isoprene monomers and the ethoxy groups on Teric X10 structure.

4.4.2.2 *XRD*

The results showed that various molar ratios of ARQUAD[®] to Teric X10 had a significant effect on the interlayer spacing expansion. The d-spacing for the admicellar polymerization-modified clay in various molar ratios of ARQUAD[®] to Teric X10 and the organoclay are listed in Table 4.4. The XRD patterns from 2 θ = 1.5 to 12 $^{\circ}$ for pristine clay, organoclay and surface-modified clay with mixed surfactant

followed by admicellar polymerization of isoprene are shown in Figures 4.12 and 4.13. All of the d-spacing values of the organoclays are larger than that of the pristine clay. This is not surprising since the nonionic surfactant molecules are larger and their uptake would almost certainly involve some interlayer expansion. Because no further cationic can enter the system, the results suggest that there must have been some intercalation of nonionic surfactant. The XRD pattern of the untreated clay showed a reflection peak at about $2\theta = 5.9^\circ$, corresponding to the basal spacing of 14.9 nm. After surface modification by cationic surfactant followed by *in situ* polymerization (P10) the reflection peak of the basal plane shifted to $2\theta = 4.7^\circ$ with a d-spacing of 18.5 nm, indicating that a swollen and intercalated structure are formed. Interestingly, in the case of clay modified by admicellar polymerization in 3:1 molar ratio of ARQUAD[®] to Teric X10 (P31) exhibited two sharp peaks at 2θ 's = 5.3° and 2.6° , respectively, suggesting that there existed two types of intercalated structure occurring separately. According to the favorable exchanging with counter ions within clay galleries, cationic surfactants tend to penetrate into silicate layer first, followed by the penetration of nonionic surfactants creating further expansion of the gallery. While the occurrence of additional peak with a lower d-spacing at $2\theta = 5.3^\circ$ is probably due to the distance between silicate layer separated by water molecules trapped within the interlayer. For XRD pattern of P11, two diffraction peaks were also observed. This support the idea that there is the co-adsorption of both cationic surfactant and nonionic surfactant on clay. The other intercalated structure corresponds to interlayer spacing that was swollen by water molecules. Interestingly, further increase in nonionic surfactant loading, as in the case of P13, the absence of the basal plane peak position at lower angle in XRD pattern was observed. It may be proposed that at such a low cationic surfactant loading, neither cationic nor nonionic surfactants can penetrate in between silicate layers. Moreover, a single peak at $2\theta = 5.5^\circ$ with a d-spacing of 15.9 nm corresponds to the layer silicate that is swollen by water molecules. It is also evident that cationic surfactant plays a more important role in enlarging the intergalleries. Without the presence of ARQUAD[®], Teric X10 themselves are not able to penetrate into the silicate layers because of their

larger size as compared to that of the clay interlayer spacing. Most of Teric X10 molecules tend to aggregate at the external surface of the clay particles. Such coverage of nonionic surfactants onto the clay particles prevent water molecules trapped within the layer to move out. This can be confirmed by a single diffraction peak at $2\theta = 6.1$ for P01. This peak corresponds to the d-spacing of clay that is swollen by water molecules. The status of the clay treated with various ratios of ARQUAD[®] to Teric X10 followed by *in situ* polymerization of isoprene in NR nanocomposites were also evaluated by X-ray diffraction. The results showed that no peak appeared in XRD spectra of NR nanocomposites (containing 10 phr of the modified clays), which could be a result of the low clay concentration and the relatively low fraction of the intercalated clusters.

4.4.2.3 TGA

In order to verify the existence of polyisoprene formed on the clay surface, all samples were examined by Thermogravimetric analysis. All organoclay and admicellar polymerization modified clay showed a weight loss below 100°C due to free water, which resides between clay particles and adsorbed on the external surface of the clay (Xie 2001). The weight loss at the temperature higher than 500°C, due to dehydroxylation of aluminosilicate and a release of residual organic carbonaceous residue product, will not be considered (Deer 1996, Osmani 2003). As evidenced from Figures 4.15 and 4.16, the decomposition temperature (T_d) of the cationic surfactant, ARQUAD[®], is around 250°C while that of the nonionic surfactant, Teric X10, is approximately 370°C. The decomposition of polyisoprene appears in the temperature range of 250 to 450°C, as shown in Figure 4.17. TGA results of untreated clay and organoclay modified clays and admicellar polymerization-modified clays are shown in Figures 4.18 to 4.28. Figure 4.29 and 4.30 depict the TGA plots and the derivative weight loss, DTG, for admicellar modified clay at different molar ratios of ARQUAD[®] to Teric X10. The DTG for organoclay with ARQUAD[®] shows two peaks at temperature ranging from 220 to 300°C and 300 to 400°C corresponding to the two-step decomposition of ARQUAD[®] adsorbed onto the clay surface. Both steps may be

attributed to the decomposition of ARQUAD[®] adsorbed on outer clay surface and in the layered silicates. According to confinement in movement, the latter tends to be degraded at a higher temperature. Obviously, the decomposition peak of polyisoprene at the temperature ranging from 250 to 450°C was observed in the case of P10 so polyisoprene was formed in this case. On the other hand, it is clearly showed that no decomposition peak of polyisoprene was detected in the case of B13 and B01. This may be due to nonpolar nature of isoprene monomers that make them difficult to adsorb within the layer of Teric X10 with partial charges on their structure. Figure 4.22 reveals that there was also the decomposition peak of polyisoprene adsorbed on 3:1 molar ratio of ARQUAD[®] to Teric X10. Evidently, in this case, the modified clay shows only two decomposition peaks. The first peak corresponds to ARQUAD[®] decomposition around 320 to 380°C. The second peak is the composition of polyisoprene obtained from admicellar polymerization-modified clay appearing around 420°C. As the nonionic surfactant content increases (i.e. from the ratio of ARQUAD[®] to Teric X10 of 1:1 to 1:3), a shoulder of the peak around 400°C was detected, implying that very small amount of polyisoprene was formed on the clay surface. This is possibly due to low adsorption of nonionic surfactant on layer silicate and there is less favorable for isoprene monomer to adsorb within. Nevertheless, there was no decomposition peak of polyisoprene in both P01 and organoclay with nonionic surfactant (B01).

4.4.3 Physical Properties of clay-rubber nanocomposites

The physical properties of vulcanizates with admicellar-modified clay and organoclay are summarized in Tables 4.5 and 4.6, respectively. The variation of the cure time with changes in the ARQUAD[®] to Teric X10 molar ratio is shown in Figure 4.31. It is observed that, in the case of 1:0 and 3:1 ARQUAD[®] to Teric X10 molar ratios, the cure time was sharply reduced by incorporation of small amount of the admicellar-modified clay. Both exhibit accelerated vulcanization with respect to pure NR and NR with untreated clay. It is deduced that such surface modified clay behave as an effective vulcanizing agent for natural rubber. These results are confirmed by the

TGA results that in the presence of polyisoprene film form on clay surface, further accelerating effect on NR curing takes place. On the contrary, an increase in the amount of Teric X10 resulted in a much increase in the cure time. Figures 4.32, 4.33, and 4.34 show the difference in the moduli of different admicellar polymerization-modified clay-filled nanocomposites at different elongational sets (i.e. 100, 200, and 300%). This is because the filler-polymer interactions play a critical role at low elongations, just as at high elongations the strain-induced crystallization of NR dominates. (Vargehese, 2003) Figures 4.35, 4.36, 4.37, and 4.38 clearly show that 1:0 and 3:1 molar ratios show noticeable increase in tensile strength, hardness, tear strength, and resilience with the least heat build up and no significant increase in the specific gravity. This shows the strong reinforcing effect of these inorganic fillers. The reinforcement is associated with the anisotropy, high aspect ratio as well as well polyisoprene film formed on clay surface that enhances the dispersion of its in NR matrix. It seems that both the modulus and the maximum strength increase with increasing molar ratio of cationic surfactant in both organoclay and admicellar-modified clay. This fact can be attributed to the good dispersion of organoclay. With the admicellar polymerization modification, the dispersion of the as-modified clay in NR matrix is further enhanced by the presence of polyisoprene film on the clay surface.

4.5 Conclusions

Nanosopic reinforcing filler has been successfully prepared by admicellar polymerization of isoprene adsolubilized in the layer of mixed surfactant with different molar ratios of cationic to nonionic surfactants adsorbed on layered alumino-silicates. Natural rubber/clay nanocomposites have been subsequently prepared using melt blending technique followed by physical property testing. The results revealed that variation in the molar ratios of cationic to nonionic surfactants had remarkable effect on the cure characteristic and the overall physical properties of the rubber compounds. Evidently, the vulcanizates filled with modified clays prepared using the molar ratio

between the cationic to nonionic surfactants of 3:1 exhibited the highest overall properties, including modulus, maximum strength, tear strength, hardness and resilience. All these results indicate the role of polyisoprene film formed on the filler surface to cause either chemical crosslinking with natural rubber matrix or a decrease in the interfacial tension of the clay particles that enhance the dispersion.

4.6 Acknowledgements

The author is particularly grateful to Postgraduate Education and Research programs in Petroleum and Petrochemical Technology (PPT Consortium) and The Research Unit: Applied Surfactant for Separation and Pollution Control from Ratchadapisak Sompote Fund, Chulalongkorn University for research funding and to the Petroleum and Petrochemical College, Chulalongkorn University, for the partial scholarship. The author would also like to acknowledge the Rubber Research Institute for providing natural rubber for this research.

4.7 References

- Yeskie, M.A., and Harwell, J.H. (1988) On the structure of aggregates of adsorbed surfactants: the surface charge density at the humimicelles / admicelle transition. The Journal of Physical Chemistry, 92(8), 2346-2352.
- Williams-Daryn, S., Thomus, R.K., Castro, M.A., and Becerro, A. (2002) The Structures of Complexes of a Vermiculite Intercalated by Cationic Surfactants, a Mixture of Cationic Surfactants, and a mixture of Cationic and Nonionic Surfactants. Journal of Colloid and Interface Science, 256, 314-324.
- Lee, S.Y. and Kim, S.J. (2002) Delamination Behavior of Silicate Layers by Adsorption of Cationic Surfactants. Journal of Colloid Interface Science, 256, 314-324.

- Lopez, M.A., Herrero, B., and Arroyo, M. (2004) Organoclay-natural rubber nanocomposites synthesized by mechanical and solution mixing methods. Polymer International, (in press)
- Wu, Y.P., Jia, Q.X., Yu., and Zhang, L.Q. (2004) Modeling Young's modulus of rubber-clay nanocomposites using composite theories. Polymer testing, 23, 908-909.
- Varghese, S., and Karger-Kocsis, J. (2003) Melt-compounded natural rubber nanocomposites with Pristine and organophilic layered silicates of natural and synthetic origin. Journal of Applied Polymer Science, 91, 813-819.
- Varghese, S., and Karger-Kocsis, J. (2003) Natural rubber-based nanocomposites by latex compounding with layered silicates. Polymer, 44, 4921-4927.
- Nabil, A.N., Kapadi, U.R., and Hundiwale, D.G. (2004) Effect of titanate coupling agent on the mechanical properties of clay-filled polubutadiene rubber. Journal of Applied Polymer Science, 93, 1299-1304.
- Wang, S., Hu, Y., Qu, S., Chen, Z., and Fan, W. (2003) Preparation and flammability properties of polyethylene/clay nanocomposites by melt intercalation method from Na⁺ montmorillonite. Material letters, 57, 2675-2678.
- Pramanik, M., Srivastava, S.K., Samantaray, B.K., and Bhowmick, A.K. (2002) Synthesis and characterization of organosoluble, thermoplastic elastomer/clay nanocomposites. Journal of Polymer Science: part B: Polymer Physics, 40, 2065-2072.
- Xie, W., Gao, Z., Pan, WP., Hunter, D., Singh, A., and Vaia, R. (2001) Thermal degradation chemistry of Alkyl Quaternary Ammonium Montmorillonite, Chemical Material, 13, 2979-2990.
- Osmann, M.A., Ploetzeb, M., and Suter, U.W. (2003) Surface treatment of clay mineral-thermal stability, basal-plane spacing and surface coverage, Journal of Material Chemistry, 13, 2359-2366.
- Deer, W.A., Howie, R.A., and Zussman. (1996) An Introduction to The Rock-Forming Minerals. China: Addison Wesley Longman Ltd.

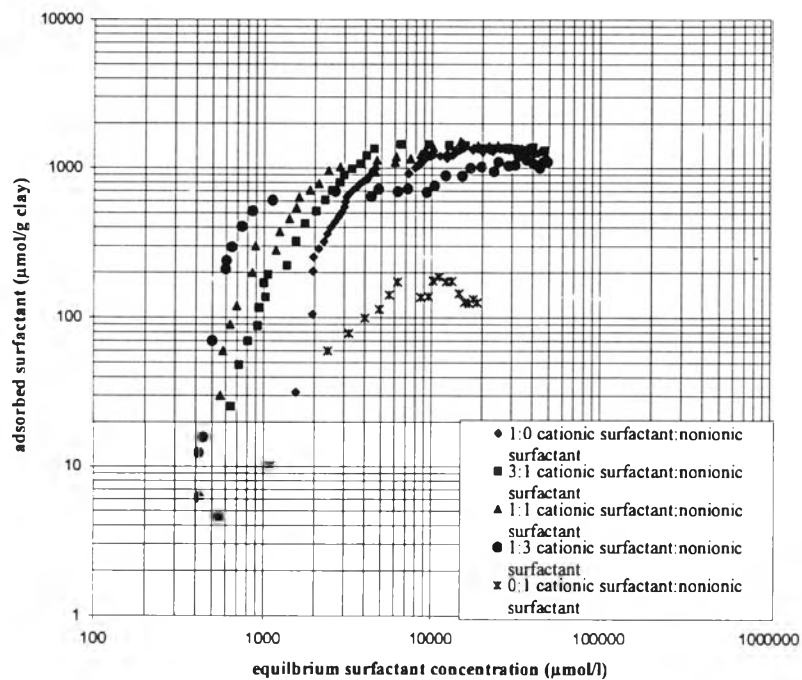


Figure 4.1 Adsorption isotherms of surfactants onto Bentonite H at 30 °C at various of ARQUAD® : Teric X10 molar ratios.

Table 4.1 Adsorption ratio of ARQUAD[®]/ Teric X10 on clay (1:1 the initial ratio of ARQUAD[®] /Teric X10)

Initial concentration ($\mu\text{mol/l}$)	Total adsorbed surfactant ($\mu\text{mol/g clay}$)	Adsorbed Teric X10 ($\mu\text{mol/g clay}$)	Adsorbed ARQUAD[®] ($\mu\text{mol/g clay}$)	ARQUAD[®] /Teric X10 ratio
5000	376.3	232.5	143.8	0.62
6000	458.9	275.1	183.8	0.67
9000	712.6	422.1	290.5	0.69
10000	788.2	464.0	324.2	0.70
14000	941.1	422.5	418.7	0.99
16000	1132.5	510.3	522.3	1.02
18000	1190.8	546.0	544.9	1.00
19000	1156.7	542.3	514.4	0.95
20000	1146.3	589.6	456.7	0.77
21000	1241.0	698.4	542.7	0.78
22500	1335.3	773.0	562.4	0.73
24000	1374.3	836.5	537.8	0.64
27000	1418.6	996.8	421.8	0.42
30000	1517.2	1135.5	381.7	0.34
33000	1422.1	1294.2	127.8	0.10

Table 4.2 Adsorption ratio of ARQUAD[®] /Teric X10 on clay (1:3 the initial ratio of ARQUAD[®]/Teric X-10)

Initial Concentration ($\mu\text{mol/l}$)	Total adsorbed surfactant ($\mu\text{mol/g clay}$)	Adsorbed Teric X10 ($\mu\text{mol/g clay}$)	Adsorbed ARQUAD[®] ($\mu\text{mol/g clay}$)	ARQUAD[®] /Teric X10 ratio
1200	70.1	65.8	4.2	0.06
2700	210.2	193.6	16.6	0.09
3000	239.5	220.4	19.1	0.09
3600	295.1	265.5	29.6	0.11
4800	405.6	353.6	52.1	0.15
6000	514.3	428.5	85.8	0.20
7200	607.4	531.8	75.6	0.14

Table 4.3 Adsorption ratio of ARQUAD[®] /Teric X10 on clay (3:1 the initial ratio of ARQUAD[®]/Teric X10)

Initial Concentration ($\mu\text{mol/l}$)	Total adsorbed surfactant ($\mu\text{mol/g clay}$)	Teric X10 ($\mu\text{mol/g clay}$)	ARQUAD[®] ($\mu\text{mol/g clay}$)	ARQUAD[®] /Teric X10 ratio
900	25.4	14.9	10.6	0.71
1800	88.1	38.1	50.0	1.31
2100	116.3	47.6	68.6	1.44
2400	137.4	55.4	82.0	1.48
2700	170.2	62.7	107.5	1.71
3000	194.2	70.6	123.6	1.75
3600	222.7	84.9	137.8	1.62
4800	325.1	115.0	210.1	1.83
6000	424.9	145.1	279.8	1.93
7200	516.3	174.8	341.6	1.95
8400	609.5	204.8	404.7	1.98
9600	706.5	233.8	472.8	2.02
10800	798.5	261.4	537.1	2.05
12000	901.1	290.1	611.0	2.11
13200	987.2	319.4	667.3	2.09
14400	1065.9	348.6	717.4	2.06
16200	1211.8	388.1	823.7	2.12
18000	1347.9	432.1	915.8	2.12
21000	1446.1	446.1	1000.5	2.24
24000	1434.7	433.1	1001.5	2.31
27000	1428.8	474.7	954.1	2.01

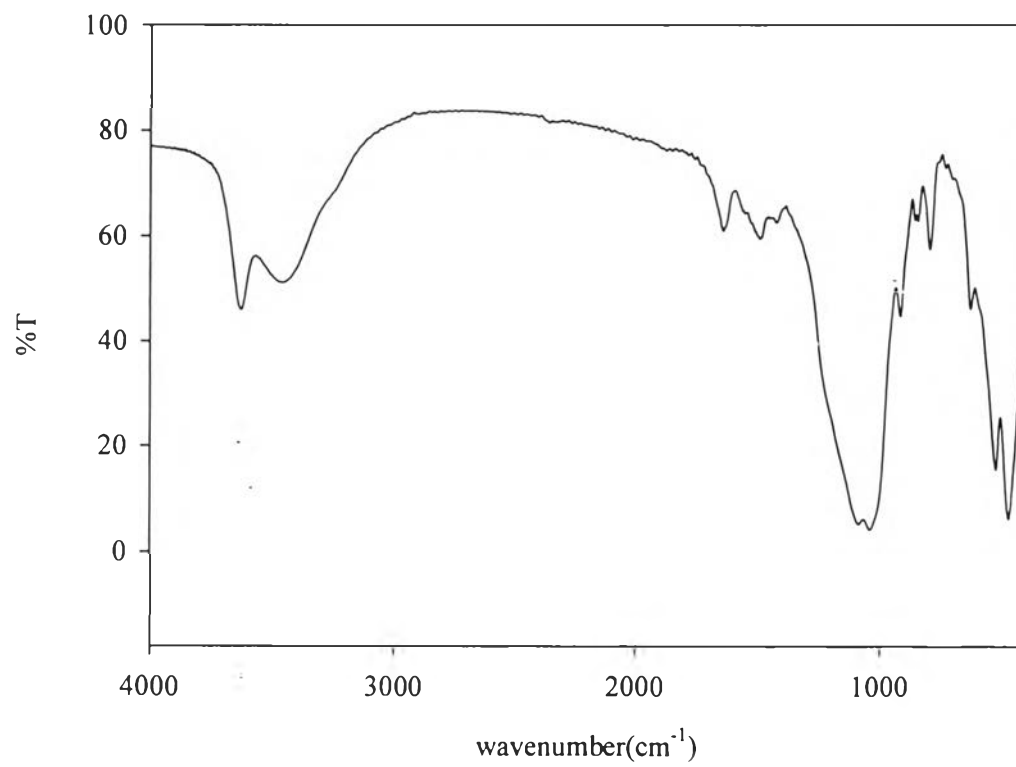


Figure 4.2 FTIR spectrum of Bentonite H.

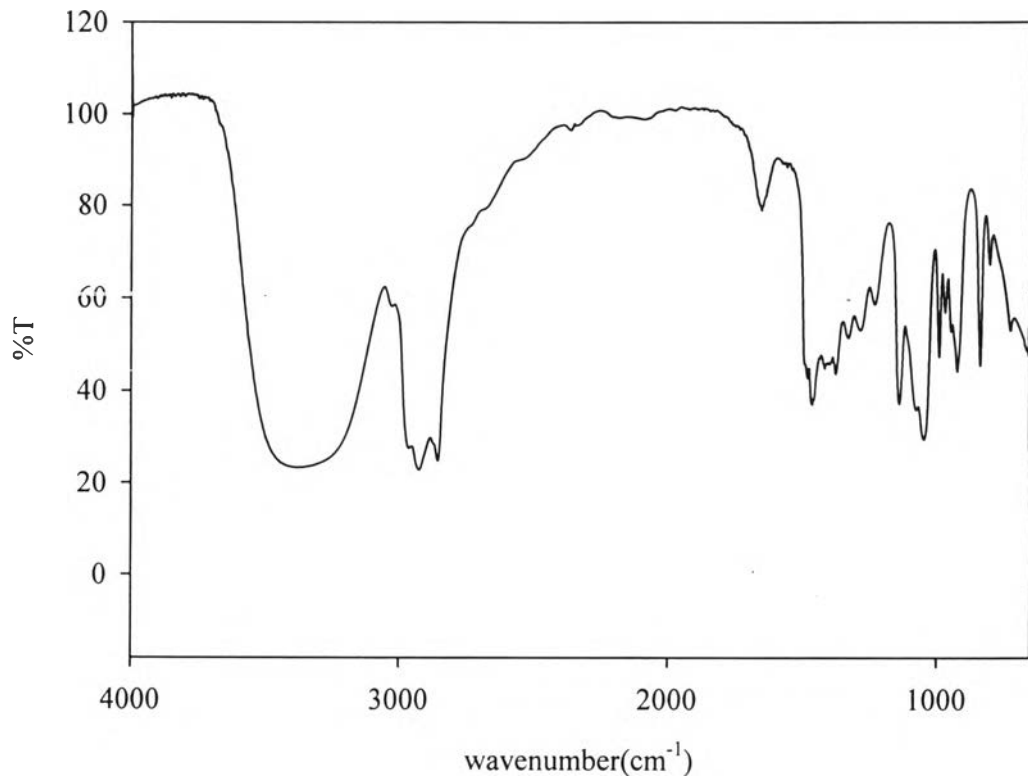


Figure 4.3 FTIR spectrum of ARQUAD®.

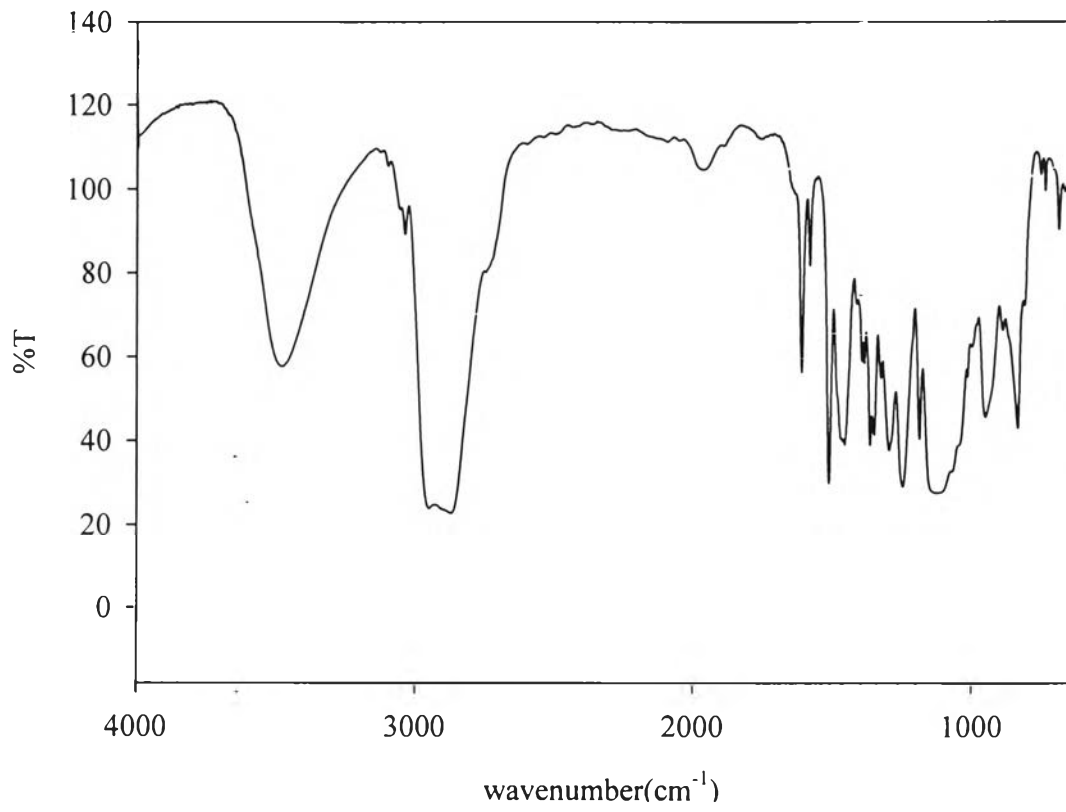


Figure 4.4 FTIR spectrum of Teric X10.

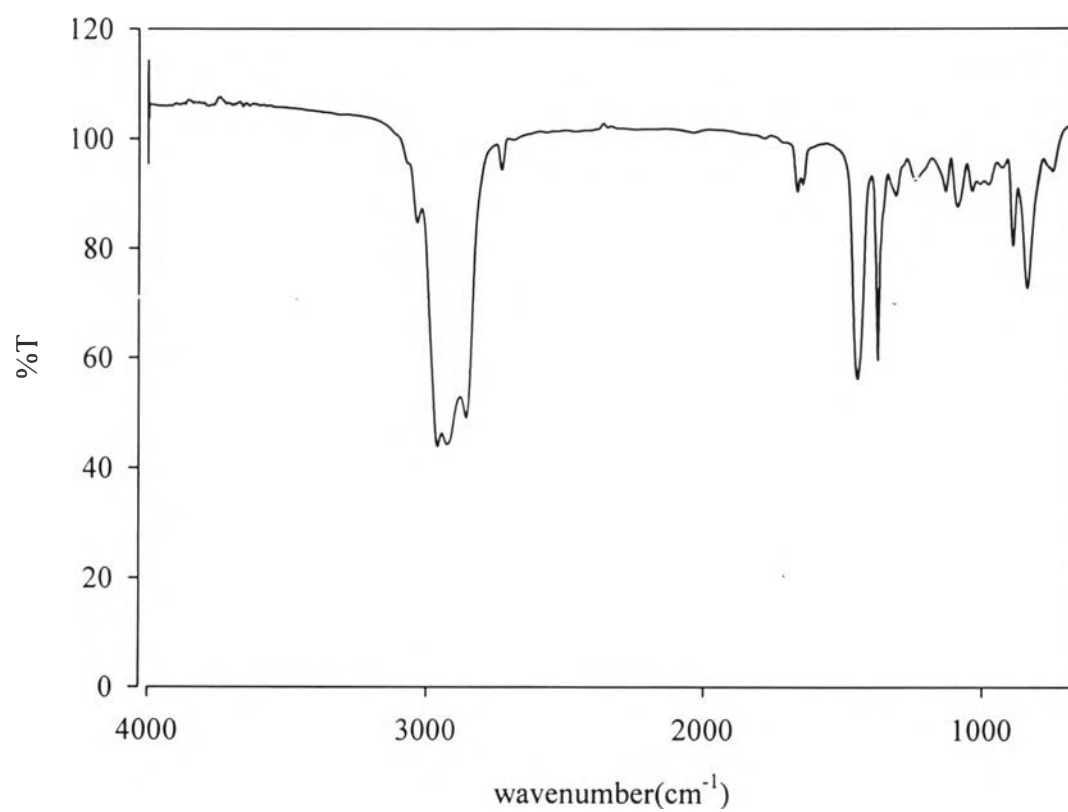


Figure 4.5 FTIR spectrum of Standard Polyisoprene.

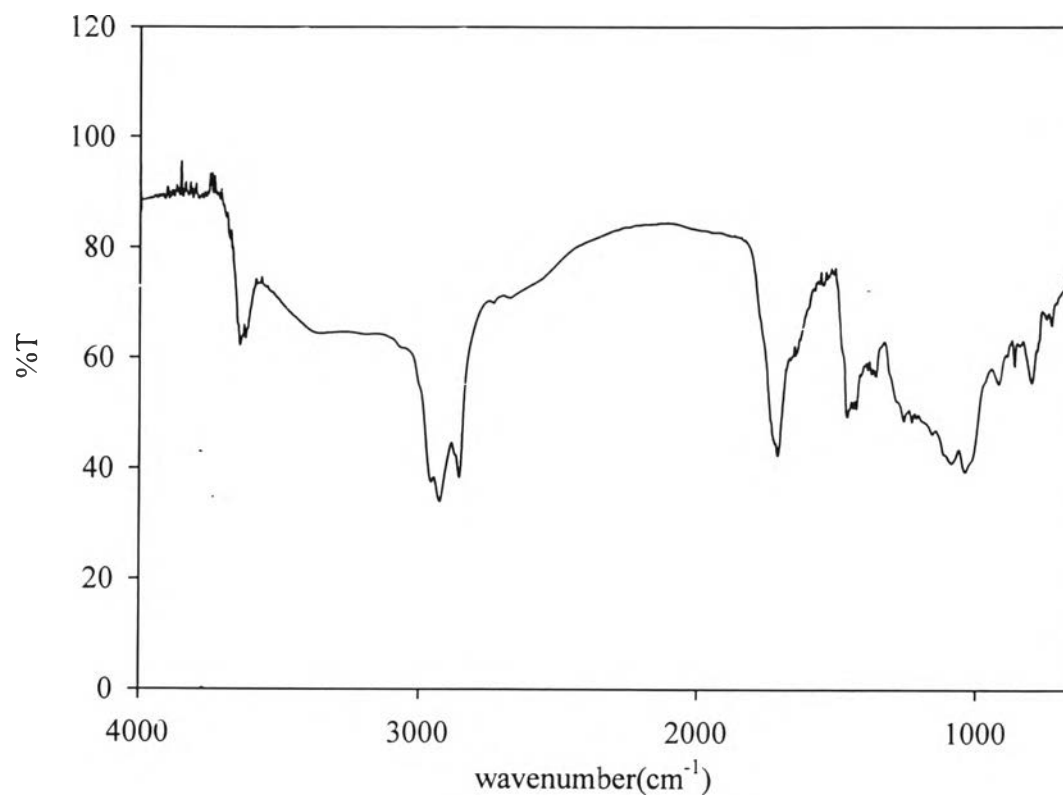


Figure 4.6 FTIR spectra of extracted material from admicellar polymerization modified clay with 1:0 the initial ratio of ARQUAD[®]/Teric X10.

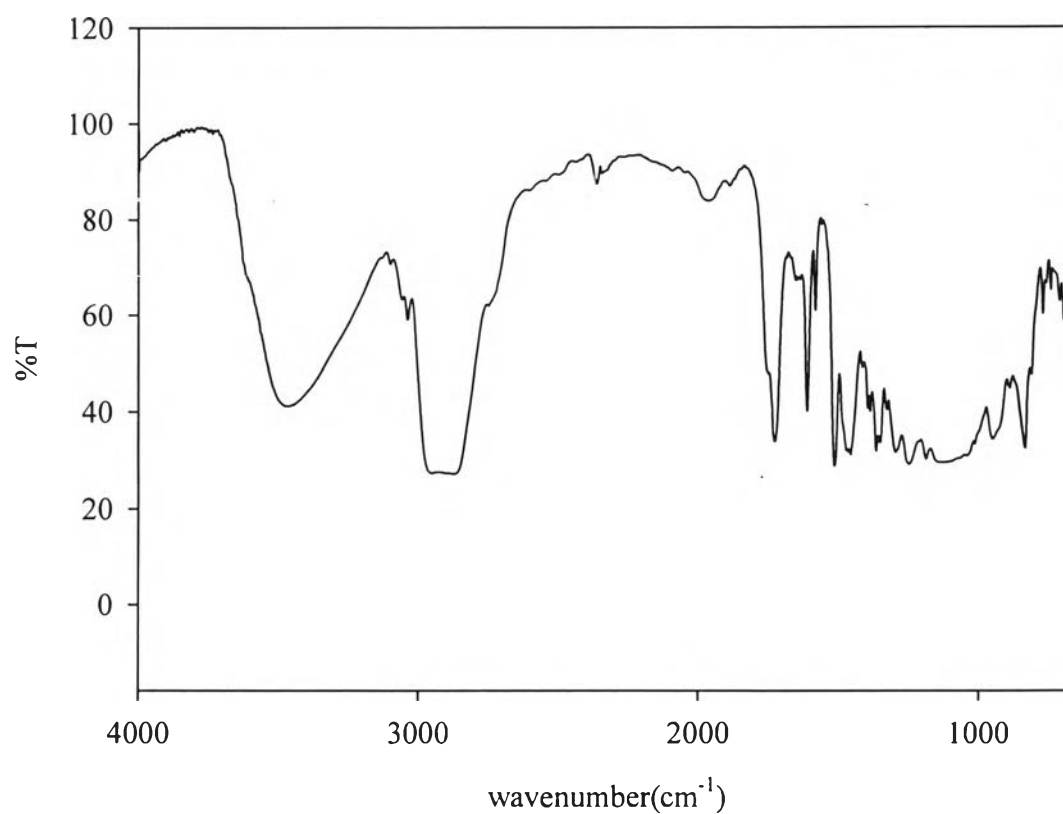


Figure 4.7 FTIR spectra of extracted material from admicellar polymerization modified clay with 3:1 the initial ratio of ARQUAD[®]/Teric X10.

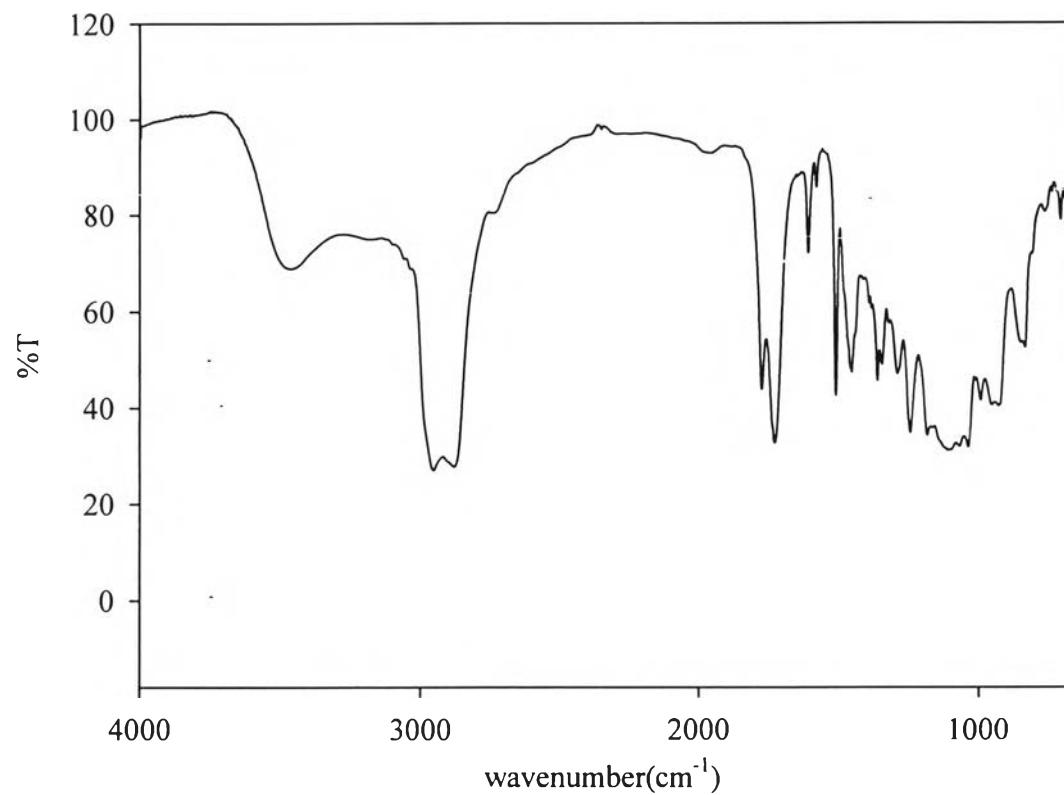


Figure 4.8 FTIR spectra of extracted material from admicellar polymerization modified clay with 1:1 the initial ratio of ARQUAD[®]/Teric X10.

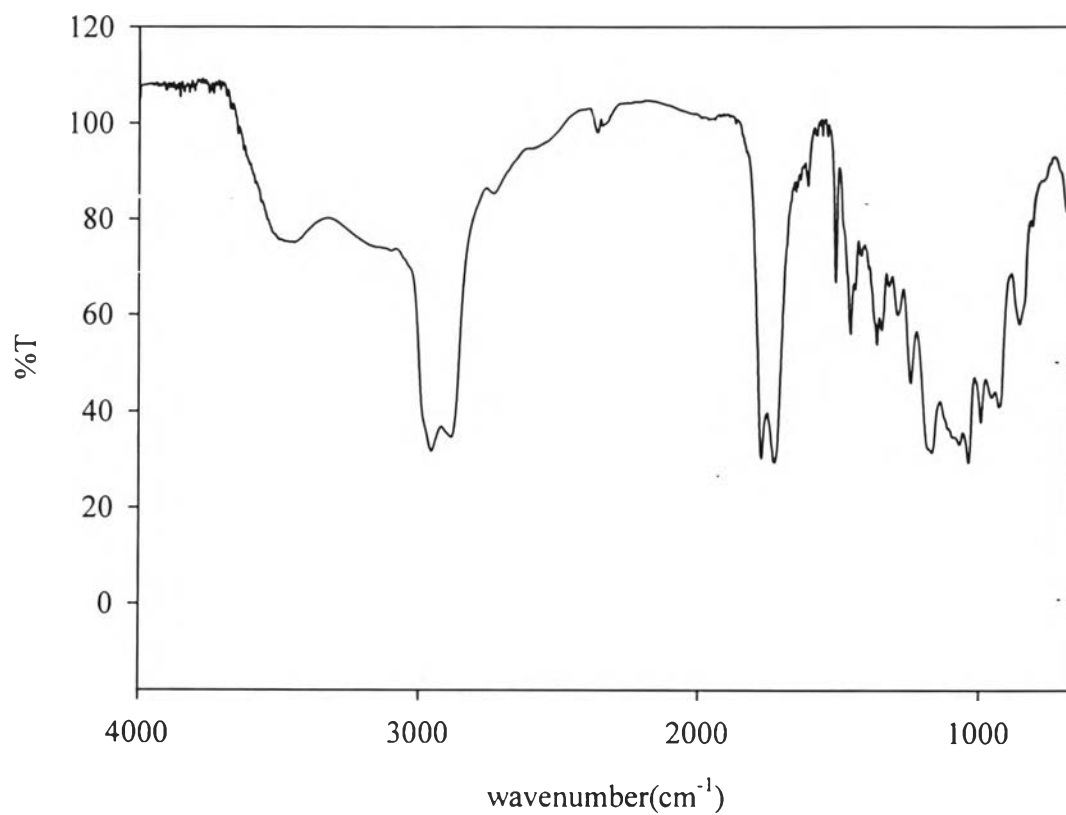


Figure 4.9 FTIR spectra of extracted material from admicellar polymerization modified clay with 1:3 the initial ratio of ARQUAD[®]/Teric X10.

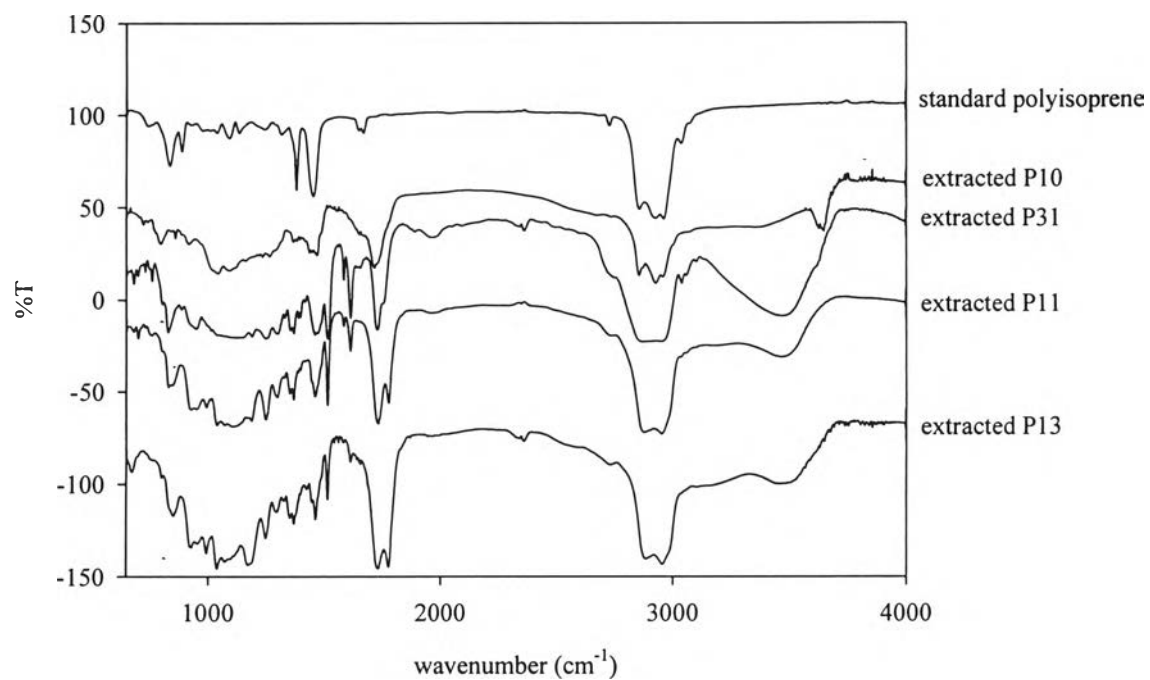


Figure 4.10 Transmission FTIR for extracted material from admicellar polymerization modified clay with different molar ratios of AQUARD[®] to Teric X10.

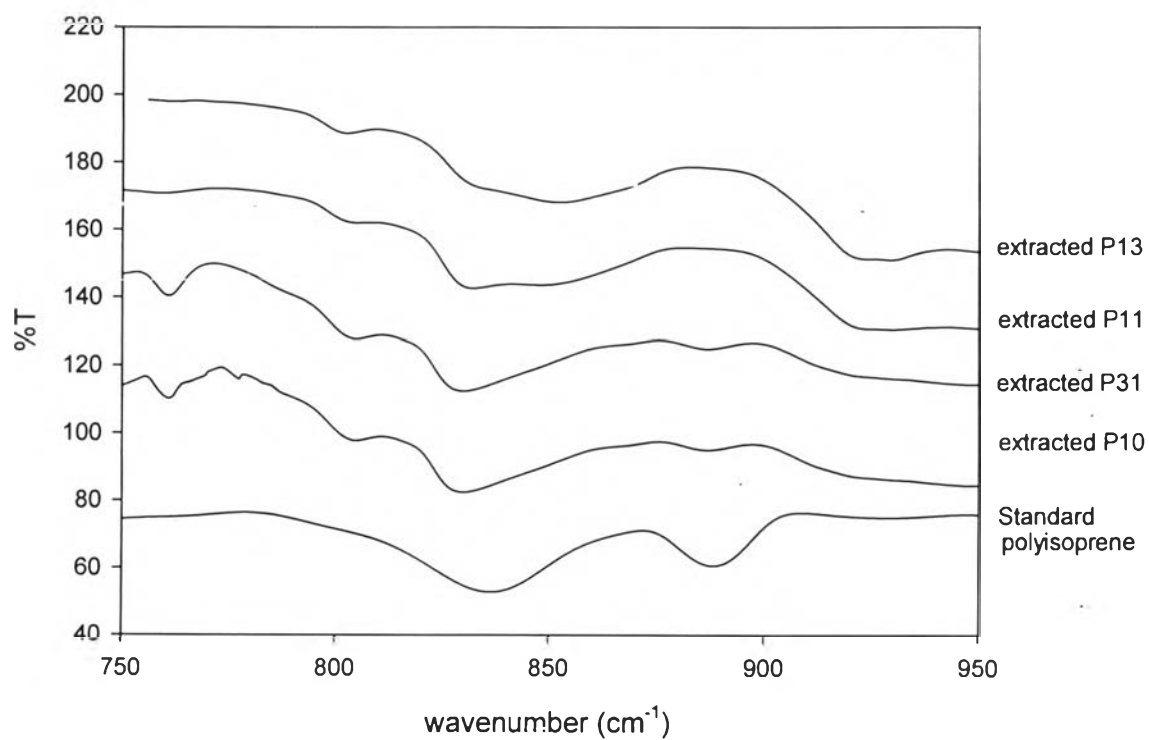


Figure 4.11 Overlay plots of transmission FTIR for extracted material from admicellar polymerization modified clay with different molar ratios of AQUARD[®] to Teric X10.

Table 4.4 XRD data for studied materials

Parameter	Untreated clay	Organoclay					Admicellar polymerization modified-clay				
		B10	B31	B11	B13	B01	P10	P31	P11	P13	P01
2 θ (degree)	5.9	4.3	2.6 5.4	2.3 5.4	5.5	5.5	4.7	2.6 5.3	2.3 5.4	5.5	5.5
d-value (nm)	14.9	19.5	33.7 16.2	37.7 16.2	16.1	16.1	18.5	34.5 16.5	37.7 16.3	15.9	16.1

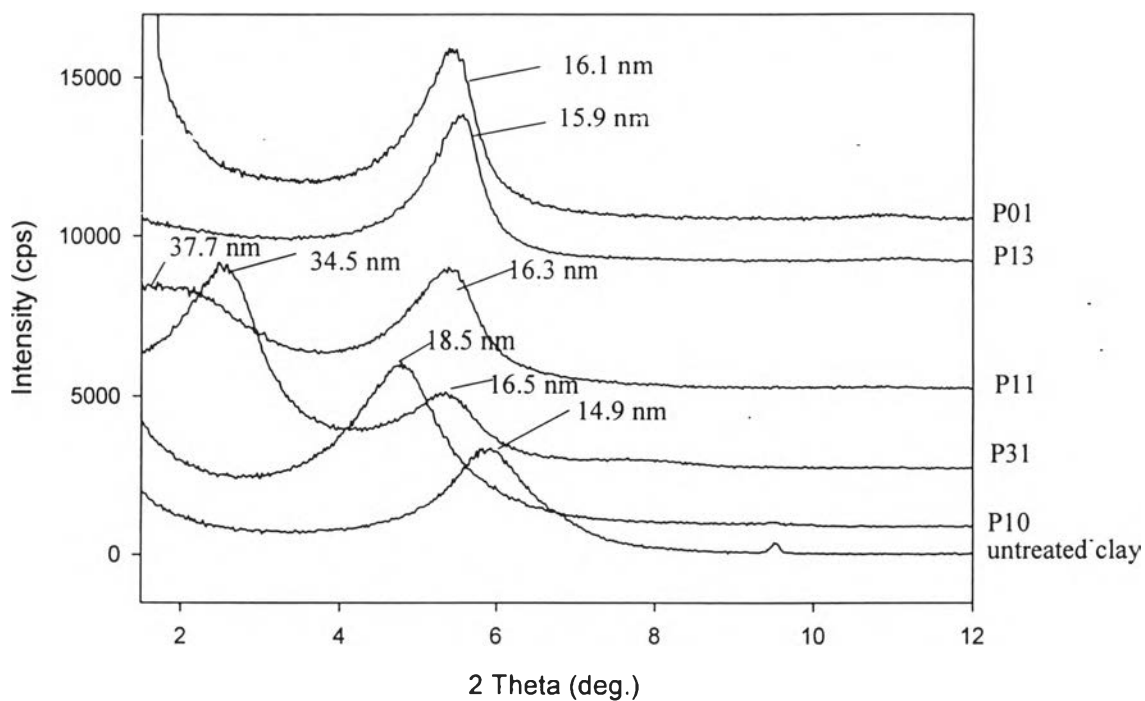


Figure 4.12 X-ray diffraction pattern for untreated clay, admicellar modified clay with 1:0 molar ratio ARQUAD[®]:Teric X10 (P10), admicellar modified clay with 3:1 molar ratio ARQUAD[®]:Teric X10 (P31), admicellar modified clay with 1:1 molar ratio ARQUAD[®]:Teric X10 (P11), admicellar modified clay with 1:3 molar ratio ARQUAD[®]:Teric X10 (P13).

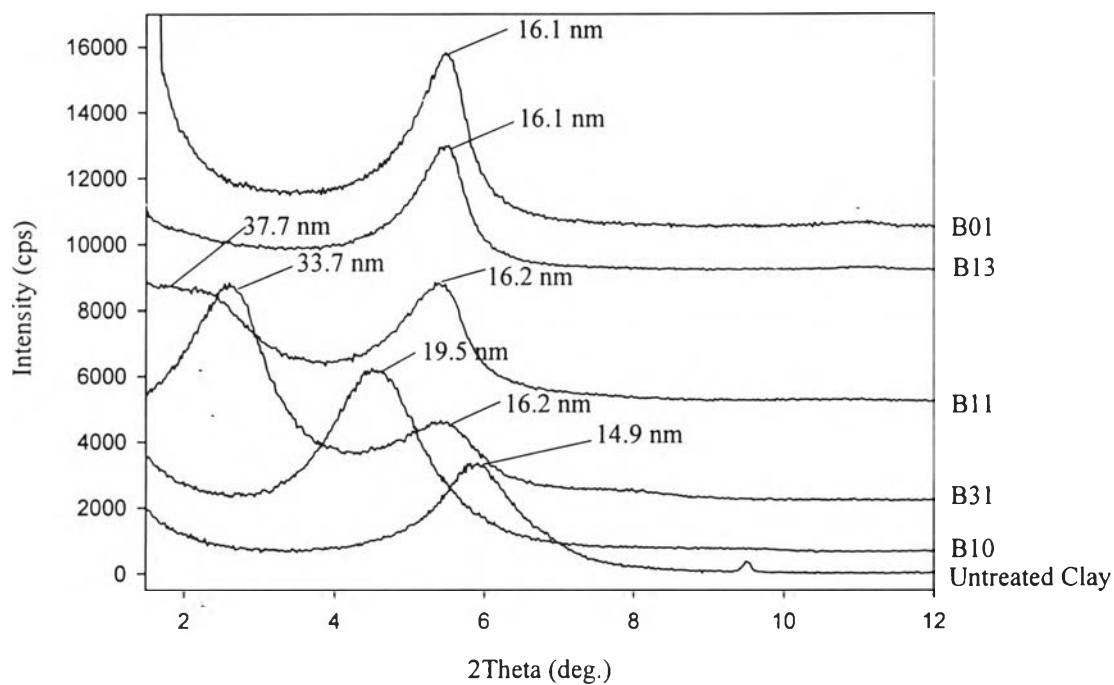


Figure 4.13 X-ray diffraction pattern for untreated clay, organoclay with 1:0 molar ratio ARQUAD[®]:Teric X10 (B10), organoclay with 3:1 molar ratio ARQUAD[®]:Teric X10 (B31), organoclay with 1:1 molar ratio ARQUAD[®]:Teric X10 (B11), organoclay with 1:3 molar ratio ARQUAD[®]:Teric X10 (B13), organoclay with 0:1 molar ratio ARQUAD[®]:Teric X10 (B01).

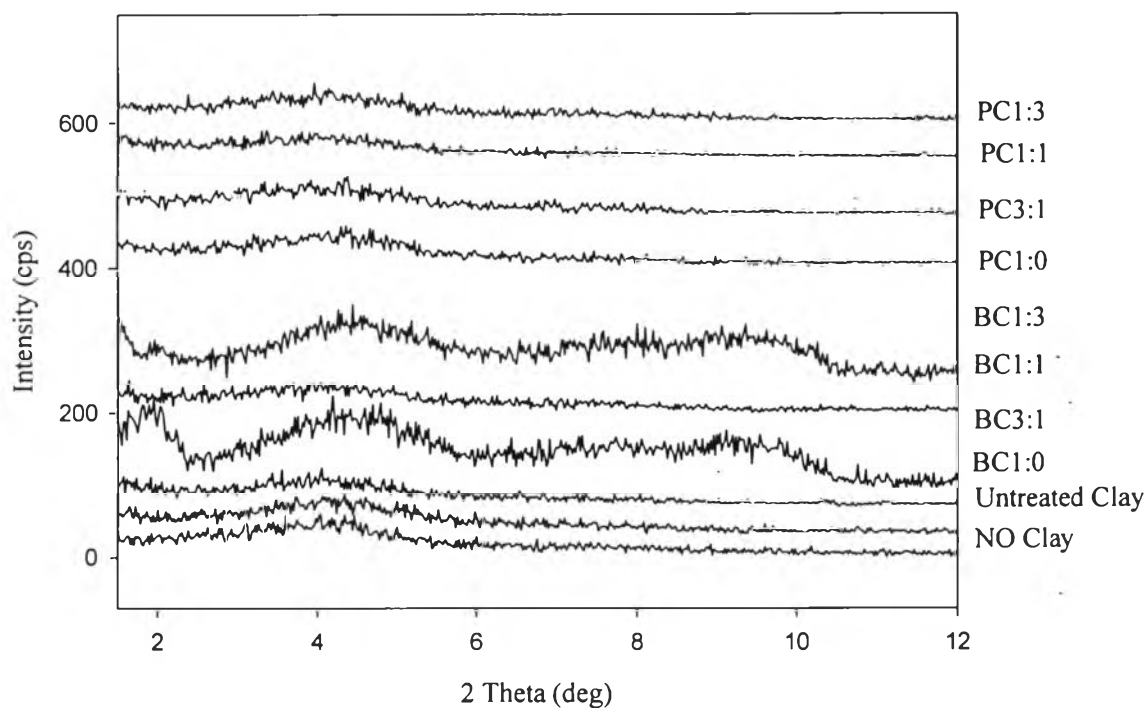


Figure 4.14 X-ray diffraction pattern for a compound without clay (No Clay), untreated clay/NR nanocomposite (Untreated Clay), admicellar modified clay with 1:0 molar ratio ARQUAD[®]:Teric X10 (P10)/ NR nanocomposite (PC1:0), organoclay with 1:0 molar ratio ARQUAD[®]:Teric X10 /NR nanocomposite (BC10), admicellar modified clay with 3:1 molar ratio ARQUAD[®]:Teric X10 /NR nanocomposite (PC31), organoclay with 3:1 molar ratio ARQUAD[®]:Teric X10/ NR nanocomposite (BC31), admicellar modified clay with 1:1 molar ratio ARQUAD[®]:Teric X10 /NR nanocomposite (PC11), organoclay with 1:1 molar ratio ARQUAD[®]:Teric X10 /NR nanocomposite (BC11), admicellar modified clay with 1:3 molar ratio ARQUAD[®]:Teric X10/ NR nanocomposite (PC13), organoclay with 1:3 molar ratio ARQUAD[®]:Teric X10/ NR nanocomposite (BC13).

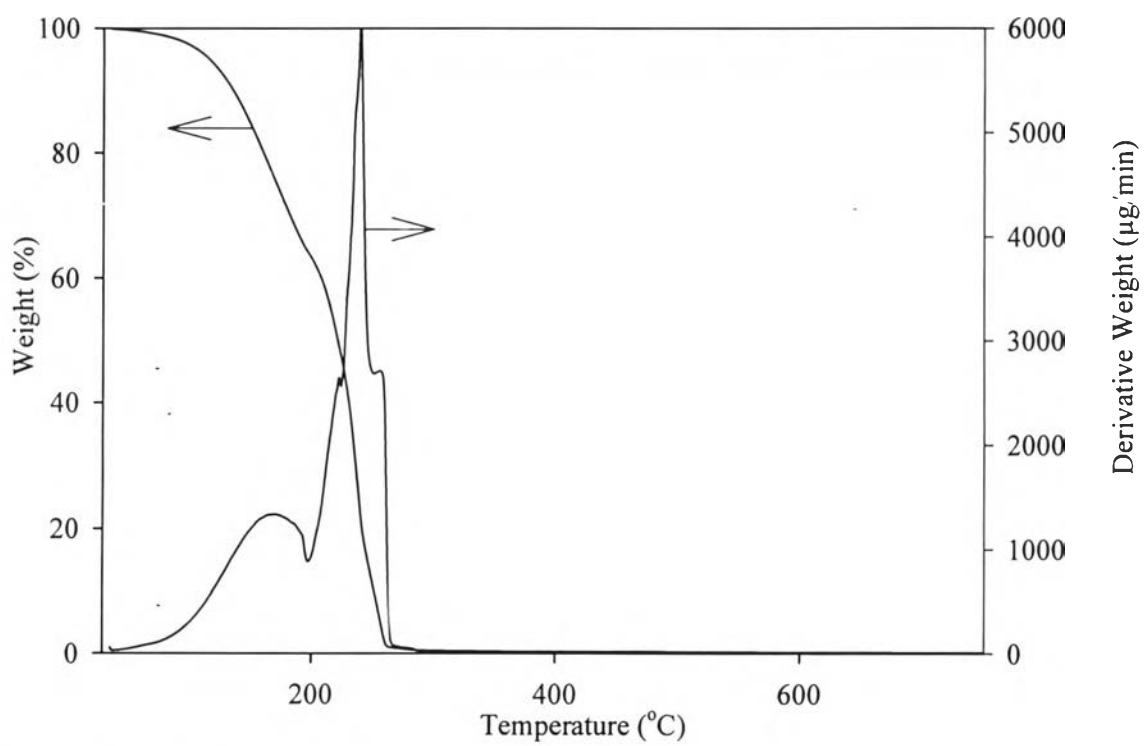


Figure 4.15 TGA result of ARQUAD®.

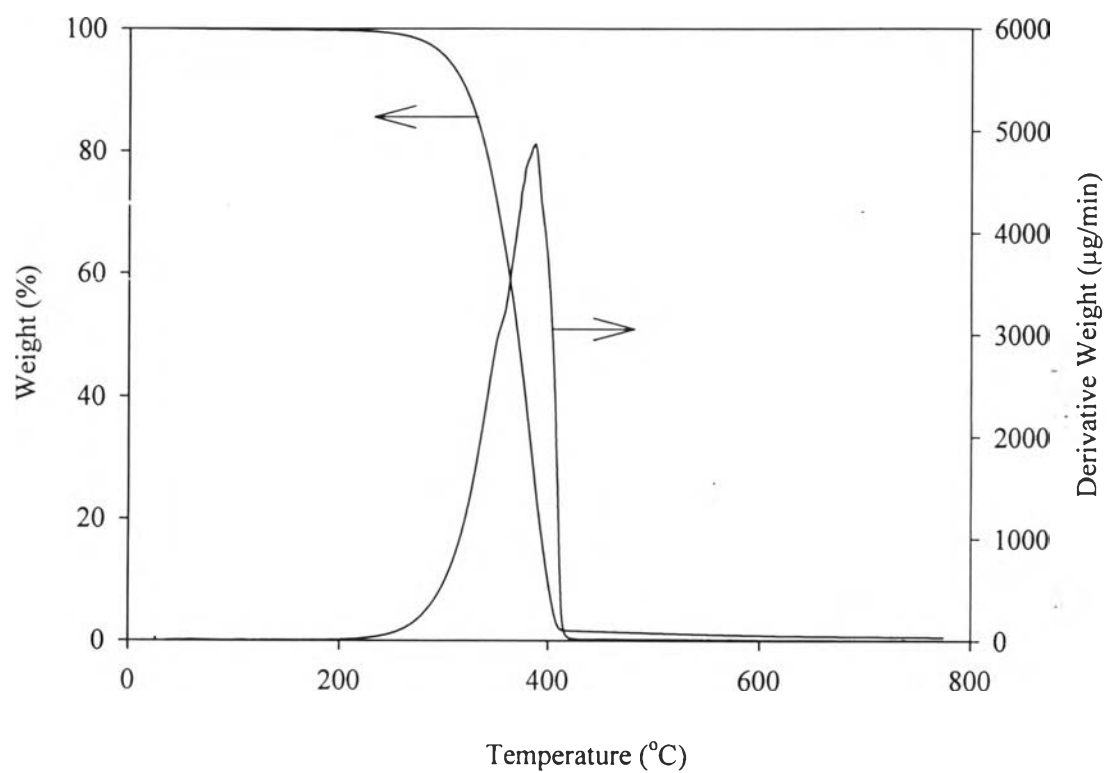


Figure 4.16 TGA result of Teric X10.

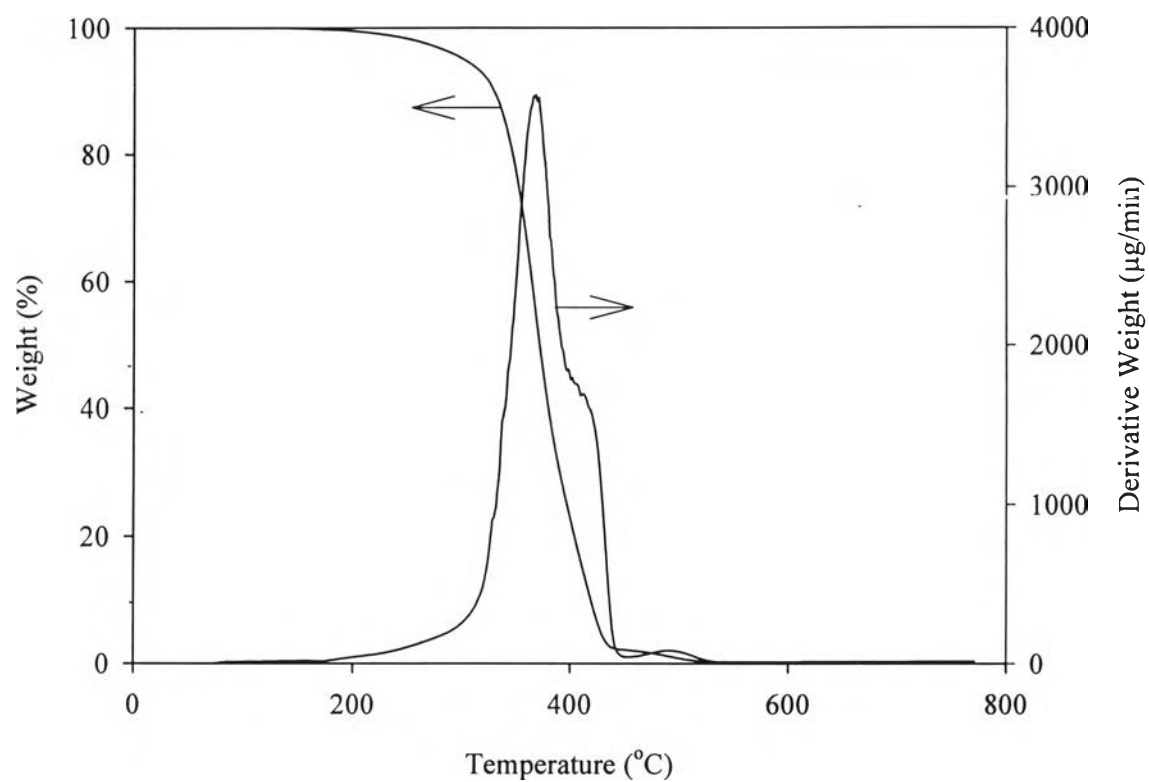


Figure 4.17 TGA result of Polyisoprene.

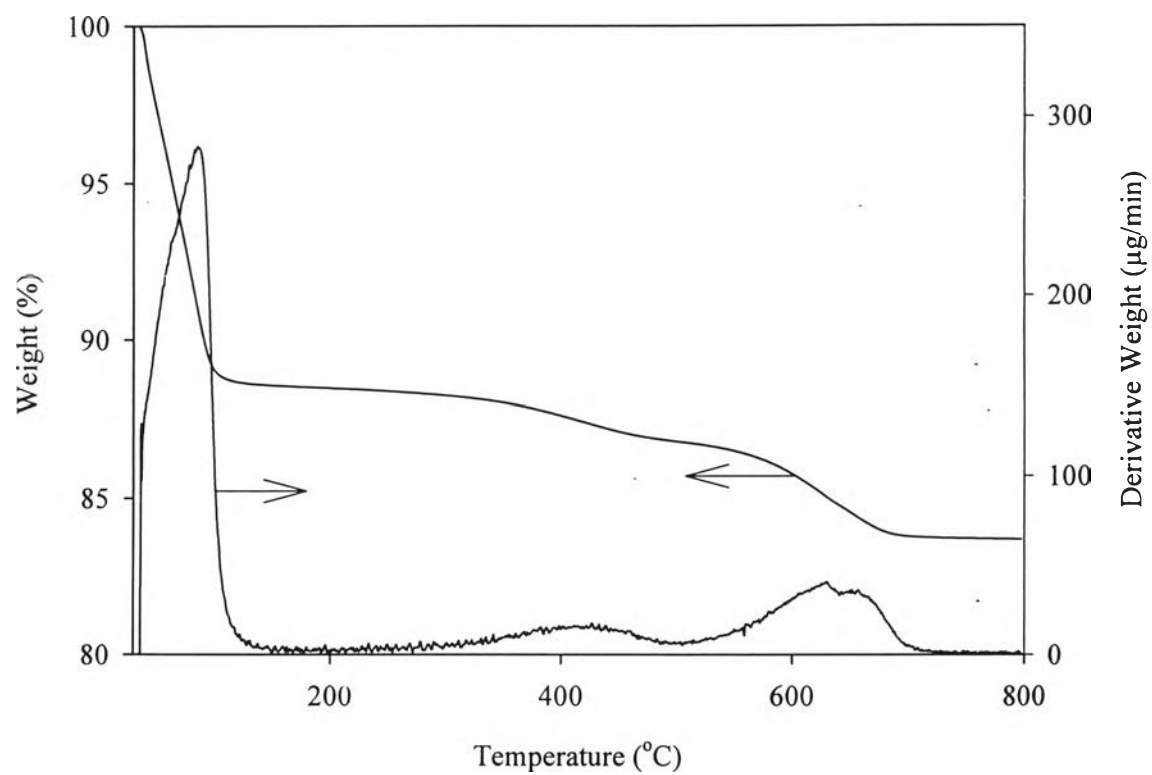


Figure 4.18 TGA result of untreated clay.

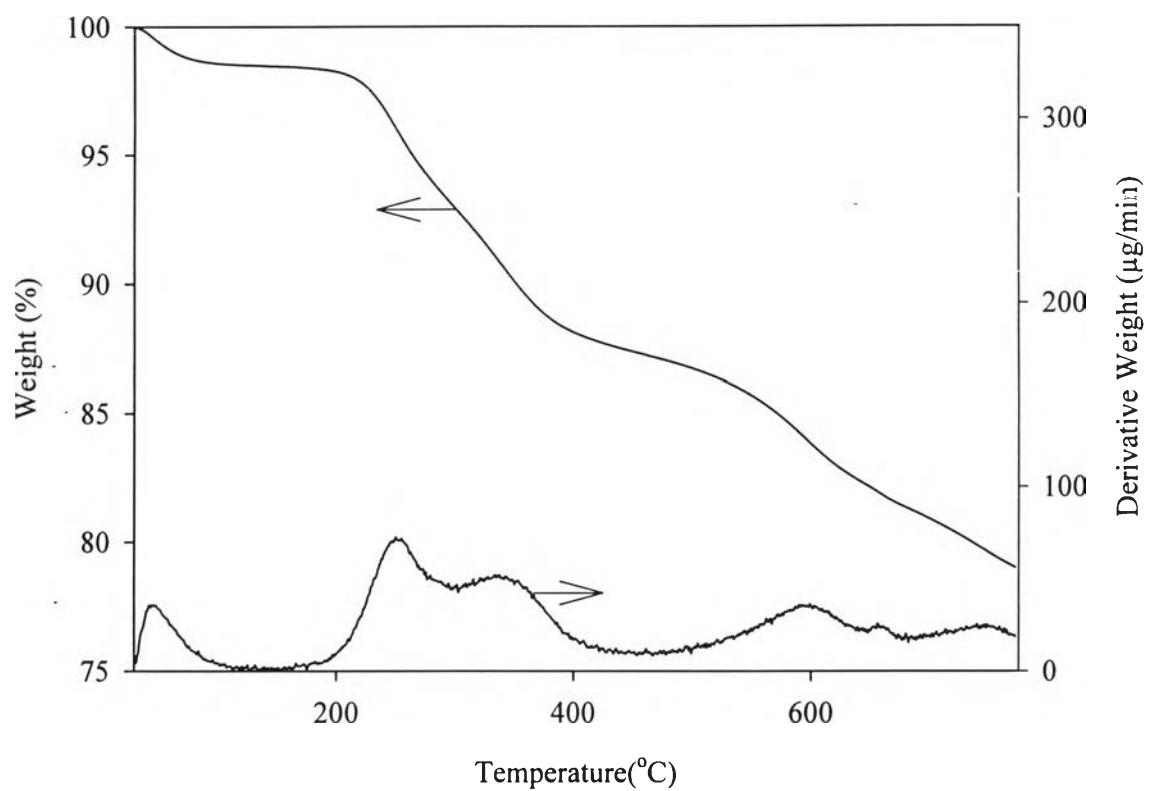


Figure 4.19 TGA result of organoclay with 1:0 molar ratio ARQUAD[®]:Teric X10.

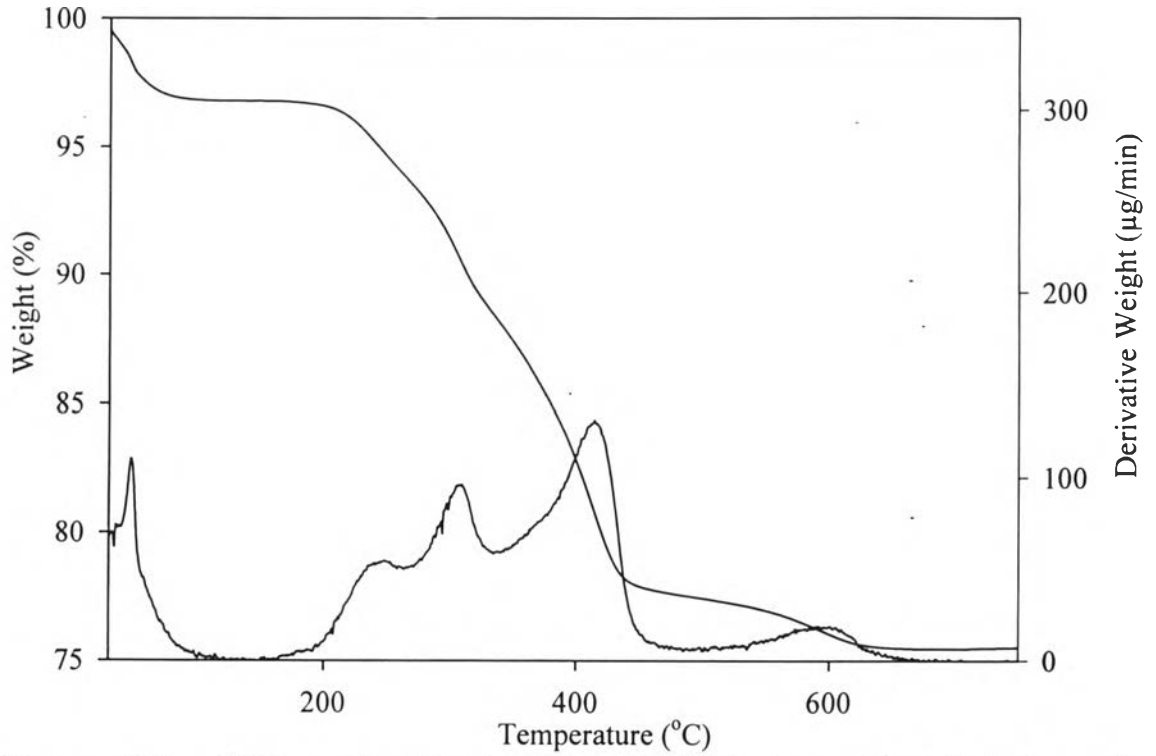


Figure 4.20 TGA result of admicellar modified clay with 1:0 molar ratio ARQUAD[®]:Teric X10.

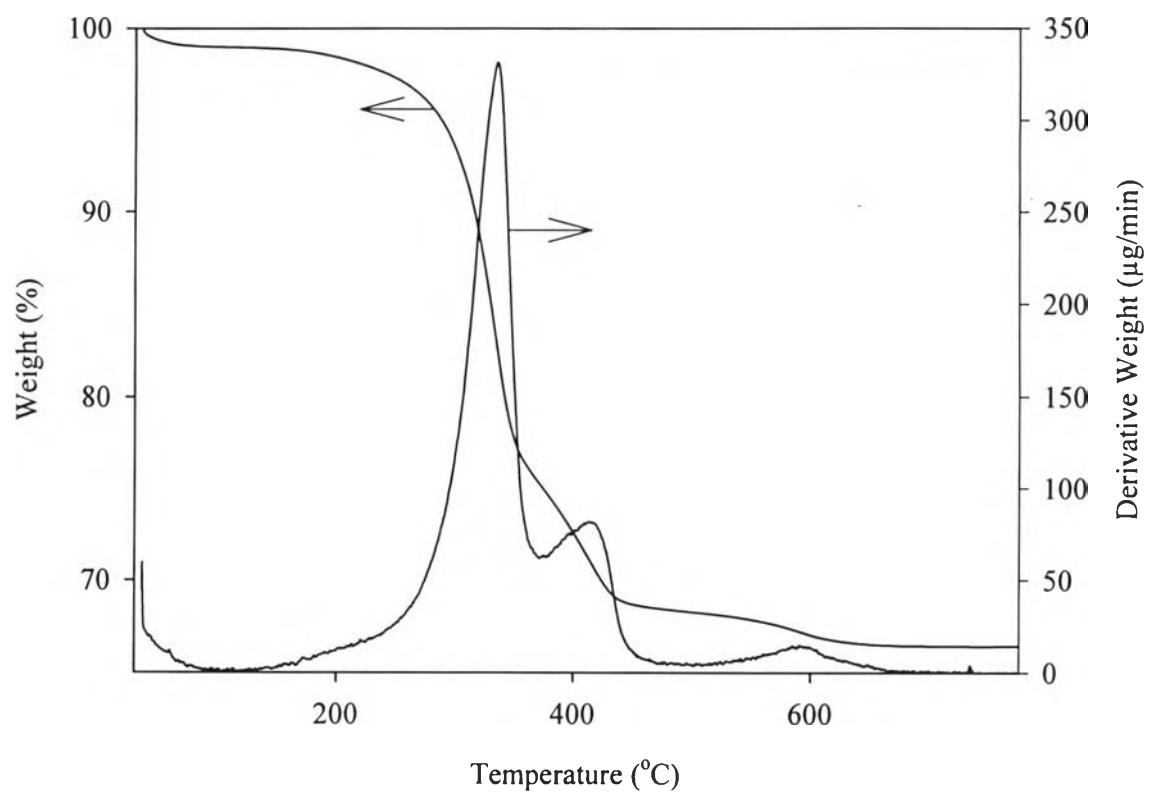


Figure 4.21 TGA result of organoclay with 3:1 molar ratio ARQUAD[®]:Teric X10.

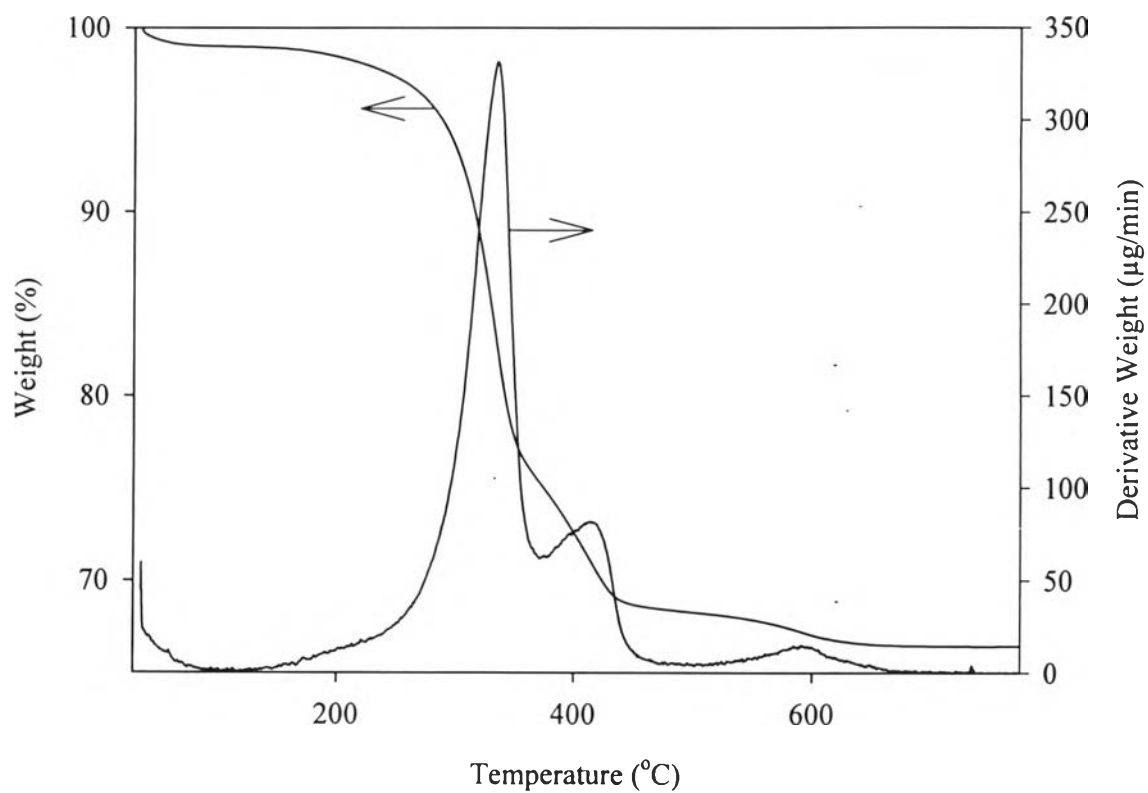


Figure 4.22 TGA result of admicellar modified clay with 3:1 molar ratio ARQUAD[®]:Teric X10.

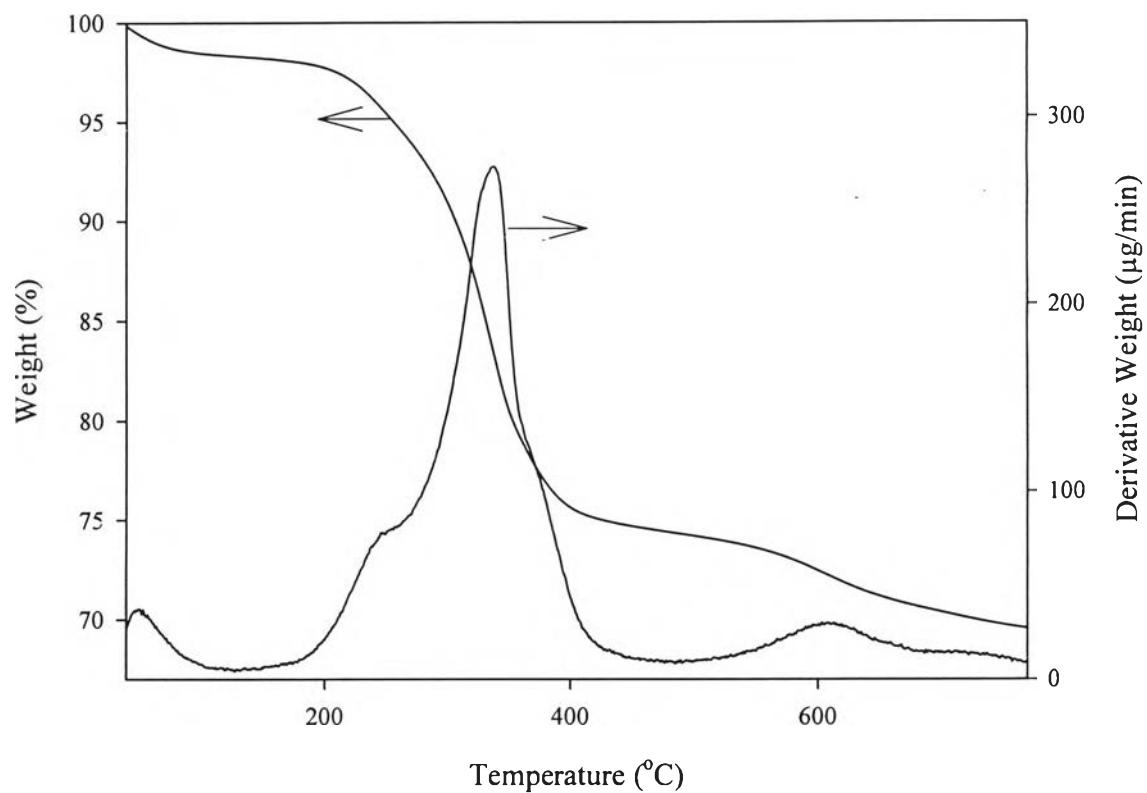


Figure 4.23 TGA result of 1 organoclay with 1:1 molar ratio ARQUAD[®]:Teric X10.

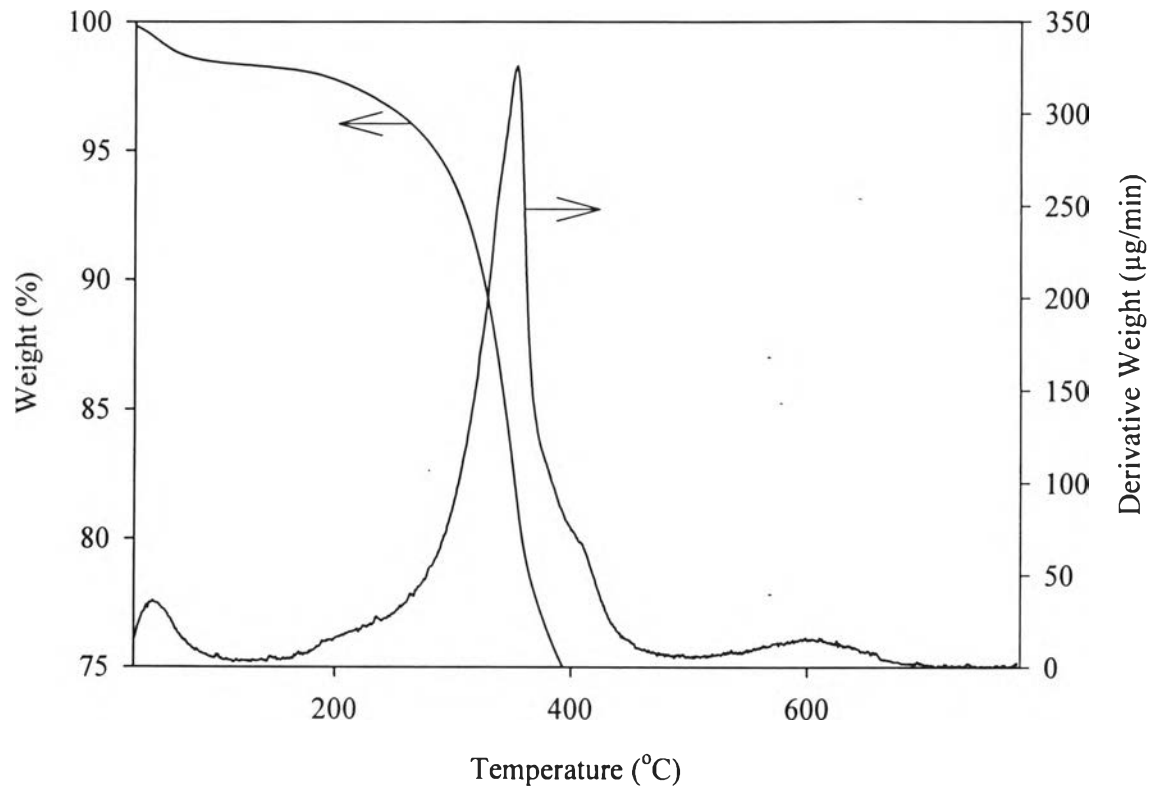


Figure 4.24 TGA result of admicellar modified clay with 1:1 molar ratio ARQUAD[®]:Teric X10.

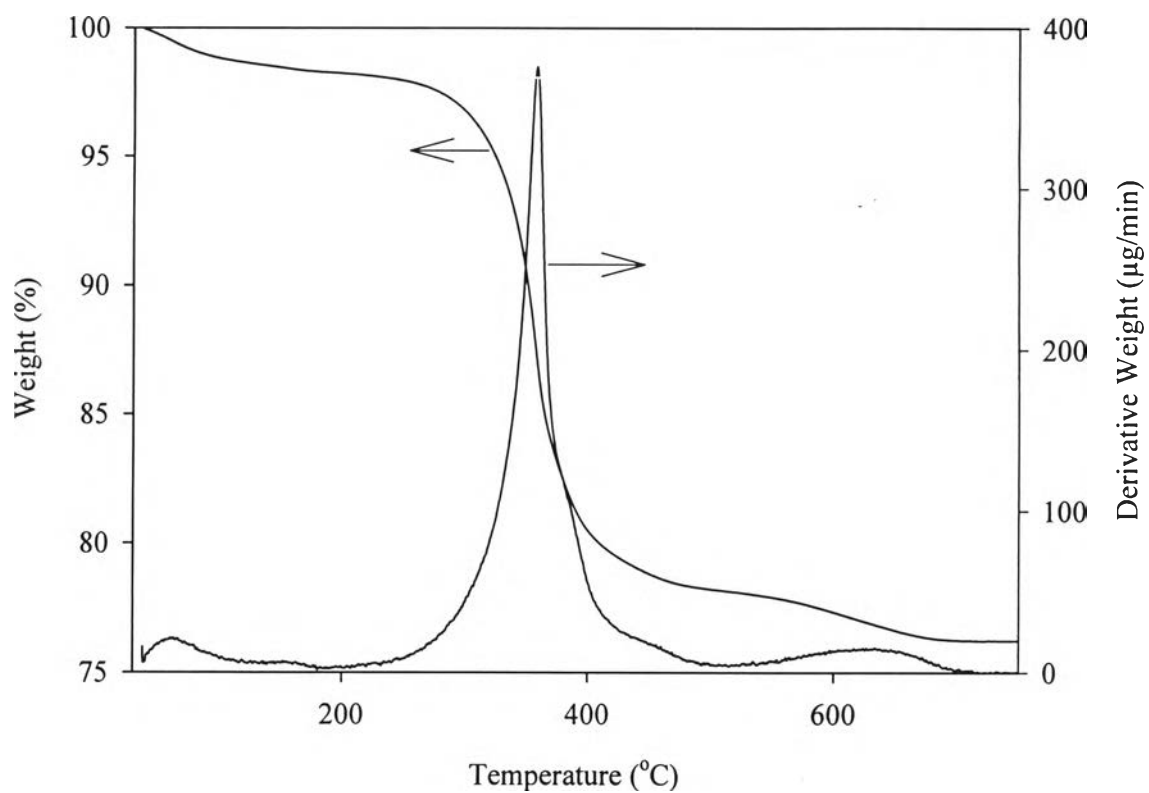


Figure 4.25 TGA result of organoclay with 1:3 molar ratio ARQUAD[®]:Teric X10.

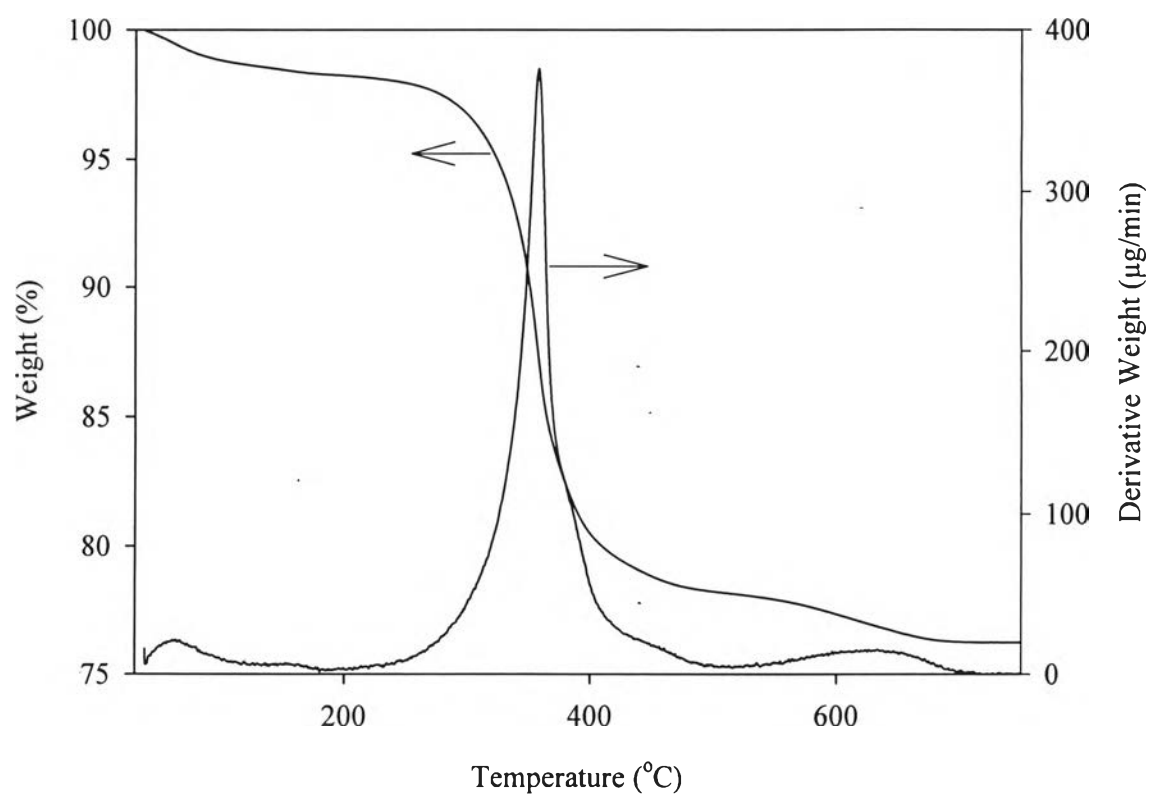


Figure 4.26 TGA result of admicellar modified clay with 1:3 molar ratio ARQUAD[®]:Teric X10.

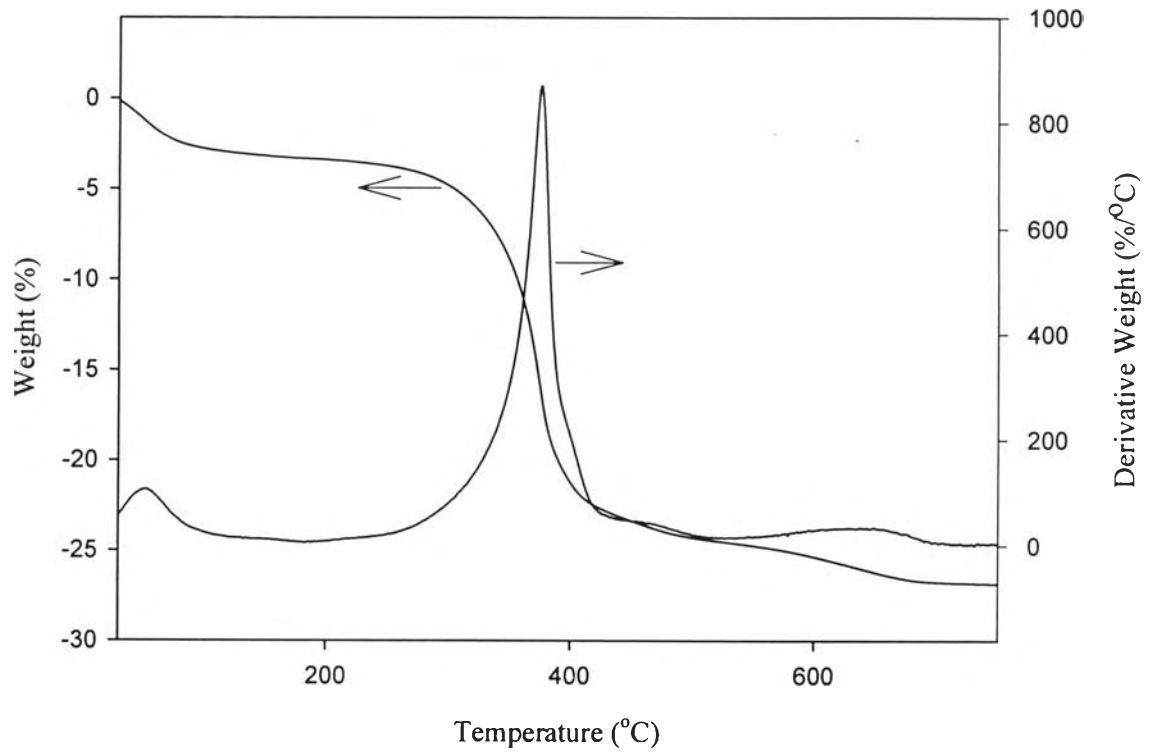


Figure 4.27 TGA result of organoclay with 0:1 molar ratio ARQUAD[®]:Teric X10.

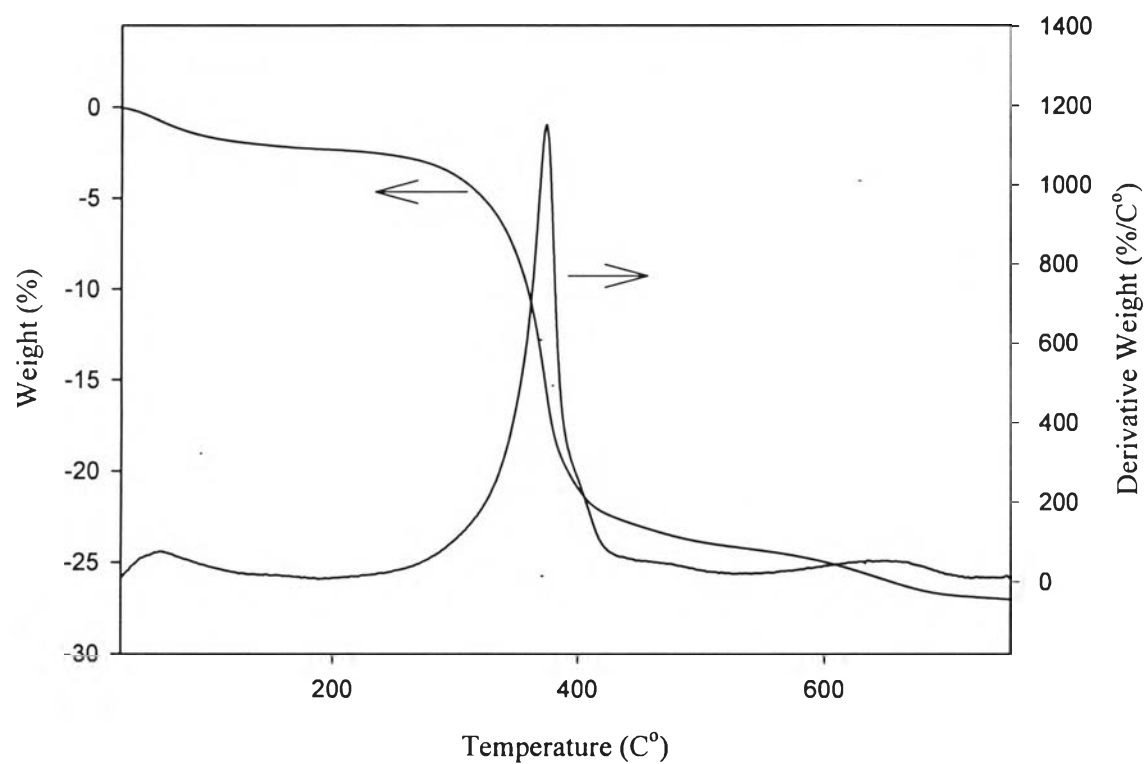


Figure 4.28 TGA result of admicellar modified clay with 0:1 molar ratio ARQUAD®:Teric X10.

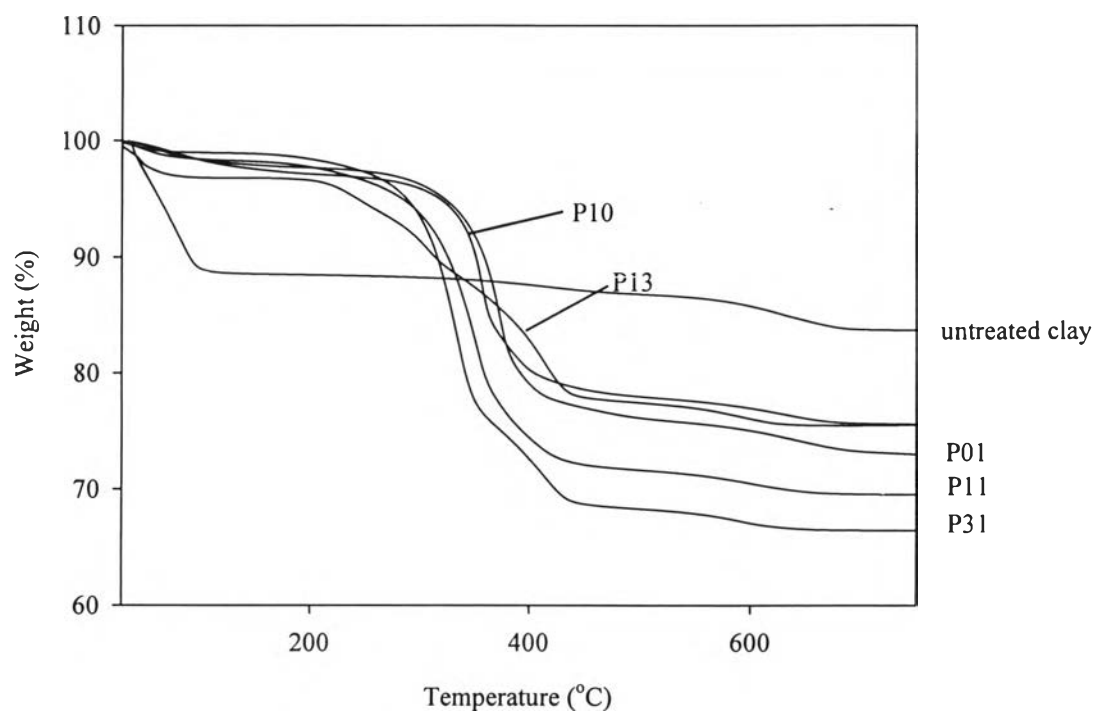


Figure 4.29 The TGA plots of admicellar modified clay at different molar ratios of ARQUAD® to Teric X10.

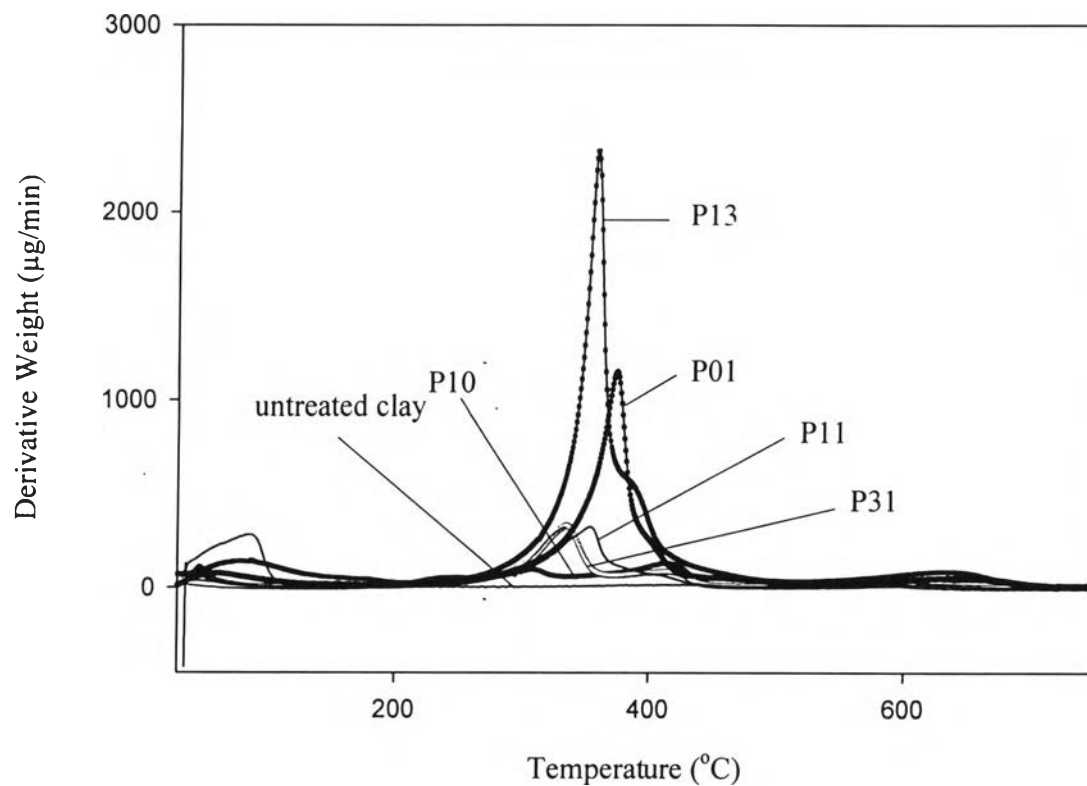


Figure 4.30 The plots of DTG of admicellar modified clay at different molar ratios of ARQUAD[®] to Teric X10.

Table 4.5 Physical Properties of modified clay/rubber nanocomposites.

Properties	No Clay	Untreated clay	P10	P31	P11	P13
Cure time (min)	13.4	13.9	10	10	14	20
100%modulus @before aging (MPa)	0.96	0.85	0.9	0.9	0.7	0.6
200%modulus @before aging (MPa)	1.35	1.28	1.5	1.3	1	0.9
300%modulus @before aging (MPa)	1.831	1.79	2.2	1.8	1.4	1.2
Tensile strength @before aging (MPa)	18.1	16.41	20	20	14	12
Hardness @before aging (Shore A)	35.8	36.1	40	42	34	33
Tear Strength (MPa)	31.5	29.3	28	33	27	26
Resilience (%)	71.9	66.8	70	68	62	60
Heat build up (°C)	7.27	9.42	8.9	8.8	9.4	12
Specific gravity (g/cm ³)	0.97	1	1	1	1	1

Table 4.6 Physical Properties of organoclay -rubber nanocomposites.

Properties	B10	B31	B11	B13
Cure time (min)	10.9	9.21	14	18.5
100%modulus @before aging (MPa)	0.89	0.92	1.09	0.63
200%modulus @before aging (MPa)	1.41	1.37	1.67	0.91
300%modulus @before aging (MPa)	1.98	1.9	2.33	1.22
Tensile strength @before aging (MPa)	19.9	15.6	19.3	9.3
Hardness @before aging (Shore A)	41.3	41.4	36.1	32.4
Tear Strength (MPa)	32.6	33.7	28.7	23.89
Resilience (%)	66.7	68.2	63.1	60.6
Heat build up (°C)	11.6	8.45	11.1	14.2
Specific gravity (g/cm ³)	0.99	1	1	1

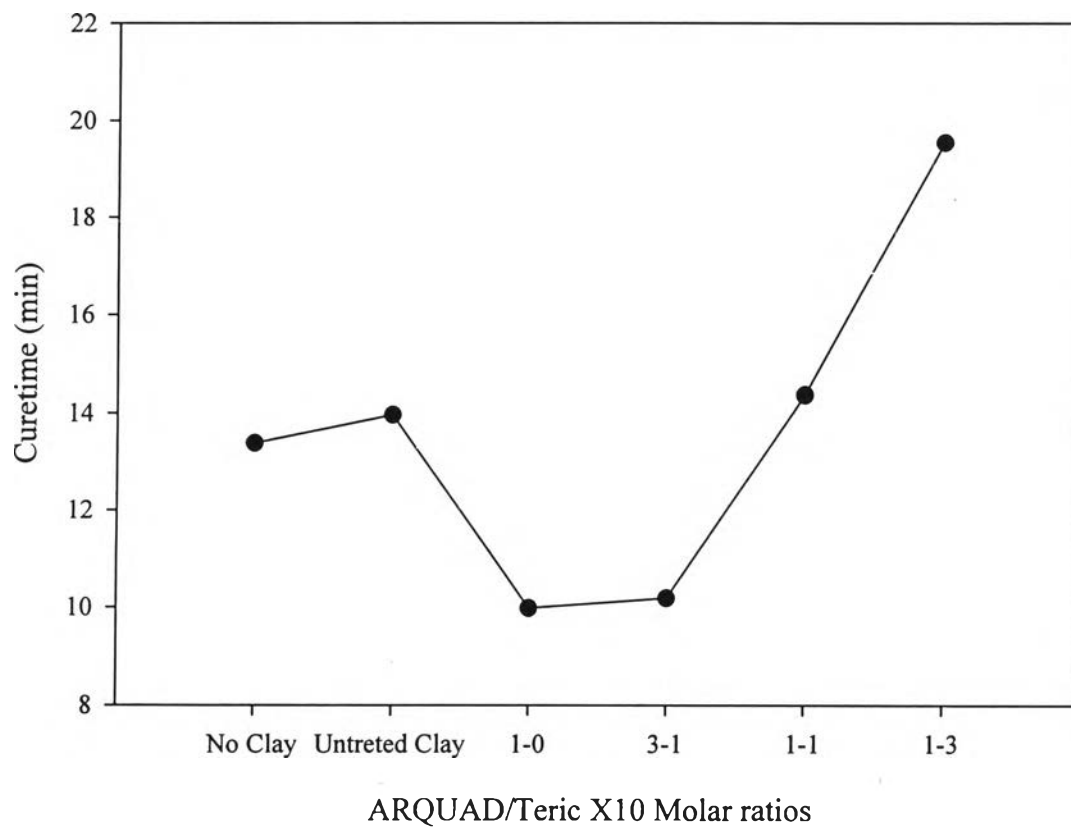


Figure 4.31 Cure time of admicellar polymerization modified clay-filled rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

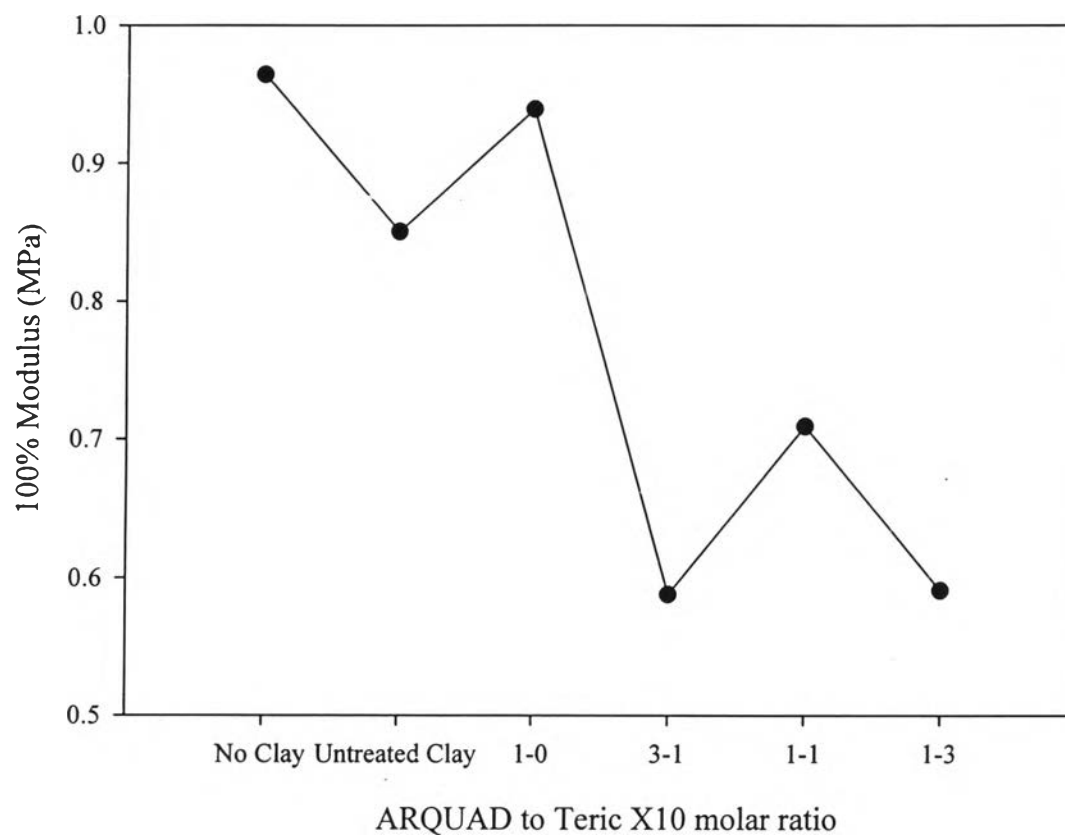


Figure 4.32 100 % modulus @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

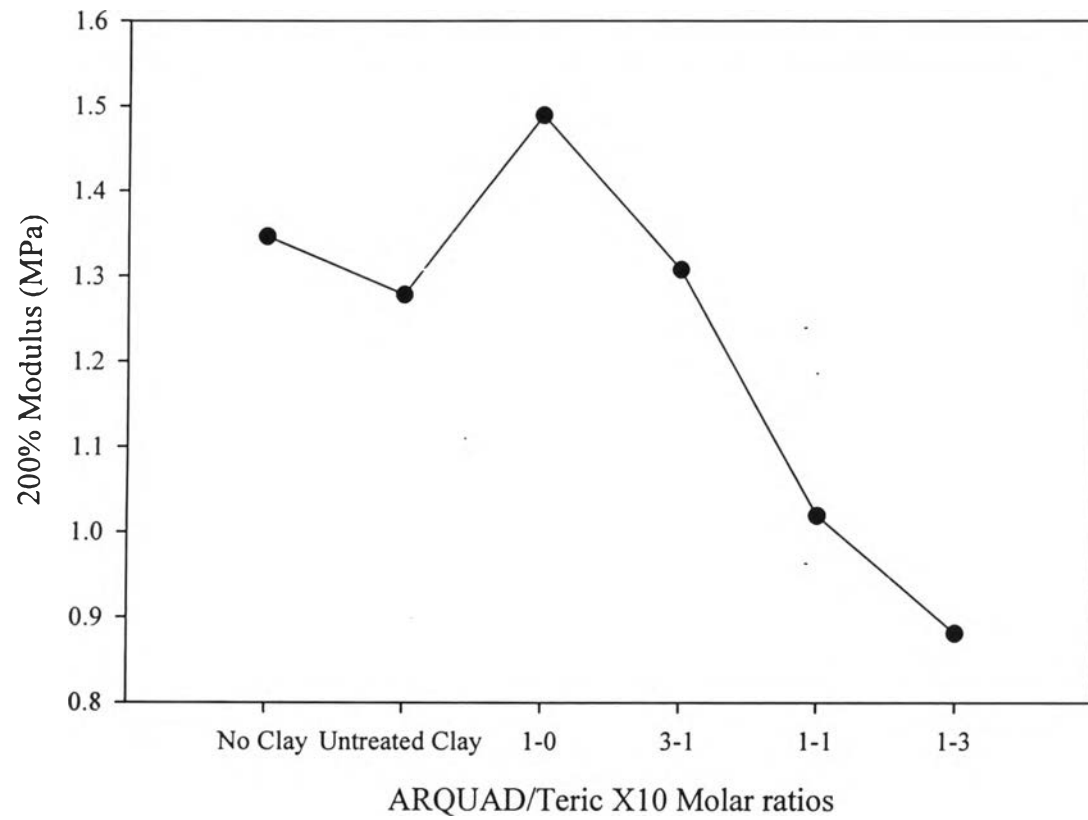


Figure 4.33 200 % moldulus @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

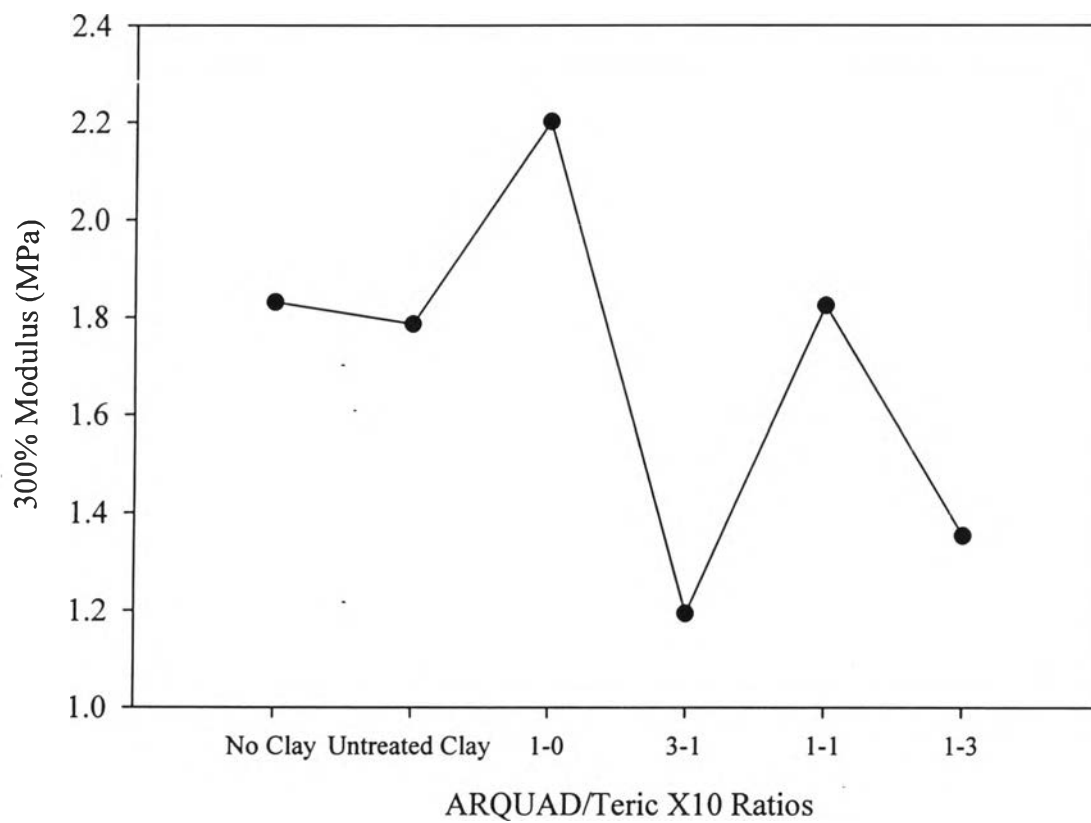


Figure 4.34 300 % modulus @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

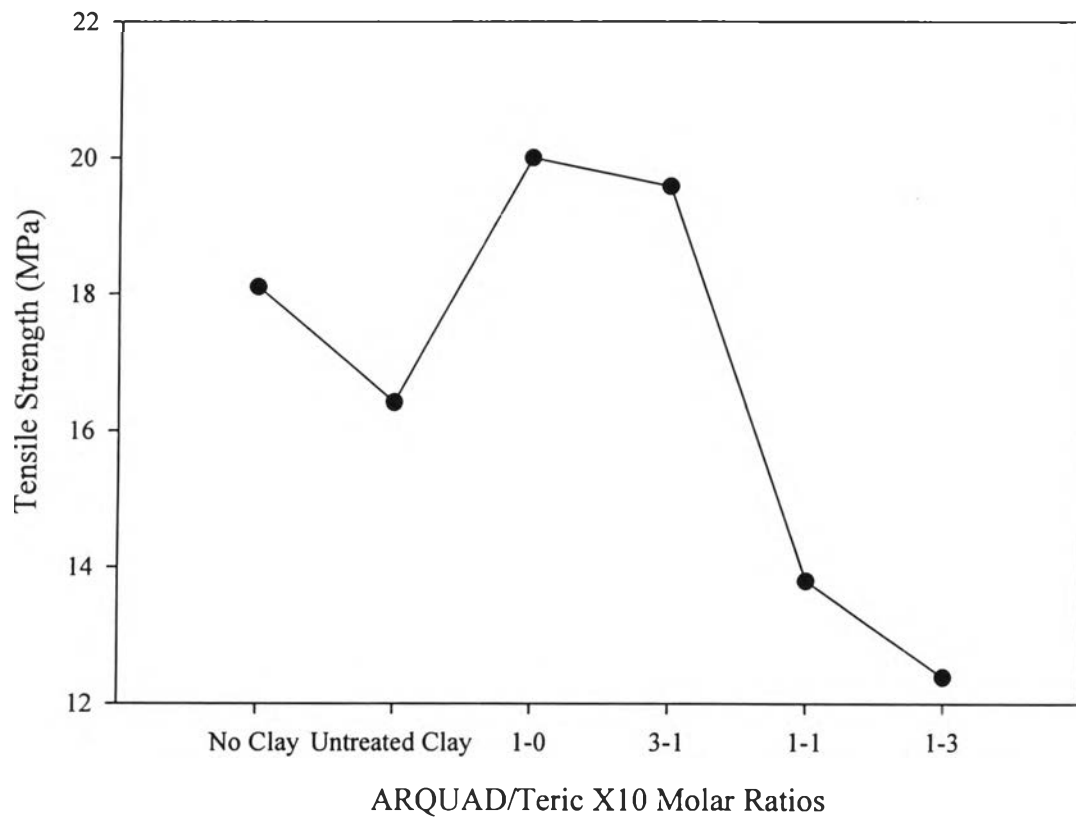


Figure 4.35 Tensile strength @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

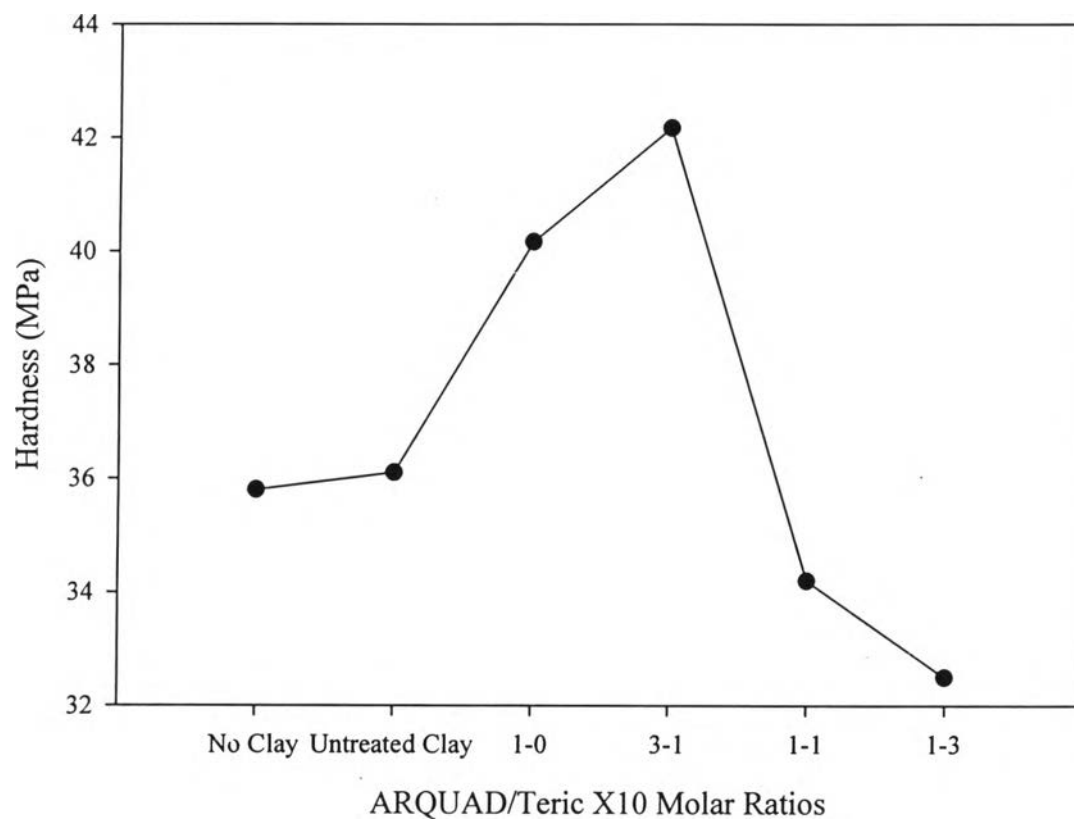


Figure 4.36 Hardness @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

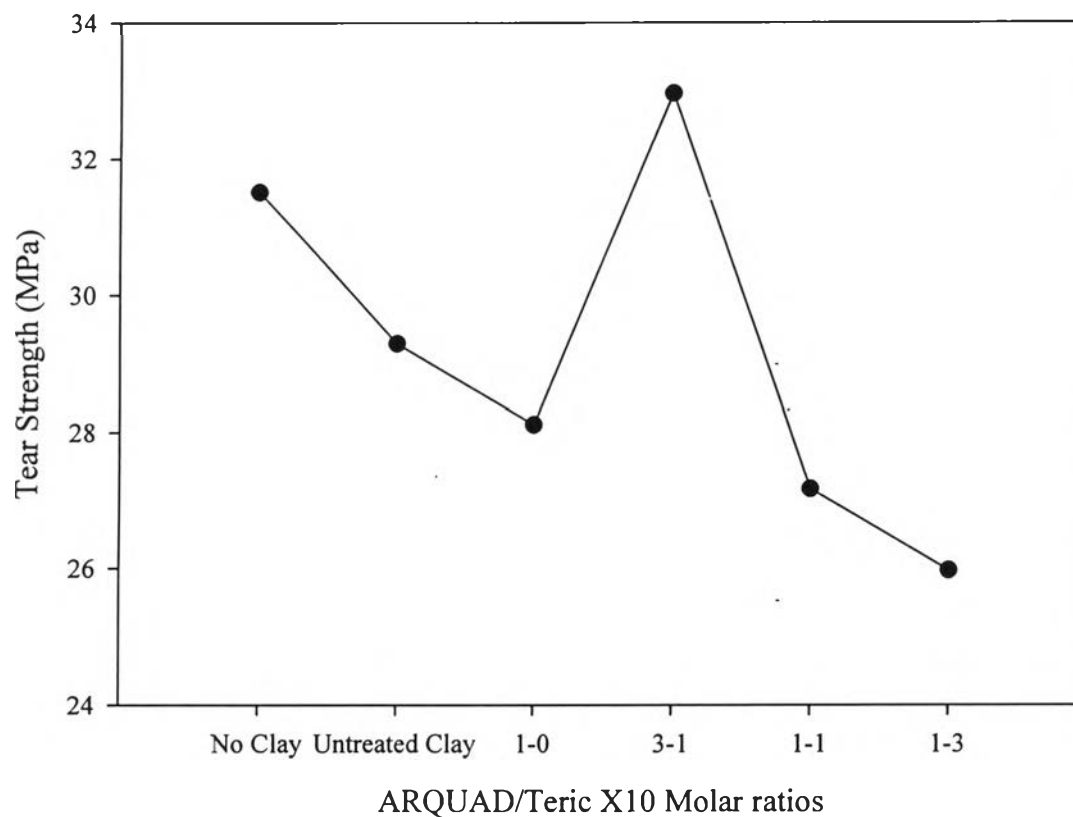


Figure 4.37 Tear strength @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

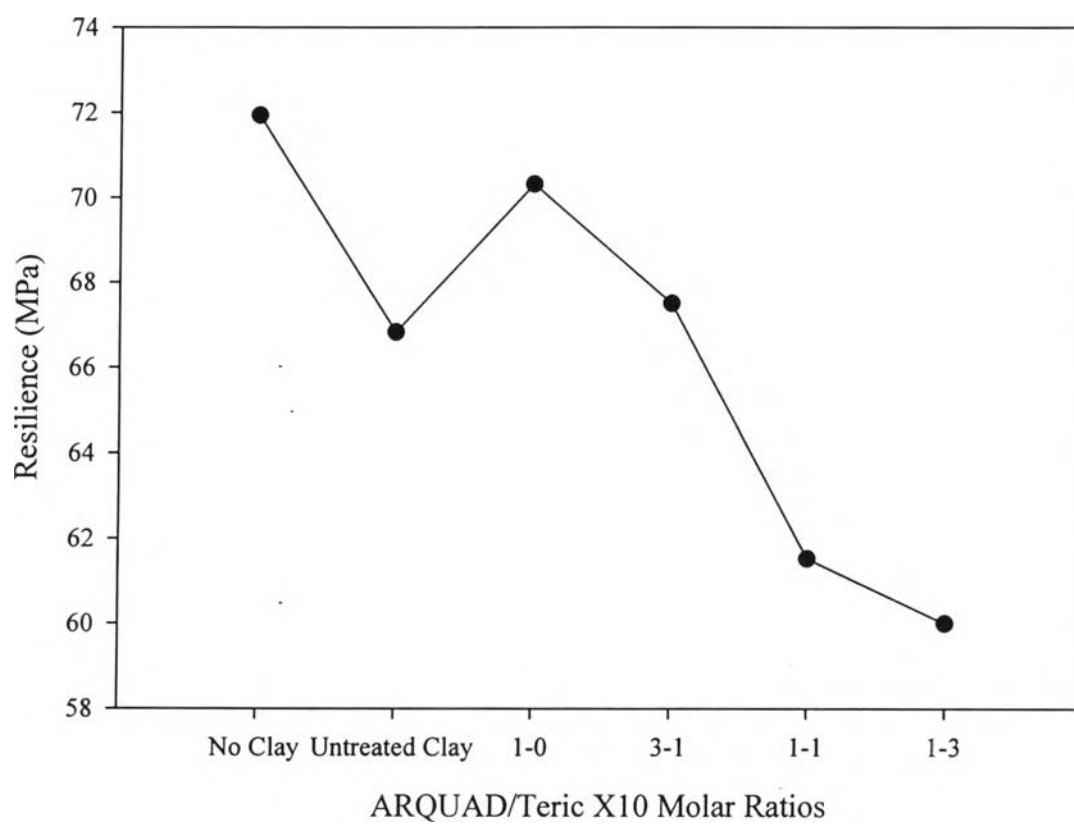


Figure 4.38 Resilience of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

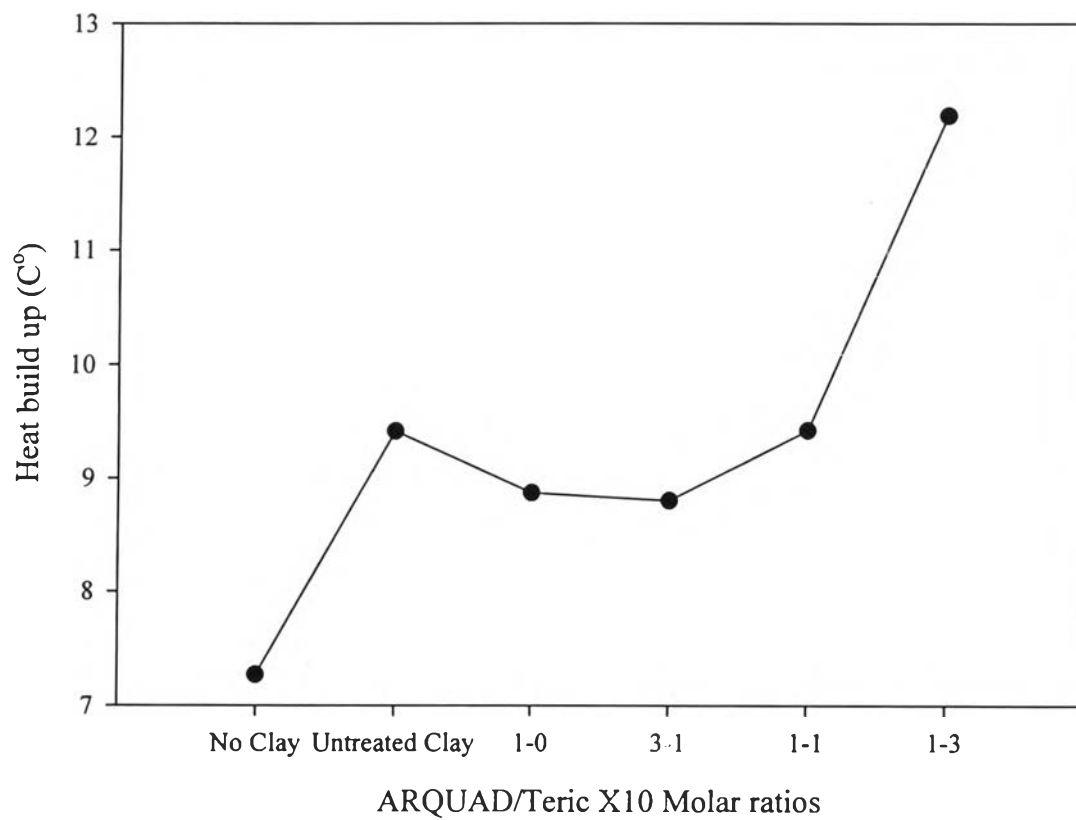


Figure 4.39 Heat build up @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.

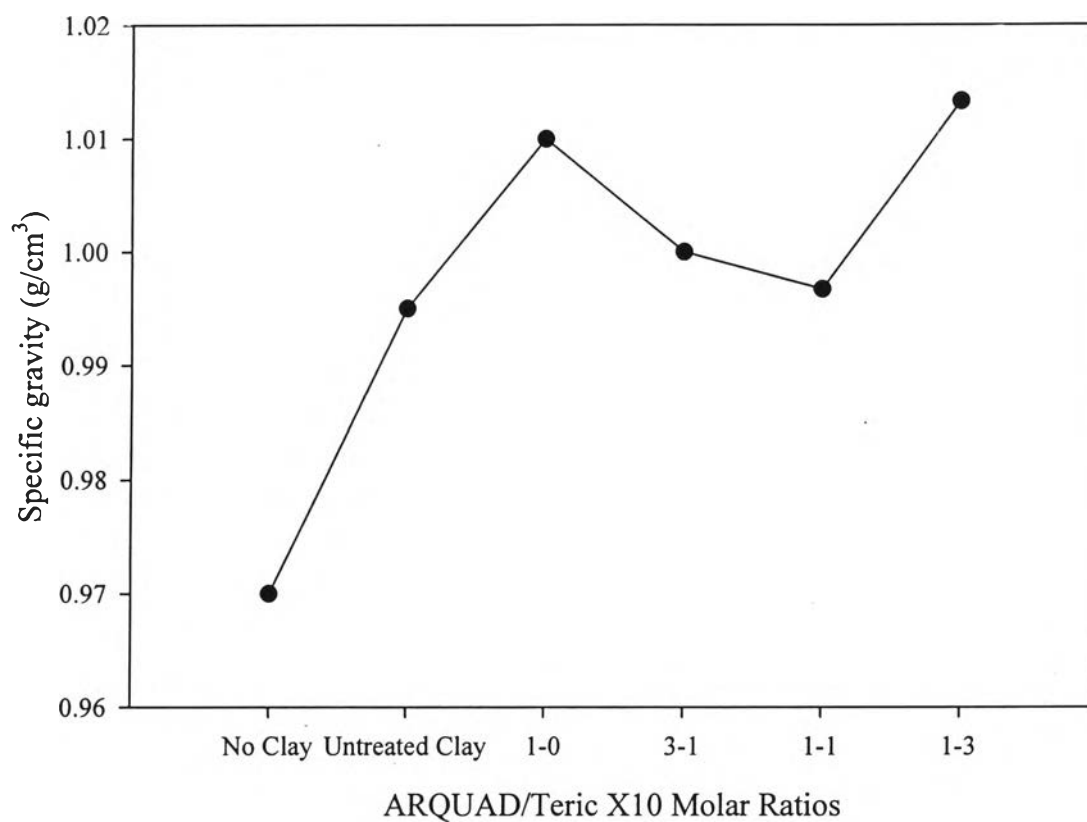


Figure 4.40 Specific gravity @ before aging of rubber compounds with different of ARQUAD[®]:Teric X10 molar ratios.