CHAPTER V

EFFECT OF ORGANOCLAY CONTENTS ON BARRIER PROPERTIES OF ENR/PVDF/PLA BLENDS

5.1 Abstract

This study is purposed to develop a thermoplastic vulcanizate (TPV) via dynamic vulcanization made of epoxidized natural rubber (ENR) and poly(vinylidene fluoride) (PVDF). The effects of contents of organoclay and poly(lactic acid) (PLA) on mechanical and oil swelling properties were studied for using in automotive and chemical industries. Rubber parts were mixed at room temperature by using two roll mill, fed in twin screw extruder with thermoplastic parts to occur dynamic vulcanization and then compressed in compression molding. This research was emphasized on the contents of organoclay (0, 3, 5, 7 and 10 phr) and the addition of PLA at fixed 10 wt%. The cure characterization results revealed that the effect of adding organoclay resulted to accelerate curing reaction in ENR which increased the maximum torque. The mechanical results showed that the increase of organoclay contents in ENR/PVDF/PLA blends have enhanced the mechanical properties (tensile and tear strength and hardness) and oil swelling resistance. Furthermore, the addition of clay made TPV stable in oil swelling by the rate of oil uptake decreased which resulted from insignificantly changing in oil swelling index within 7 days in both of 25 °C and 100 °C.

5.2 Introduction

Dynamic vulcanization is the vulcanization process of an elastomer during its melt mixing with a thermoplastic, which results to a new class of materials called thermoplastic vulcanizates (TPV). The initial stage of vulcanization show co-continuous morphology, then apply any torque or shear rate, rubber phases are going to be separated gradually until the final stage which exist the fine dispersed morphology of rubber particles within thermoplastic matrix.

Organoclay/polymer nanocomposites have been known for many years ago. Organoclay can act as both of reinforcing agent and compatibilizer. Then organoclay-filled dynamically vulcanized blends of epoxidized natural rubber (ENR) and poly(vinylidene fluoride) (PVDF) have been recognized as TPV materials which were purposed to increase mechanical and oil resistant properties.

Ranumas Thipmanee *et al.* [1] studied mechanical properties and morphology of poly(lactic acid) (PLA) / epoxidized natural rubber (ENR) / organoclay nanocomposites. The results found that the addition of organoclay improved the tensile strength and modulus of the PLA/ENR blend because the organoclay acted as reinforcing agent. P. L. TEH *et al.* [2] found that cure time (t_{90}) decreased with increasing filler content from 0 -10 phr but showed slight increases in maximum torque. The mechanical properties: tensile strength increased gradually up to 2 phr filler loading due to uniformly dispersed in the natural rubber matrix. The filler has high aspect ratio which tends to improve interfacial bonding and form filler-rubber interaction because of the high specific surface area. Further increase in filler loading after 6 phr of organoclay resulted in a reduction in the tensile properties because when the filler content is high, the filler tends to form agglomerate. The same trends are observed for elongation at breaks and tear strength.

In this study, PVDF and PLA used as thermoplastic parts to provide oil and chemical resistant properties and make it more environmental friendly, respectively. ENR used as rubber part to provide the elastomeric properties. This research reports the effects of organoclay contents (0, 3, 5, 7 and 10 phr) and addition of PLA at fixed 10 wt% on mechanical properties (tensile and tear strength and hardness), thermal properties (DMA), curing properties (MDR), oil swelling resistant properties and morphology (SEM) of the blends.

5.3 Experimental section

5.3.1 Materials

The materials used in this study were ENR with 25 % epoxidation, supplied by Muang Mai Guthrie PCL., PVDF (grade Z100), supplied by Asambly Chemicals Company, PLA (grade 2002D), supplied by NatureWorks LLC. The selected additives (Fluka reagent grades) were calcium hydroxide ($Ca(OH)_2$) and 2,5–bis(tert–butylperoxy)–2,5–dimethylhexane (DBPH). Triacetin was supplied by Sigma-Aldrich Co. LLC. Stearic acid and triallyl isocyanurate (TAIC) were purchased from Neo plastomer Co.,Ltd. Organoclay with surfactant type of DEHYQUART® F 75 was prepared in-house. Gasohol 91, 95, E20 and E85 were supplied by PTT PCL.

5.3.2 Preparation of the blends

5.3.2.1 Preparation of rubber parts

The organoclay-filled ENR compounds were prepared for curing characterization by using MDR. They were blended by using an internal mixer at room temperature with a rotor speed of 50 rpm. The ENR was charged first into the mixing chamber, then stearic acid, $Ca(OH)_2$, organoclay, TAIC and DBPH were added, respectively. Mixing was then continued until a constant torque was obtained. The total mixing time was 12 minutes. The compound was removed from the mixer and was tested in next steps. The formulations were shown in table 5.1.

5.3.2.2 Preparation of thermoplastic parts

The thermoplastic parts which contain PVDF, triacetin (5 phr) and PLA, if any, were prepared by melt-mixing in a co-rotating twin screw extruder (LTE20-40 model). In case of adding PLA, the PVDF/PLA blends were mixed at composition of 80/20. The temperature profile from the feed zone to die is 175, 180, 185, 185, 190, 190, 195, 195, 200, 210 °C. The screw speed was used at 50 rpm. The extrudate was cooled in water bath and then cut into pellet by pelletizer.

5.3.2.3 Preparation of Thermoplastic vulcanizate (TPV)

The formulations of the TPV blends are given in Table 5.2. First step, the rubber parts were prepared at room temperature by using two roll mill

(LRM 110 model). The ENR was mixed with stearic acid, $Ca(OH)_2$, organoclay, TAIC, DBPH and triacetin, respectively. The total mixing time was 45 min. The compound was removed from two roll mill, cut it to be small strips, put thermoplastic blends pellets which obtained from 5.3.2.2 on top of rubber compound surface and fed in twin screw extruder, respectively.

Table 5.1 Formulations of organoclay-filled ENR compounds for curing characterization

Materials	**Quantity, phr**^{a}	**Mixing times, min**
ENR	100	0 - 2
Stearic acid	0.25	2 - 3
$Ca(OH)_2$	3	3 - 6
Organoclay	X	6 - 8
TAIC	2.5	8 - 10
DBPH	5	10 - 12

Note: ^{a}phr is part per hundred part of rubber and X is the varying organoclay contents at 0, 3, 5, 7 and 10 phr.

Last step, the TPV was achieved by blending thermoplastic and rubber via twin screw extruder by using temperature profile from the feed zone to die of 185, 188, 188, 178, 180, 182, 185, 188, 190, 190 °C. The screw speed was used at 70 rpm. Then the extrudate was cooled in water bath and then cut into pellets by pelletizer. The TPV blends pellets were compressed in a compression mold (Wabash MPI, V50H–18–CX model, USA). Hot-press procedures involved pre-heating at 190 °C for 5 min, followed by compressing for 5 min at the same temperature with pressure of 20 tons.

Table 5.2 Formulations of organoclay-filled TPV blends

Materials	Blends (wt %)	
	I	II
ENR	50	50
PVDF	40	50
PLA	10	-
DBPH [a]	5	5
TAIC [a]	2.5	2.5
Stearic acid [a]	0.25	0.25
$Ca(OH)_2$ [a]	3	3
Organoclay [a]	X	X
Triacetin [a]	2.5	2.5
Triacetin [b]	2.5	2.5

Note: X is the varying organoclay content at 0, 3, 5, 7 and 10 phr, [a] At phr of rubber and [b] At php of plastic.

5.3.3 Study of curing properties

The curing properties of organoclay-filled ENR including cure rate index (CRI), cure time (t_{90}) and maximum torque were observed by using MDR. For MDR (rheoTECH MD+,Tech pro, A022S), they were tested under operation of constant conditions (0.5 deg arc strain amplitude, rotor size L) at various temperatures ranging from 180 – 200 °C.

5.3.4 Study of mechanical properties

The mechanical properties including the tensile strength, tear strength and hardness (shore A). Tensile test was done according to ASTM D412-06a or ISO 37 (type 1), tear test was done according to ASTM D624-00 or ISO 34 by using the universal testing machine (Instron, 4206-006 model) with load cell of 5 kN and crosshead speed of 500 mm/min. The hardness was determined according to ASTM D2240 by using shore A durometer (Zwick, type 7206). Five specimens were used in each case.

5.3.5 Study of thermal properties by using dynamic mechanical analyzer (DMA)

The storage modulus (E'), the loss modulus (E"), and the dissipation factor (tan δ) are measured by DMA (GABO-EPLEXOR 100N model) using a constant frequency of 1 Hz and a temperature range of -80°C to +120°C. The measurements were carried out under tension mode with a static load of 10 N and a dynamic load of 5 N. The dimensions of the test samples were in width*length*thickness (10*50*2 mm).

5.3.6 Study of oil swelling resistance properties

The oil resistance of the blends was studied after immersing sample in oil at temperature of 25 °C and 100 °C for 24 hours and 7 days according to ASTM D471-06 or ISO 2285 (Method A). In this study, gasohol 91, gasohol 95, E20 and E85 which contain 10, 10, 20 and 85 % ethanol, respectively, were used. After removal from the oil, the test pieces were wiped with tissue paper to remove excess oil from the surface and weighed immediately. The swelling index and percentage of swelling were calculated using equation 5.1 and 5.2, respectively:

$$Swelling\ index = \frac{Final\ mass}{Initial\ mass} \qquad (5.1)$$

$$\%\ Swelling = \frac{Ws - Wo}{Wo} \times 10 \qquad (5.2)$$

Where Ws refer to a swelling weight and Wo refer to an original weight.

5.3.7 Study of morphology

The morphology of rubber and plastic phases, the vulcanized rubber particles size and the dispersion of vulcanized rubber particles was examined by using the field emission scanning electron microscope (FE-SEM) HITACHI S-4800 model which contributed the images in the magnification range of 1,000 to 10,000 times at 10 kV. The samples must be coated with platinum under vacuum condition before observation to make them electrically conductive.

5.4 Results and discussion

5.4.1 Curing properties of organoclay-filled ENR

Curing characteristics of organoclay-filled ENR in terms of cure rate index (CRI), cure time (t_{90}), maximum elastic torque (S'@MH), minimum elastic torque (S'@ML) and maximum viscous torque (S"@MH) obtained from MDR were shown in table 5.3. Figure 5.1 shows the influence of organoclay content on the cure characteristics. It can be seen that the addition of organoclay resulted in increase of cure rate index. This can be attributed to the amine functionality in the organoclay after the modification process or ion exchange process. The amine containing compounds facilitate the curing reaction of ENR stocks supported by literature of P.L. TEH *et al.* [2]. The cure rate index increases to a maximum at 3 phr, then further increase in loading, organoclay tends to form agglomerate and this leads to the reduction of efficiency of curing reaction. T_{90} showed the same trend as cure rate index.

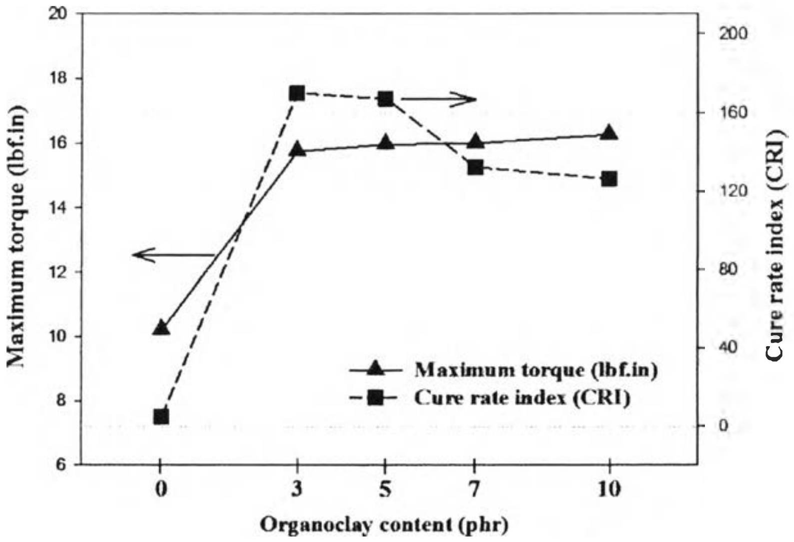


Figure 5.1 Maximum torque and cure rate index of the compounds with the different organoclay content (phr) obtained from MDR at 190 °C.

Maximum torque, which indicates the stock modulus, increased due to the organoclay/rubber interactions because the maximum torque depended on both the extent of crosslinking and reinforcement by the filler particles in the polymer matrix. This result shows the strong reinforcing effect of organoclay and the good interfacial adhesion between ENR and organoclay. H. Ismail and R. Ramli [7] reported a similar observation. There was enhancement in maximum viscous torque with increasing organoclay loading which indicated the increase of damping characteristics.

Table 5.3 Cure characteristic of organoclay-filled ENR obtained from MDR

Organoclay, phr	**Upper and Lower die, °C**	**S'@ML, lbf·in**	**S'@MH, lbf·in**	**S"@MH, lbf·in**	**t_{90}, min**	**Cure rate index (CRI)**
0	**180**	1.34	10.91	0.32	5.34	1.94
	190	1.20	10.24	0.28	2.26	4.71
	200	0.77	9.26	0.30	1.03	10.75
3	**180**	0.72	19.11	0.76	3.26	34.35
	190	0.41	15.77	0.51	0.56	169.92
	200	0.67	15.98	0.43	0.44	229.78
5	**180**	1.70	19.88	0.53	3.50	31.16
	190	1.01	15.98	0.58	1.00	167.12
	200	0.90	15.55	0.52	0.44	231.10
7	**180**	1.71	18.64	0.90	3.00	42.22
	190	0.36	16.02	0.75	1.08	132.14
	200	0.62	10.23	0.75	0.45	212.19
10	**180**	0.54	18.78	1.10	3.08	37.71
	190	1.09	16.28	0.92	1.14	126.32
	200	0.61	15.68	0.87	0.48	193.56

5.4.2 Mechanical properties of organoclay-filled TPV

Mechanical properties in terms of tensile strength, young's modulus at 0.2 % strain and percent elongation at break were shown in table 5.4. There are 10 different formulations by varying contents of PLA and organoclay.

From figure 5.3, the results showed that the tensile strength increased with increasing organoclay loading in ENR/PVDF/PLA system until a maximum point at 3 phr because the organoclay particles are no longer sufficiently separated or wetted by the polymer phase, L. E. Yahaya *et al.* [3] also suggested similar observations. Since, there was high amount agglomerate in high organoclay-filled TPV, these agglomerates played the role of an obstacle to molecular chain movement, thereby initiating failure under stress. In contrast to ENR/PVDF system, the tensile strength decreased as organoclay loading due to no strong interaction between PVDF phase and organoclay layer which help to generate some crystallinity at the interface that was responsible for the effect of reinforcement, whereas these strong interactions may occur between hydroxyl groups of PLA and hydroxyl groups of modified organoclay. The possible interaction was proposed in figure 5.2. Resulted from no these interaction, the organoclay-filled ENR/PVDF system gave lower properties such as tensile strength, young's modulus and tear strength.

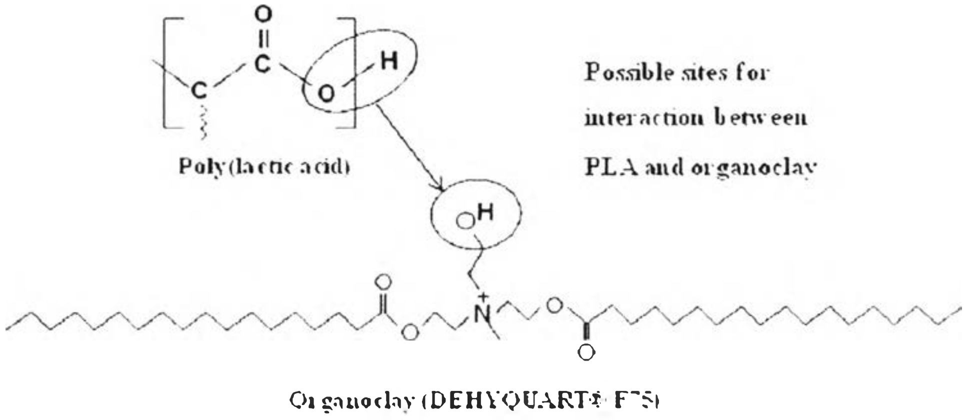


Figure 5.2 Proposed interaction between PLA and organoclay.

Focusing on ENR/PVDF/PLA system in figure 5.4, it can be seen that the increase of modulus at organoclay 3 phr was undeniable due to the contribution from organoclay which it acted as reinforcing agent and then resulted to increase the stiffness, Thipmanee *et al.* [1] also revealed the similar results. As seen from figure 5.5, the effect of adding organoclay resulted to decrease of elongation at break. It was found by Chen *et al.* [4] that the increase in the modulus of the polymer-clay composites would result in a reduction in the elongation at break because of the improvement in strength. Moreover, P. L. TEH *et al.* [2] also suggested that the decrease of elongation at break related to the intercalation process of the clay that caused more crosslink between ENR and clay. Our results agreed with these observations.

Table 5.4 The tensile strength, Young's modulus and percent elongation at break of the organoclay-filled TPV at fixed DBPH 5 phr

ENR/PVDF/PLA, % wt	Organoclay, phr	Tensile strength, MPa	Young's modulus, MPa	Elongation at break, %
50/40/10	0	5.08 ± 0.44	83.50 ± 3.17	38.13 ± 8.99
	3	6.72 ± 0.15	98.78 ± 5.17	10.82 ± 0.52
	5	5.91 ± 0.27	86.86 ± 3.68	9.65 ± 1.28
	7	5.50 ± 0.52	77.76 ± 2.80	9.08 ± 0.42
	10	5.60 ± 0.11	76.59 ± 4.06	9.03 ± 0.65
50/50/0	0	9.28 ± 0.39	250.36 ± 7.54	10.39 ± 1.59
	3	9.13 ± 0.40	156.80 ± 4.01	11.20 ± 0.62
	5	8.54 ± 0.41	146.77 ± 3.46	10.99 ± 0.78
	7	8.18 ± 0.54	148.8 ± 2.56	10.04 ± 0.21
	10	7.44 ± 0.46	133.72 ± 5.07	10.82 ± 0.99

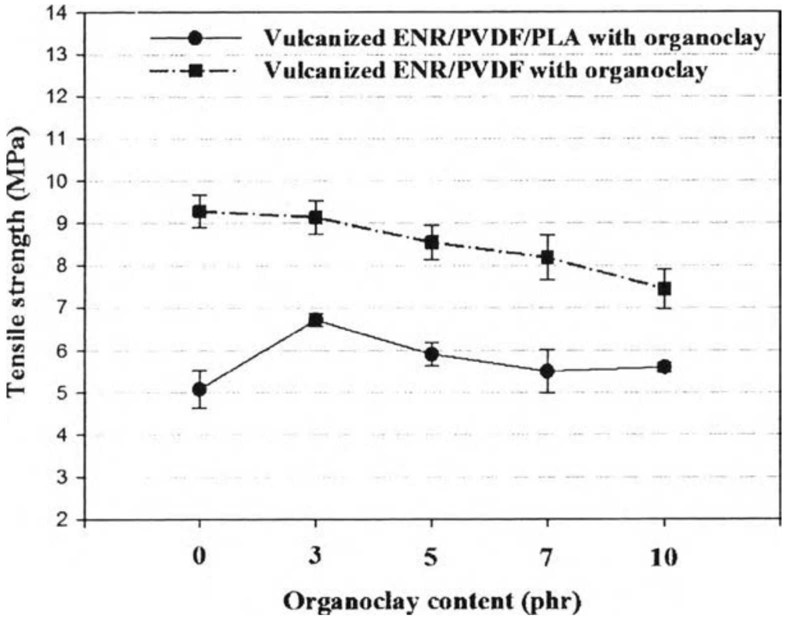


Figure 5.3 Tensile strength of the organoclay-filled TPV with the different organoclay content (phr).

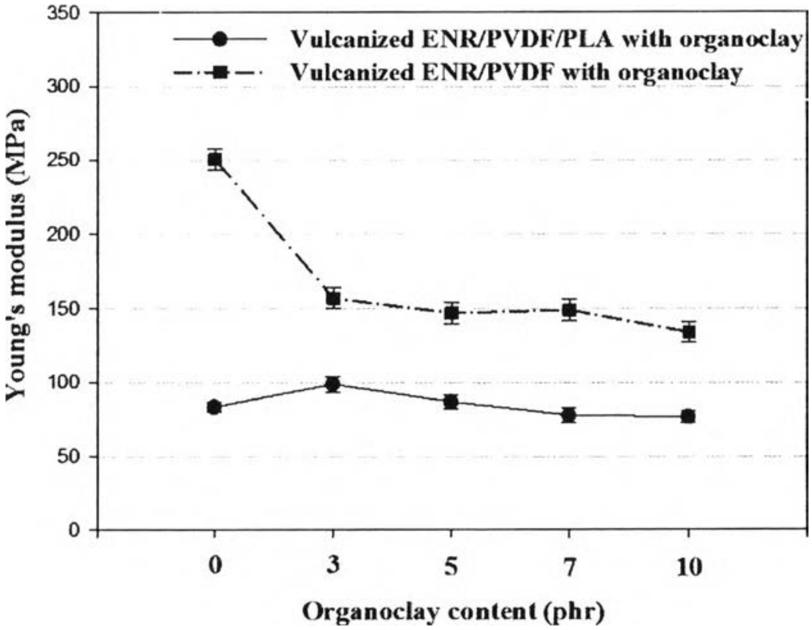


Figure 5.4 Young's modulus of the organoclay-filled TPV with the different organoclay content (phr).

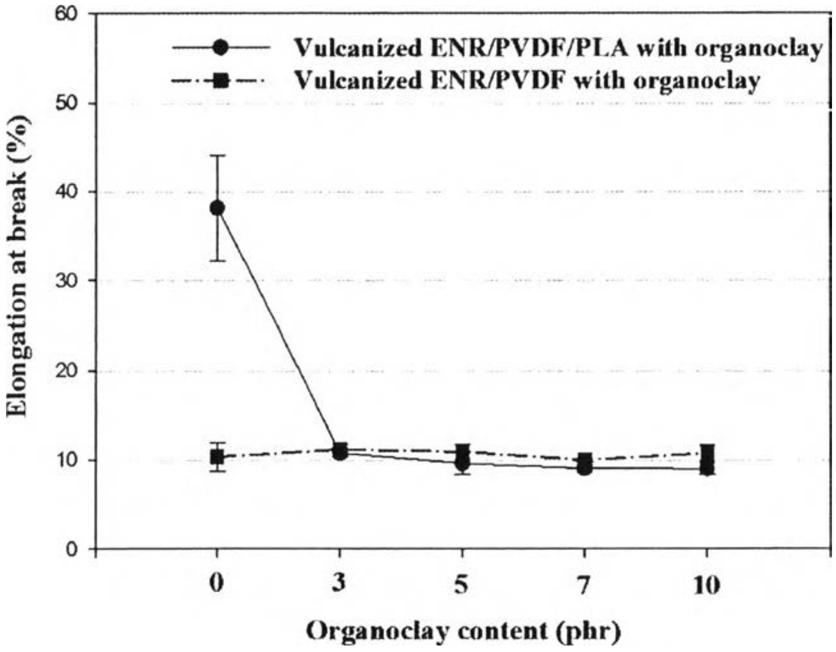


Figure 5.5 Percent elongation at break of the organoclay-filled TPV with the different organoclay content (phr).

Table 5.5 The tear strength of the organoclay-filled TPV at fixed DBPH 5 phr

ENR/PVDF/ PLA, % wt	Organoclay, phr	Tear strength, kN/m
50/40/10	0	29.40 ± 2.35
	3	31.81 ± 1.19
	5	33.39 ± 4.24
	7	33.28 ± 2.71
	10	34.47 ± 5.29
50/50/0	0	63.47 ± 8.98
	3	55.93 ± 3.26
	5	54.23 ± 1.28
	7	55.18 ± 3.24
	10	50.54 ± 2.23

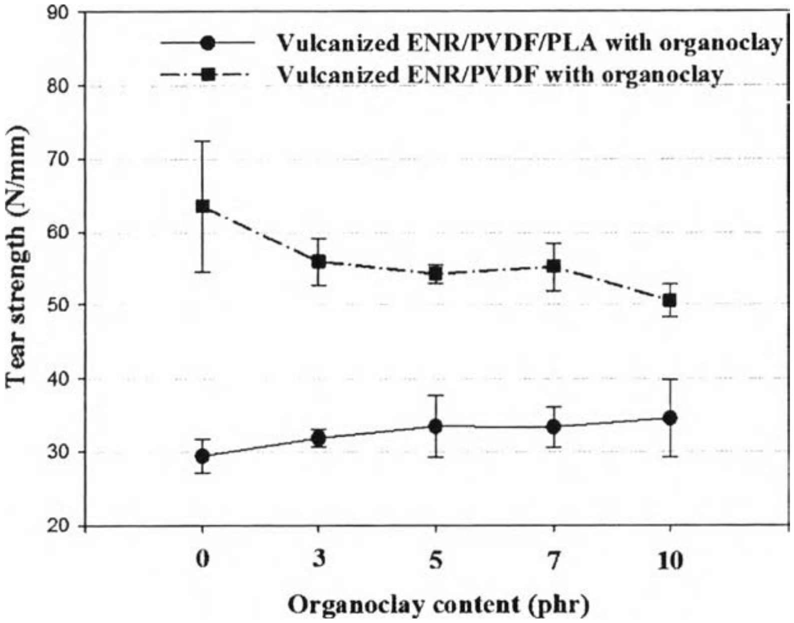


Figure 5.6 Tear strength of the organoclay-filled TPV with the different organoclay content (phr).

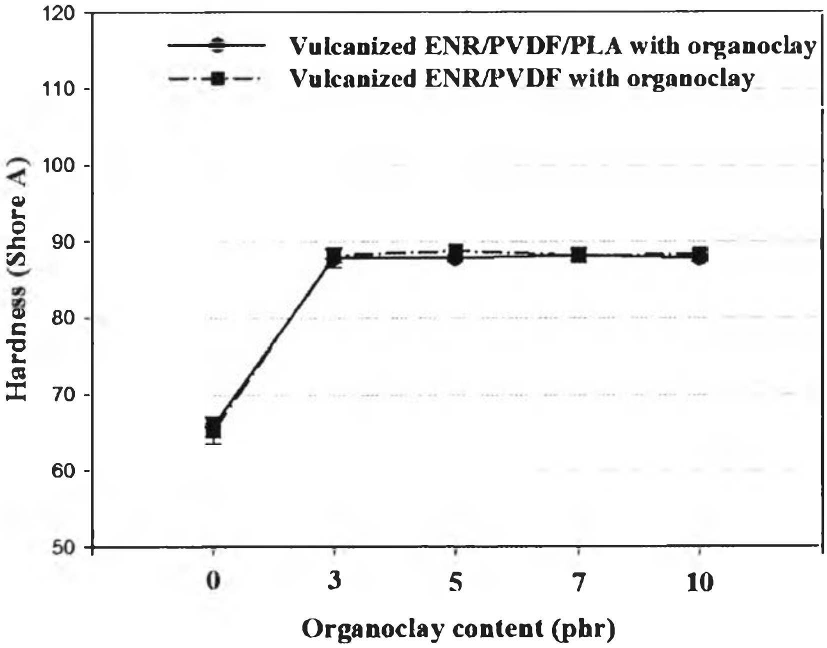


Figure 5.7 Hardness of the organoclay-filled TPV with the different organoclay content (phr).

Table 5.6 The hardness of the organoclay-filled TPV at fixed DBPH 5 phr

ENR/PVDF/ PLA, % wt	**Organoclay, phr**	**Hardness (Shore A)**
50/40/10	0	65.8 ± 1.30
	3	87.8 ± 1.16
	5	87.8 ± 0.40
	7	88.2 ± 0.75
50/50/0	10	87.8 ± 0.40
	0	65.2 ± 1.64
	3	88.2 ± 0.98
	5	88.8 ± 0.75
	7	88.2 ± 0.98
	10	88.4 ± 0.49

Table 5.5 and 5.6 reported the tear strength and hardness. As seen from figure 5.6, the improvement of tear strength with organoclay loading in ENR/PVDF/PLA system was directly related to the intercalation of the organoclay-filled the TPV which also attributed to the strong interaction between organoclay and ENR, L. E. Yahaya *et al.* [3] also revealed the same results, so it can be concluded that organoclay can extend further propagation. The effect of adding organoclay resulted to higher hardness whereas the organoclay content insignificantly affected the hardness as seen from figure 5.7.

5.4.3 Dynamic mechanical properties

Figure 5.8 and 5.9 represented the temperature dependence of storage modulus (E') and loss factor (tan delta), respectively on the effects of organoclay contents and addition of PLA. The explanations of the sample name were shown here, for example, 0 Organoclay-PLA means the TPV with PLA without organoclay and 10 Organoclay-NO PLA means the TPV without PLA with organoclay 10 phr.

Focusing on TPV without PLA system, the increase of organoclay showed significant increase in storage modulus (5 organoclay-NO PLA) compared to without organoclay due to the incorporation of organoclay into ENR phase, whereas the increase of organoclay contents resulted to lower storage modulus (10 organoclay-NO PLA). This may be attributed to the increase of organoclay loading that formed agglomerates at few spots inside ENR phase. R. Rajasekar *et al.* [5] also reported that the agglomeration can introduce some voids and pores during the sample preparation, which may be responsible for decrease in the storage modulus. As seen from the curves, the storage modulus of organoclay-filled TPV with PLA was lower than that of without PLA at the lower temperature region (below 0°C). This may be attributed to incorporate of PLA that formed some cracks and voids between PVDF and PLA phases due to the immiscibility, which may be responsible for decreased in the storage modulus. In case of TPV with PLA, the storage modulus showed close values in all of organoclay contents because some of organoclay layers could intercalate into PLA which resulted to the reduction of organoclay in overall ENR phase, thereby the storage modulus below 0 °C showed quite similar values. All blends gave similar storage modulus values at region around 20 – 40 °C which related to the insignificant change of Young's modulus with increasing organoclay contents.

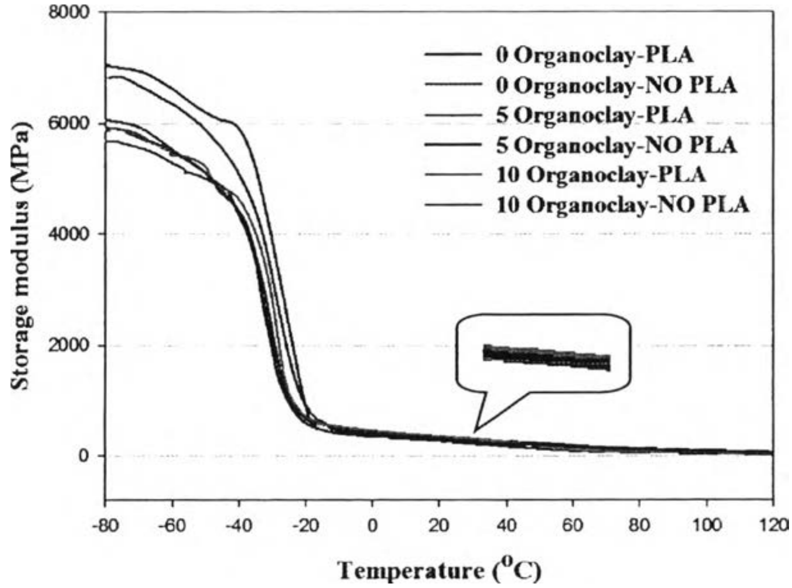


Figure 5.8 Effects of the organoclay contents and addition of PLA on the storage modulus as a function of temperature.

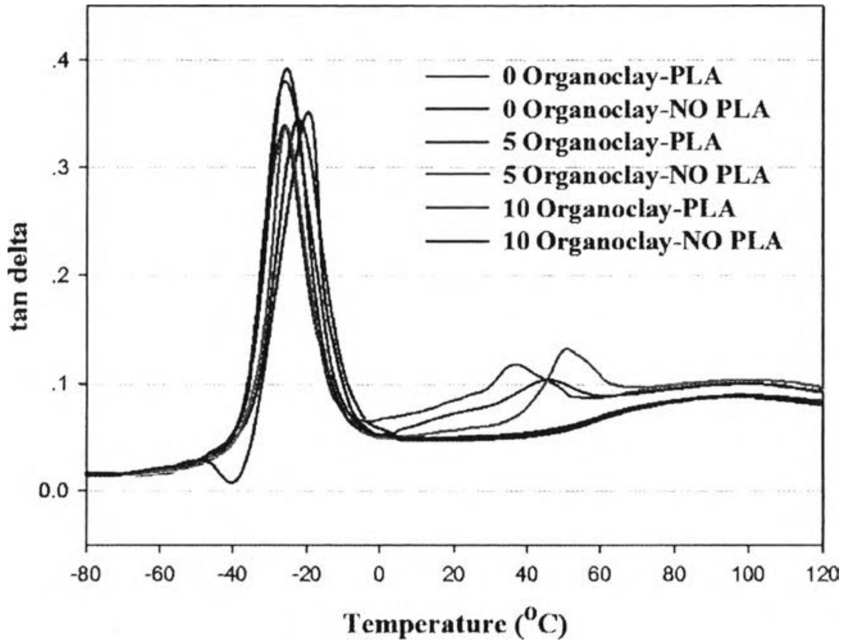


Figure 5.9 Effects of the organoclay contents and addition of PLA on the tan delta as a function of temperature.

From the dynamic mechanical properties in previous chapter, the tan delta peak around -25 °C belong to the glass transition temperature of ENR phases. The blends with increasing organoclay contents showed significant decrease in tan delta peak. This corresponds to reinforcing tendency of the nanofiller in the matrix. Das A. *et al.* [6] reported that the reduction of chain mobility resulted to physical and chemical adsorption of the rubber molecules on the organoclay surface caused a height reduction of tan delta peak during dynamic mechanical deformation. The decrease in tan delta peak revealed minimum heat buildup which resulted to the lower damping characteristics for the blends containing organoclay. The incorporation of organoclay in the blends showed increase in glass transition temperature. Generally, strong interactions between the organoclay layers and the polymer matrix can restrict the movement of polymer segments near to the filler surface, thereby resulting in an increase of the glass transition temperature of the matrix, the literature of R. Rajasekar *et al.* [5] also supported these observations.

Moreover, the dynamic mechanical investigation was used to predict the miscibility of the system. The TPV with PLA blends showed two tan delta peak around -25 and +50 °C, which corresponded to the Tg of ENR and PLA, respectively. Two clearly separated peaks indicated that the ENR and PLA phases were not fully compatible. The obtained glass transition temperature of ENR is at -25 °C. The Tg of PVDF is at -35 °C reported by R. D. Simoes *et al.* [8]. There was a single tan delta peak in between the Tg of these two components but it can't be concluded that the ENR and PVDF phases were miscible because the Tg of them were close (< 20 °C), miscibility can't be judged from Tg measurements. SEM morphology studies could help to indicate the miscibility by observing the phase separation and interfacial adhesion. The Tg of PLA in 10 phr organoclay-filled TPV (10 Organoclay-PLA) was shifted to a higher temperature which attributed to the restriction of the PLA molecular chain mobility. This may be due to the intercalation of organoclay layers into PLA, Thipmanee *et al.* [1] also supported the possibility of this observation.

5.4.4 Oil swelling properties

Oil swelling test was done in gasohol 91, gasohol 95, E20 and E85 at room temperature and 100 °C for 24 hours and 7 days. Figure 5.10 – 5.13 studied the effects of the organoclay contents and addition of PLA on the oil resistance in 4 oil types. The explanations of the sample name were shown here, for example, 5 Organoclay-NO PLA means the TPV without PLA with organoclay 5 phr. According to the oil swelling resistance related to the extent of crosslinking, it were revealed that the addition of organoclay helped to decrease the rate of oil uptake after immersed for 7 days which showed similar results as that of 24 hours, especially clearly be seen in ENR/PVDF/PLA system, whereas the organoclay insignificantly improved the oil resistance comparing to without organoclay in the immersion for 24 hours. L. E. Yahaya *et al.* [3] also reported the observation that the rate of oil uptake decreased with the incorporation of the organoclay into NR matrix. This trend can be attributed to the presence of the nanodispersed impermeable clay layers, which decreased the rate of transportation by increasing the average diffusion path length in the NR matrix, the literature of Peiyao *et al.*, [10] also reported the similar results. The higher temperature of immersion resulted to increase in swelling index in all of the blends.

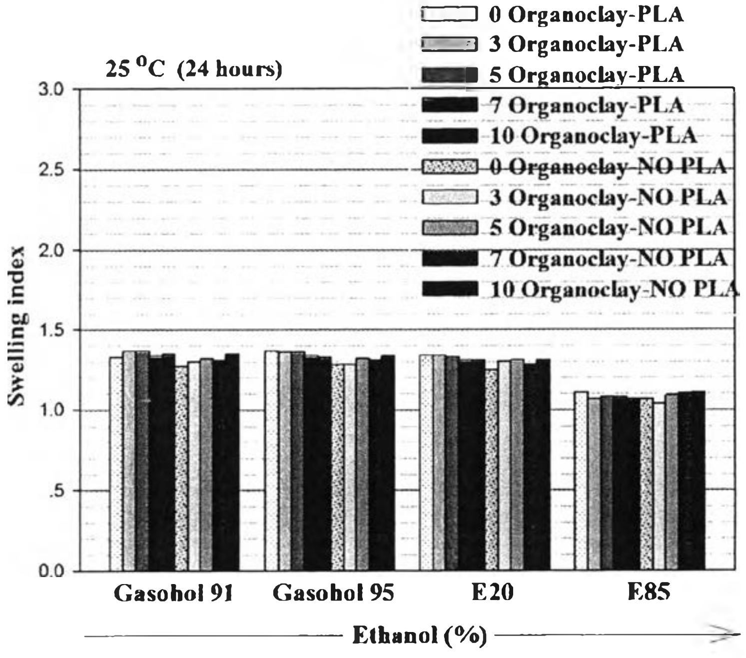


Figure 5.10 Oil swelling index using ENR/plastic/DBPH ratio of 50/50/5 by varying the organoclay content at room temperature for 24 hours.

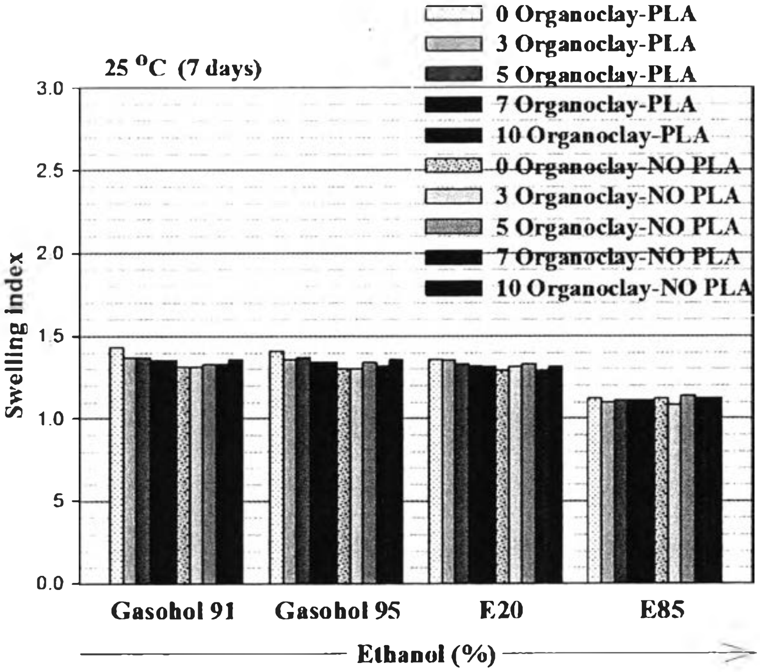


Figure 5.11 Oil swelling index using ENR/plastic/DBPH ratio of 50/50/5 by varying the organoclay content at room temperature for 7 days.

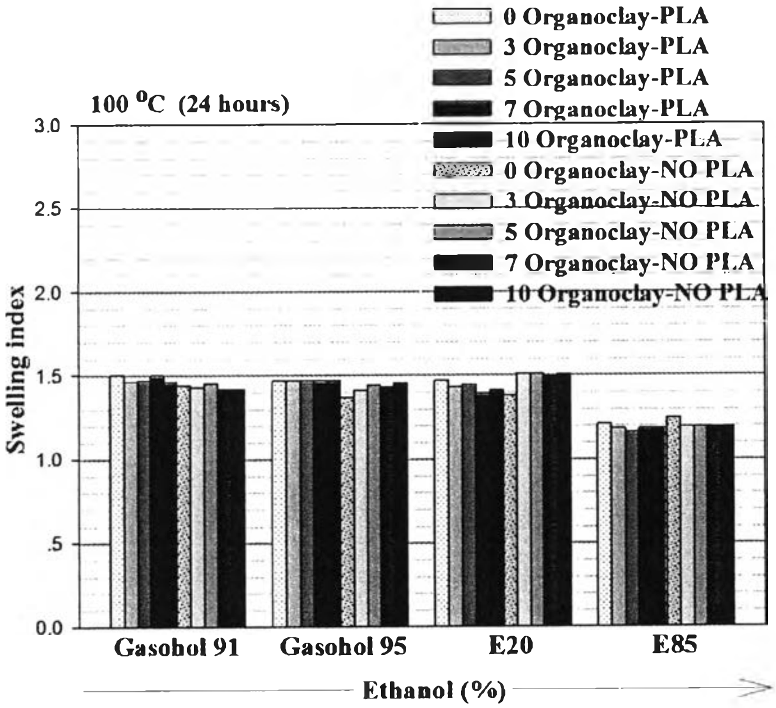


Figure 5.12 Oil swelling index using ENR/plastic/DBPH ratio of 50/50/5 by varying the organoclay content at 100 °C for 24 hours.

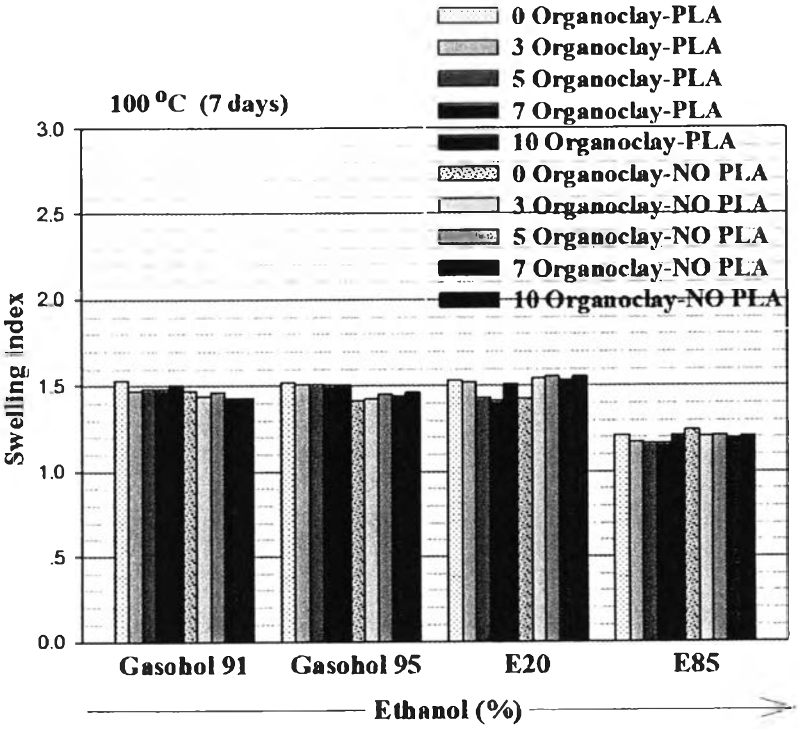
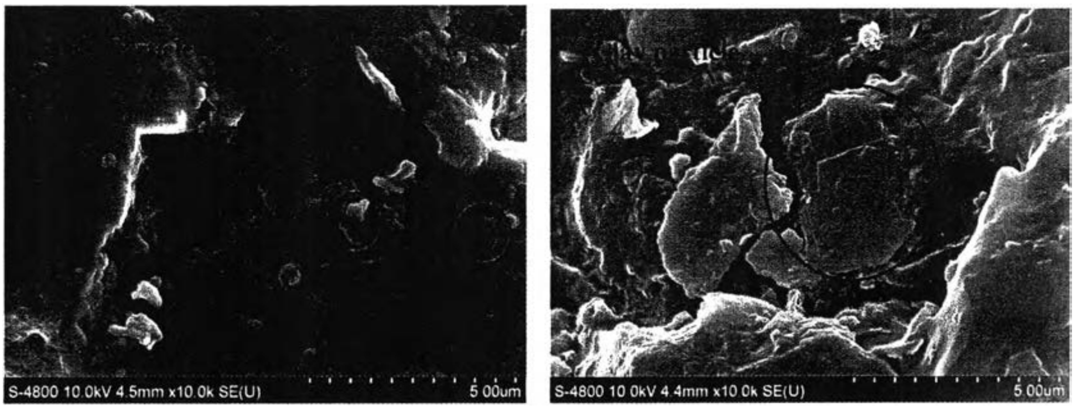


Figure 5.13 Oil swelling index using ENR/plastic/DBPH ratio of 50/50/5 by varying the organoclay content at 100 °C for 7 days.

5.4.5 SEM morphology

SEM images recorded by scanning the samples along the cross section of fractured surface provided further details of the morphology of the blends. They revealed that the morphology observed at the cross section was similar to that found at the volume of the blends, which is important information.

Focusing on the dispersion of organoclay particles in ENR domain, the SEM morphology revealed that the low contents of organoclay (at 3 phr) showed the clay particle size around 1 micron (1 μm) while the high contents of organoclay (at 10 phr) showed particle size around 4 micron. This attributed to the agglomeration of organoclay happened at high loading that effected to the less of mechanical properties.



(a) (b)

Figure 5.14 The SEM morphology with 10000x magnification; (a) 3 Organoclay-NO PLA and (b) 10 Organoclay-NO PLA.

5.5 Conclusion

The effects of organoclay and PLA contents on the cure characteristics, mechanical, oil resistant and morphological properties have been studied. The results showed that the increase of organoclay in the ENR compounds gave higher cure rate index and maximum torque. The effect of loading organoclay significantly improved mechanical and oil resistant properties in ENR/PVDF/PLA. The highest properties obtained at organoclay 3 phr. The SEM morphology of the ENR phase revealed that in case of organoclay 3 phr loading, the organoclay well dispersed in the matrix and particle size was around 1 micron, whereas in case of 10 phr the organoclay became agglomerates.

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5.7 References

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