

CHAPTER VI
CHARACTERIZATION AND COMPARISON OF ENR/PVDF/PLA AND
NBR/PVDF/PLA THERMOPLASTIC VULCANIZATE ON MECHANICAL
AND OIL RESISTANT PROPERTIES

6.1 Abstract

This study is purposed to compare a thermoplastic vulcanizate (TPV) via dynamic vulcanization made of epoxidized natural rubber (ENR) and poly(vinylidene fluoride) (PVDF) to acrylonitrile butadiene rubber (NBR) and PVDF. The effects of rubber types and addition of PLA on mechanical and oil swelling properties were studied for comparing between natural and synthetic rubber. 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 rubber types (ENR and NBR) at fixed 50 wt% and the addition of PLA at fixed 10 wt%. Curing agents (DBPH) was fixed at 5 phr. The results showed that tensile strength and tear strength of NBR/PVDF system were higher than NBR/PVDF/PLA system and TPV of NBR type gave better properties than ENR type in both of them. In contrast to the young's modulus, the NBR/PVDF/PLA showed higher modulus than NBR/PVDF. The addition of PLA into NBR/PVDF insignificantly affected the hardness. The oil resistant properties of NBR system gave better results than ENR system in both of adding and non-adding PLA but the swelling in E85 gave similar resistance results. The addition of PLA in NBR/PVDF insignificantly changed the swelling index.

6.2 Introduction

The production of rubber parts become a big market because they have highly consumed in fuel and chemical transmission line in automotive and chemical industries such as, gasket, suspension bush, oil tank plug and drain pipe. The rubbers for special applications like these have prominent properties for example, flexibility,

thermal resistance, chemical and oil resistance, compressibility, impact resistance, and friction resistance. In the present, synthetic rubber mostly use as major raw materials.

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 dynamically vulcanized blends of epoxidized natural rubber (ENR) and poly(vinylidene fluoride) (PVDF) have been recognized as TPV materials which are promising candidates to be able to use instead of synthetic rubber. Supri and H. Ismail [1] reported dynamically vulcanized blends of poly(vinyl chloride)/acrylonitrile butadiene rubber (PVC/NBR) gave better results than binary blends in terms of mechanical properties, swelling resistance, thermal stability and interaction between PVC and NBR. Sachiko Ishida *et al.* [2] revealed that NBR was possible to melt blend with PLA due to the low interfacial tension between them.

In this work, 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 comparing with that of NBR. This research report the effects of rubber types (ENR and NBR) at fixed 50 wt% and the addition of PLA at fixed 10 wt% on the mechanical properties (tensile and tear strength and hardness), thermal properties (DMA), curing properties (MDR), oil swelling resistant properties and morphology (SEM) of the blends.

6.3 Experimental section

6.3.1 Materials

The materials used in this study were ENR with 25 % epoxidation, supplied by Muang Mai Guthrie PCL., NBR (grade KRYNAC 3345F), supplied by PI Industry Ltd., PVDF (grade Z100), supplied by Asambly Chemicals Company, PLA (grade 2002D), supplied by NatureWorks LLC. The selected additives (Fluka reagent grades) were calcium hydroxide ($\text{Ca}(\text{OH})_2$) 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. Gasohol 91, 95, E20 and E85 were supplied by PTT PCL.

6.3.2 Preparation of the blends

6.3.2.1 *Preparation of rubber parts*

The ENR and NBR 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 (or NBR) was charged first into the mixing chamber, then stearic acid, $\text{Ca}(\text{OH})_2$, 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 6.1.

6.3.2.2 *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.

6.3.2.3 *Preparation of Thermoplastic vulcanizate (TPV)*

The formulations of the TPV blends are given in Table 6.2. First step, the rubber parts were prepared at room temperature by using two roll mill (LRM 110 model). The ENR or NBR was mixed with stearic acid, $\text{Ca}(\text{OH})_2$, 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 6.3.2.2 on top of rubber compound surface and fed in twin screw extruder, respectively.

Table 6.1 Formulations of ENR and NBR compounds for curing characterization

Materials	Quantity, phr ^a	Mixing times, min
ENR or NBR	100	0 - 2
Stearic acid	0.25	2 - 3
Ca(OH) ₂	3	3 - 6
TAIC	X/2	6 - 8
DBPH	X	8 - 10

Note: ^aphr is part per hundred part of rubber and X = the varying DBPH content at 3, 5 and 7 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 6.2 Formulations of TPV blends of ENR and NBR

Materials	Blends (wt %)	
	I	II
ENR or NBR	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
Triacetin ^a	2.5	2.5
Triacetin ^b	2.5	2.5

Note: ^a At phr of rubber and ^b At php of plastic.

6.3.3 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.

6.3.4 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.

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

The storage modulus (E'), the loss modulus (E''), and the dissipation factor ($\tan \delta$) are measured by DMA (GABO-EPLEXOR 100N model) using a constant frequency of 1 Hz and a temperature range of -80°C to $+120^{\circ}\text{C}$. 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).

6.3.6 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 6.1 and 6.2, respectively:

$$\text{Swelling index} = \frac{\text{Final mass}}{\text{Initial mass}} \quad (6.1)$$

$$\% \text{ Swelling} = \frac{W_s - W_o}{W_o} \times 10 \quad (6.2)$$

Where W_s refer to a swelling weight and W_o refer to an original weight.

6.3.7 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.

6.4 Results and discussion

6.4.1 Curing properties of ENR and NBR

Curing characteristics of ENR and NBR using DBPH at 5 phr in terms of cure rate index (CRI), cure time (t_{90}), maximum elastic torque ($S'@MH$ or MH), minimum elastic torque ($S'@ML$ or ML) and maximum viscous torque ($S''@MH$) obtained from MDR were shown in table 6.3. It can be seen that the increase of temperature resulted to higher CRI and lower t_{90} because the higher temperature accelerated the curing reaction in both of ENR and NBR systems, as seen a clear trend of increasing CRI in figure 6.1. The NBR showed faster curing reaction than ENR due to its high degree of unsaturation. Focusing on MH, the NBR gave higher MH than ENR which mean higher stock modulus due to the nature of NBR structure that has high polarity and strong intermolecular bond. These reasons also explained the higher $S''@MH$ of NBR than that of ENR which mean higher damping properties.

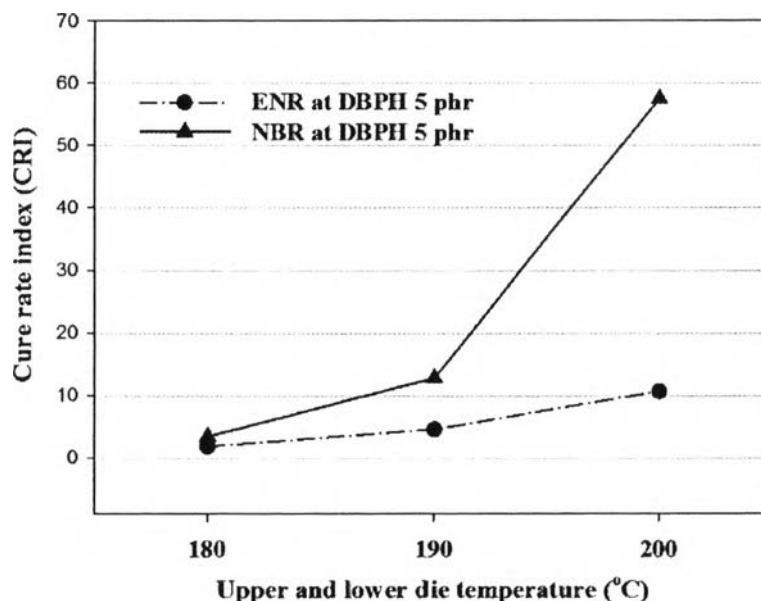


Figure 6.1 Cure rate index of the ENR and NBR compounds using DBPH 5 phr at the different temperature obtained from MDR.

Table 6.3 Cure characteristics of ENR and NBR at DBPH 5 phr obtained from MDR.

Rubber types	Upper and Lower die, °C	S'@ML, lbf·in	S'@MH, lbf·in	S''@MH, lbf·in	t ₉₀ , min	Cure rate index (CRI)
ENR	180	1.34	10.91	0.40	5.34	1.94
	190	1.20	10.24	0.34	2.26	4.71
	200	0.77	9.26	0.24	1.03	10.75
NBR	180	0.67	17.5	0.70	5.22	3.45
	190	0.54	17.7	0.84	1.58	12.8
	200	0.45	17.7	0.74	0.49	57.5

6.4.2 Mechanical properties

Mechanical properties in terms of tensile strength, young's modulus at 0.2 % strain and percent elongation at break were shown in table 6.4.

Table 6.4 The tensile strength, Young's modulus and percent elongation at break of the blends at fixed DBPH 5 phr comparing between ENR and NBR

NBR/PVDF/ PLA, % wt	Tensile strength, MPa	Young's modulus, MPa	Elongation at break, %
50/40/10	9.53 ± 0.42	190.52 ± 5.48	20.28 ± 5.76
50/50/0	11.32 ± 0.23	161.34 ± 2.70	30.75 ± 4.24
ENR/PVDF/ PLA, % wt	Tensile strength, MPa	Young's modulus, MPa	Elongation at break, %
50/40/10	5.08 ± 0.44	83.50 ± 3.17	38.13 ± 8.99
50/50/0	9.28 ± 0.39	250.36 ± 7.54	10.39 ± 1.59

From figure 6.2, the results showed that the NBR systems gave better tensile strength than that of ENR systems in both with and without PLA which can be attributed to the cyano group of NBR is more polar than epoxy group of ENR. As seen from figure 6.3 and 6.4, the NBR/PVDF/PLA gave higher young's modulus and lower elongation at break than NBR/PVDF resulted from the polar segments of NBR and PLA which interactions could take place. Sachiko Ishida *et al.* [2] also reported that the interfacial tension between NBR and PLA was very low. As seen from figure 6.5, the surface energy and interfacial tension between PLA and rubbers were reported. Therefore, there is no method available for measuring directly the interfacial tension in their blends. So this research estimated the values of the interfacial tension via contact-angle measurements at room temperature. It can be seen than the interfacial tension between PLA and rubber decreased in the order of IR > EPM > AEM > NBR. If the interfacial tension is low, the repulsion of chain segments in the presence of incompatible chain segments due to the interaction energy is low. Moreover, the surface free energies of rubbers seem to become high when the polarity becomes high. Because PLA has hydroxyl groups, it is thought that the polar segments of rubbers might enhance the compatibility and reduce the repulsion forces under melt-blending conditions.

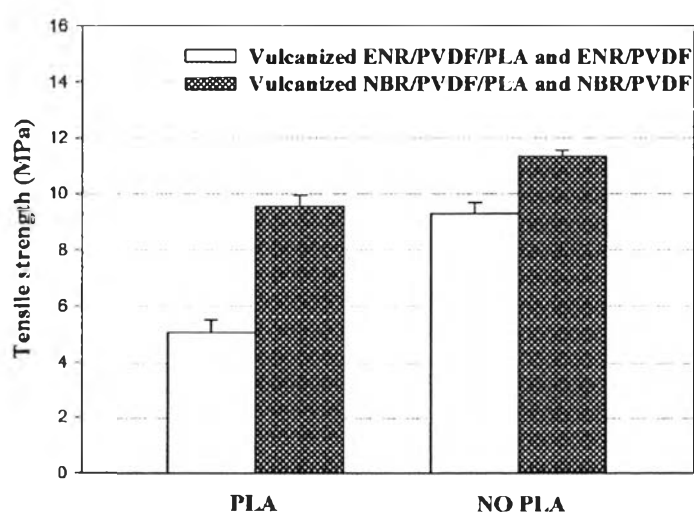


Figure 6.2 The comparison of tensile strength of vulcanized ENR/PVDF and NBR/PVDF with and without PLA.

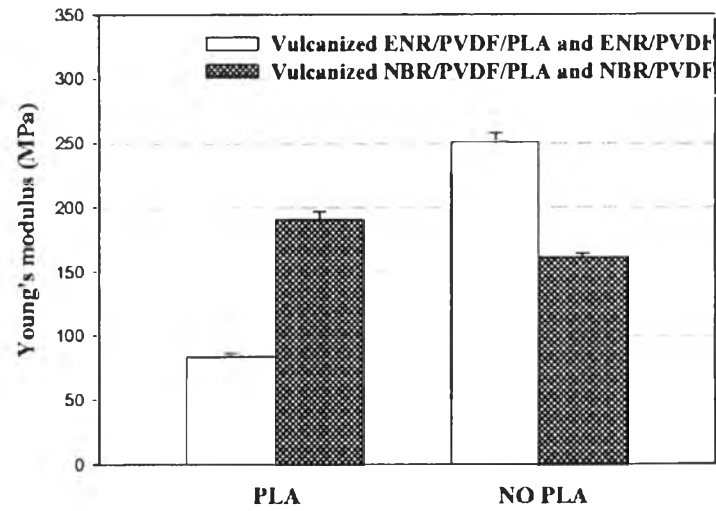


Figure 6.3 The comparison of young's modulus of vulcanized ENR/PVDF and NBR/PVDF with and without PLA.

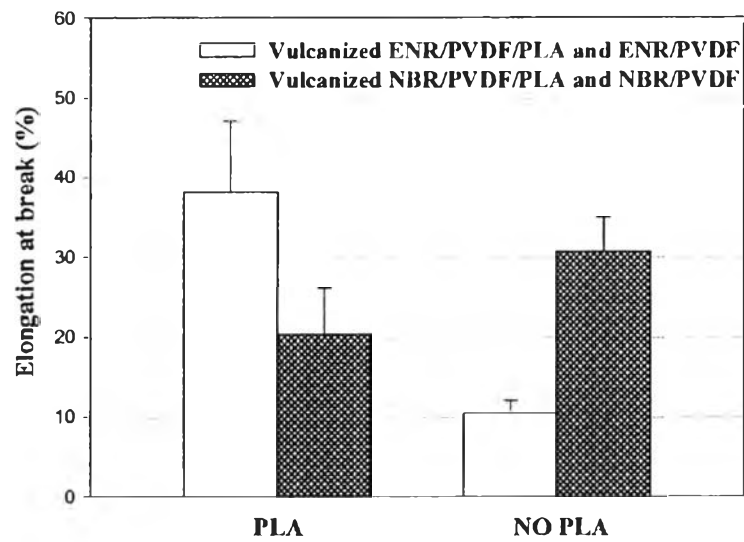


Figure 6.4 The comparison of elongation at break of vulcanized ENR/PVDF and NBR/PVDF with and without PLA.

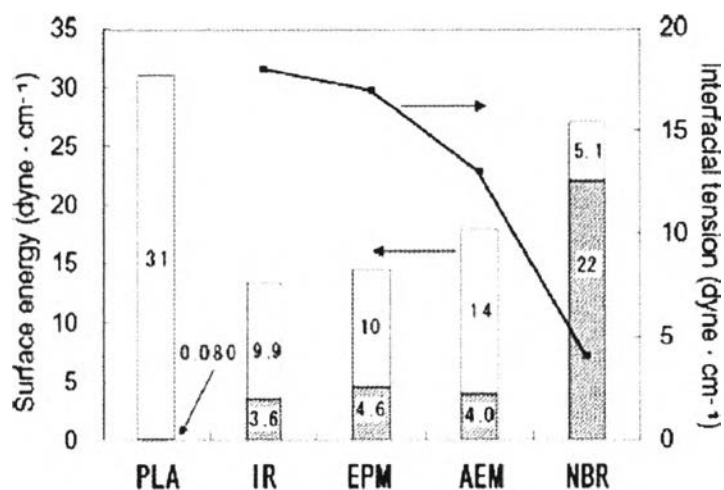


Figure 6.5 Surface energy and interfacial tension between PLA and rubbers.

Table 6.5 and 6.6 showed the tear strength and hardness. It can be seen from figure 6.6 and 6.7 that the NBR systems gave better values than that of ENR systems in both adding and non-adding PLA which can be attributed to the cyano group of NBR is more polar than epoxy group of ENR, thereby the stronger interaction of NBR helped to resist the crack propagation.

Table 6.5 The tear strength of the blends at fixed DBPH 5 phr comparing between ENR and NBR

NBR/PVDF/PLA, % wt	Tear strength, kN/m
50/40/10	63.92 ± 4.76
50/50/0	87.84 ± 9.19
ENR/PVDF/PLA, % wt	Tear strength, kN/m
50/40/10	29.40 ± 2.35
50/50/0	63.47 ± 8.98

Table 6.6 The hardness of the blends at fixed DBPH 5 phr comparing between ENR and NBR

NBR/PVDF/PLA, % wt	Hardness (Shore A)
50/40/10	88.0 ± 0.89
50/50/0	88.8 ± 1.17
ENR/PVDF/PLA, % wt	Hardness (Shore A)
50/40/10	65.8 ± 1.30
50/50/0	65.2 ± 1.64

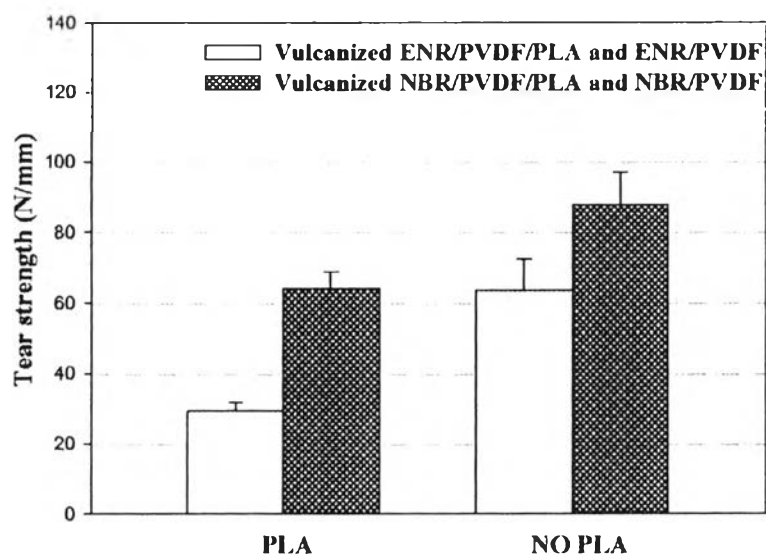


Figure 6.6 The comparison of tear strength of vulcanized ENR/PVDF and NBR/PVDF with and without PLA.

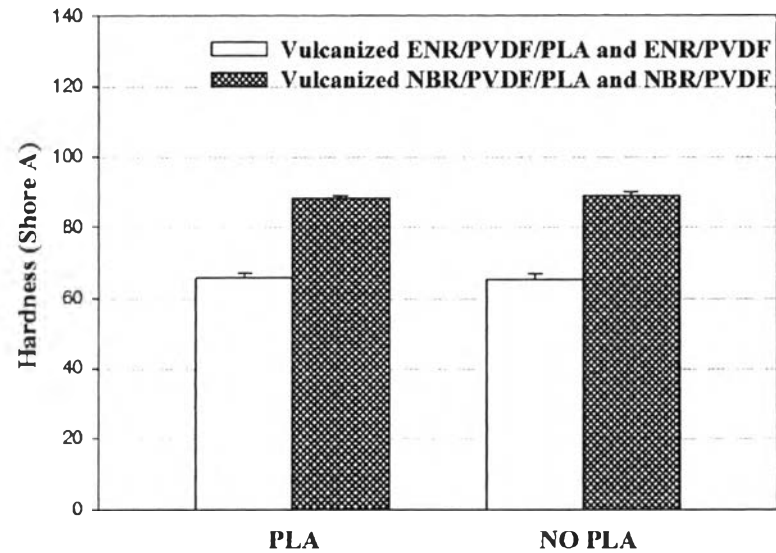


Figure 6.7 The comparison of hardness of vulcanized ENR/PVDF and NBR/PVDF with and without PLA.

6.4.3 Dynamic mechanical properties

Figure 6.8 and 6.9 represented the temperature dependence of storage modulus (E') and loss factor ($\tan \delta$), respectively on the effects of rubber types. The explanation example of the sample name was shown here, ENR-50505-PLA means the TPV with PLA of ENR rubber type at rubber/plastic/DBPH ratio of 50/50/5. The storage modulus of ENR system at below 0°C region showed higher modulus than that of NBR system due to the nature of them. At $20 - 40^{\circ}\text{C}$, the NBR system showed higher storage modulus than that of ENR which also related to the higher Young's modulus of NBR system than that of ENR.

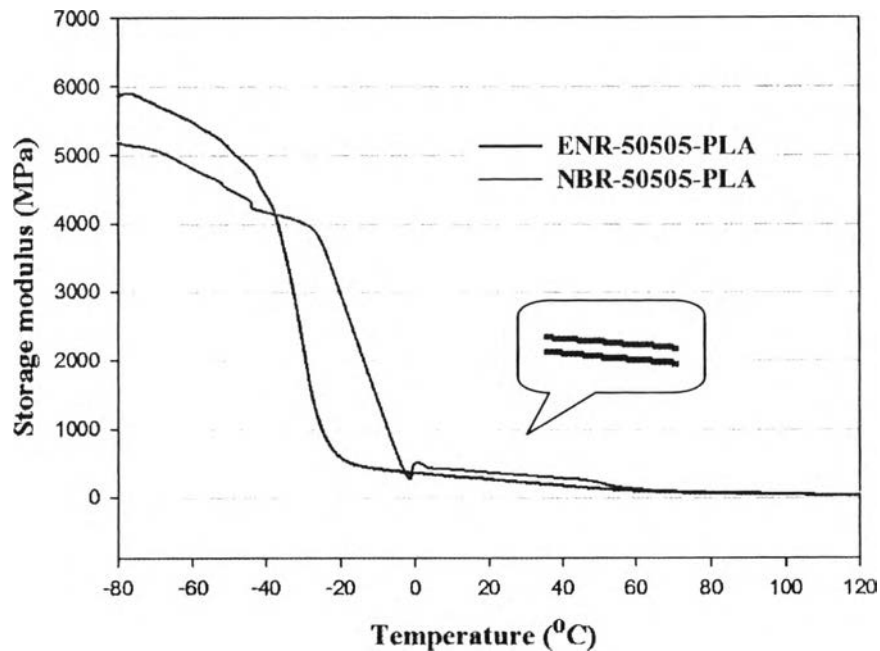


Figure 6.8 Effects of the rubber types on the storage modulus as a function of temperature.

According to the dynamic mechanical investigation was used to predict the miscibility of the system. The TPV both of ENR and NBR systems showed two tan delta peak, in case of ENR showing peak around -25 and $+45$ °C, whereas that of NBR showing peak around -6 and $+53$ °C. Two clearly separated peaks indicated that the ENR (and NBR) and PLA phases were not fully compatible. The obtained glass transition temperature of ENR is at -25 °C. The T_g of PVDF is at -35 °C reported by R. D. Simoes *et al.* [3]. There was a single tan delta peak in between the T_g of these two components but it can't be concluded that the ENR and PVDF phases were miscible because the T_g of them were close (< 20 °C), miscibility can't be judged from T_g measurements. In case of NBR system, there was a single tan delta peak in between the T_g of them but it also can't be concluded the miscibility.

The area under peak related to the damping characteristics. The damping properties of NBR system was lower than that of ENR which attributed to the higher crosslinking density of NBR supported by the cure rate index from MDR which results were shown above (6.4.1).

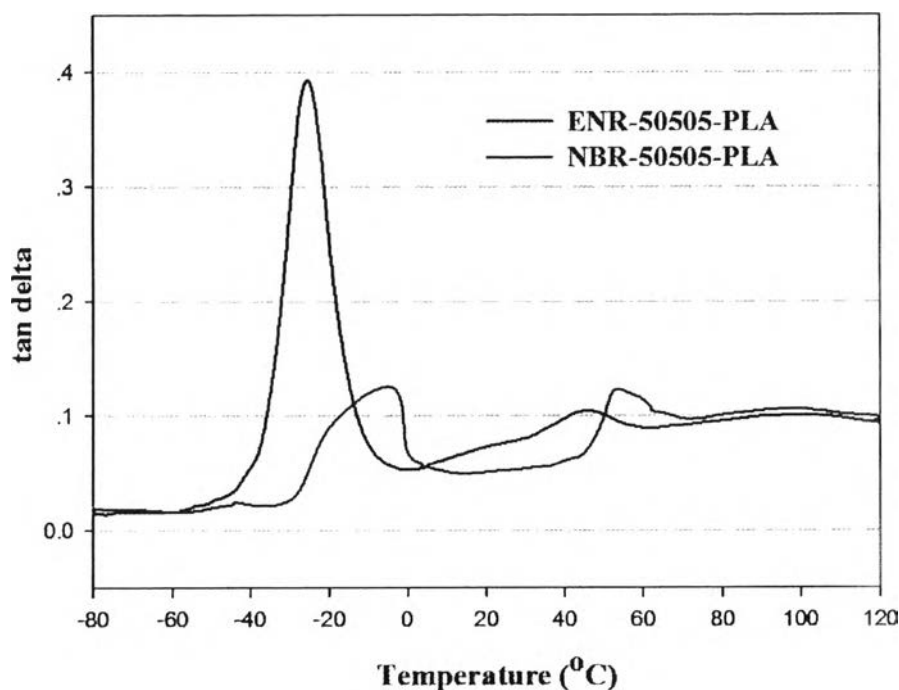


Figure 6.9 Effects of the rubber types on the tan delta as a function of temperature.

6.4.4 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 6.10 – 6.13 studied the effects of the rubber types (ENR and NBR) and addition of PLA on the oil resistance in 4 oil types including effects of higher temperature and longer time of immersion. The explanations of the sample name were shown here, for example, ENR-PLA means the TPV with PLA using ENR as rubber part and NBR-NO PLA means TPV without PLA using NBR as rubber part.

The results revealed that the TPV of NBR systems gave lower oil swelling index in all of conditions than that of the TPV of ENR systems which attributed to the nature of NBR structure which had more polarity and the higher extent of crosslink which showed in cure characteristics obtained from MDR, the results were shown above. Thereby the swelling index of NBR systems after immersed for 7 days insignificantly changed due to the stability in oil uptake. The higher temperature of immersion resulted to slightly increase in swelling index of NBR systems but significantly increase in that of ENR systems.

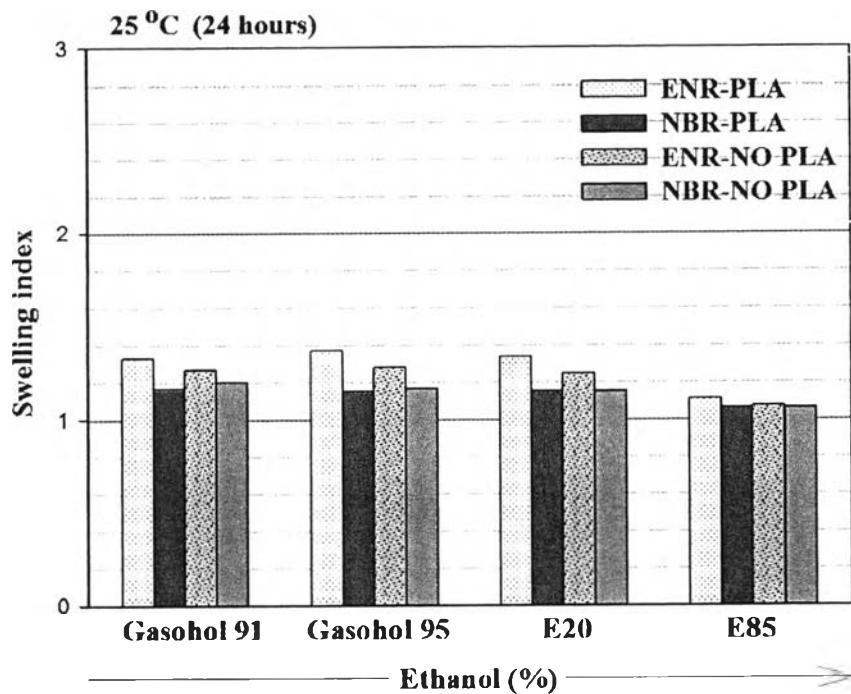


Figure 6.10 Oil swelling index using rubber/plastic/DBPH ratio of 50/50/5 by varying the rubber types at room temperature for 24 hours.

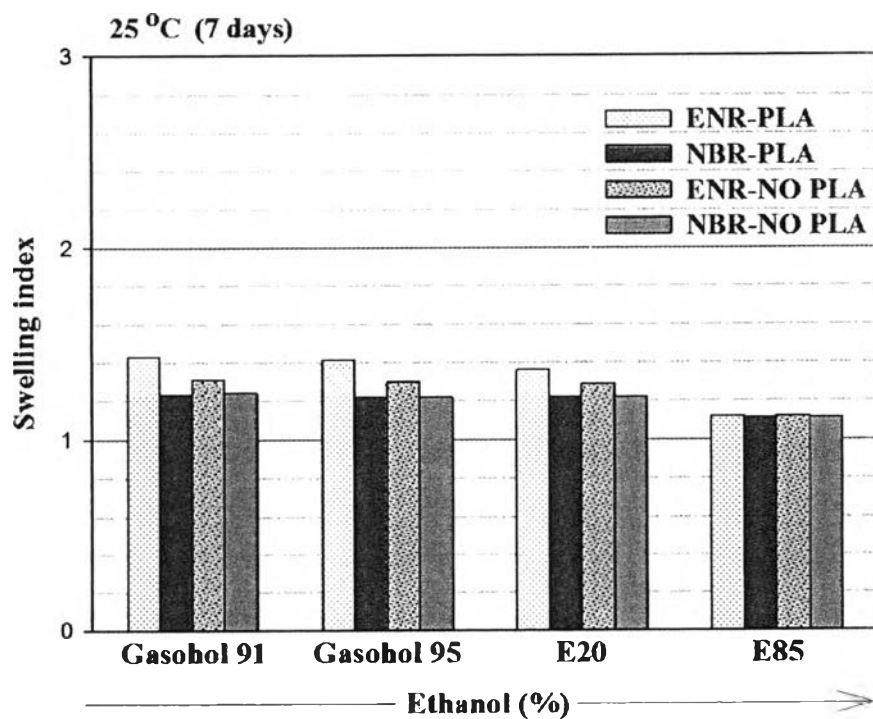


Figure 6.11 Oil swelling index using rubber/plastic/DBPH ratio of 50/50/5 by varying the rubber types at room temperature for 7 days.

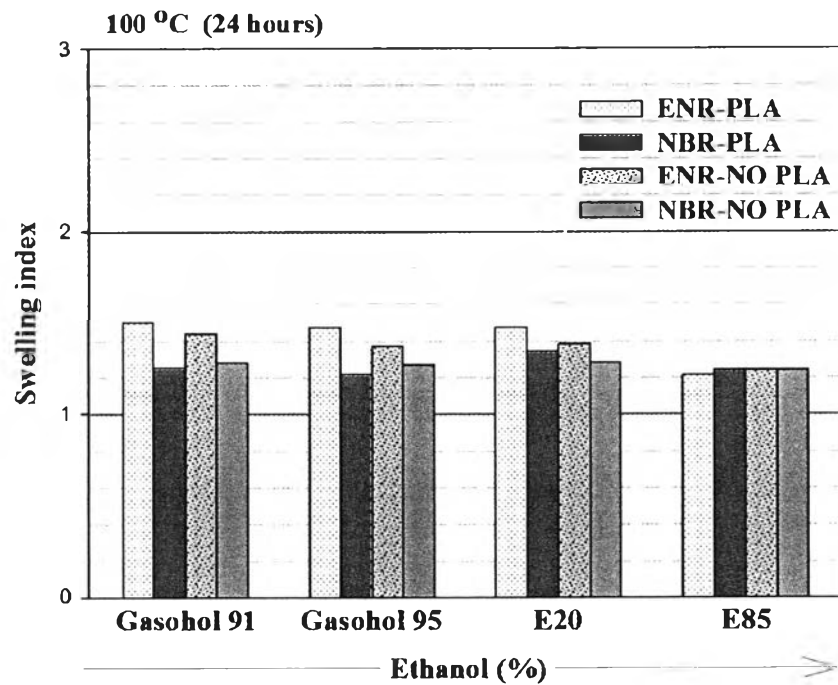


Figure 6.12 Oil swelling index using rubber/plastic/DBPH ratio of 50/50/5 by varying the rubber types at 100 °C for 24 hours.

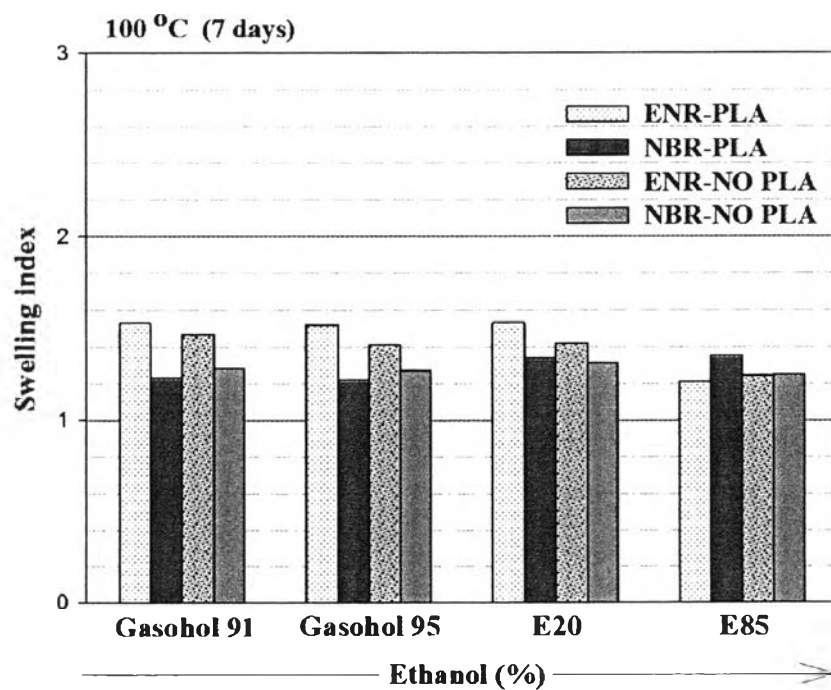


Figure 6.13 Oil swelling index using rubber/plastic/DBPH ratio of 50/50/5 by varying the rubber types at 100 °C for 7 days.

6.4.5 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. Figure 6.14 revealed the studies of SEM morphology of TPV blends in different types of rubber. According to the literature of R.D. Simoes *et al.* [3], the rougher region was PVDF phase while the smoother region was rubber phase. It can be seen that the morphology showed the co-continuous phases (at the rubber/plastic ratio of 50/50) in both of figure (a) and (b). Focusing on the interface of figure (a), the clear edge between NBR and thermoplastic domain not appeared compared to that of ENR system in figure (b) which may attributed to better interfacial adhesion. Moreover, Sachiko Ishida *et al.* [2] found that if the interfacial tension is low, the repulsion of chain segments in the presence of incompatible chain segments due to the interaction energy is low; therefore, the particle size of rubber phases decrease.

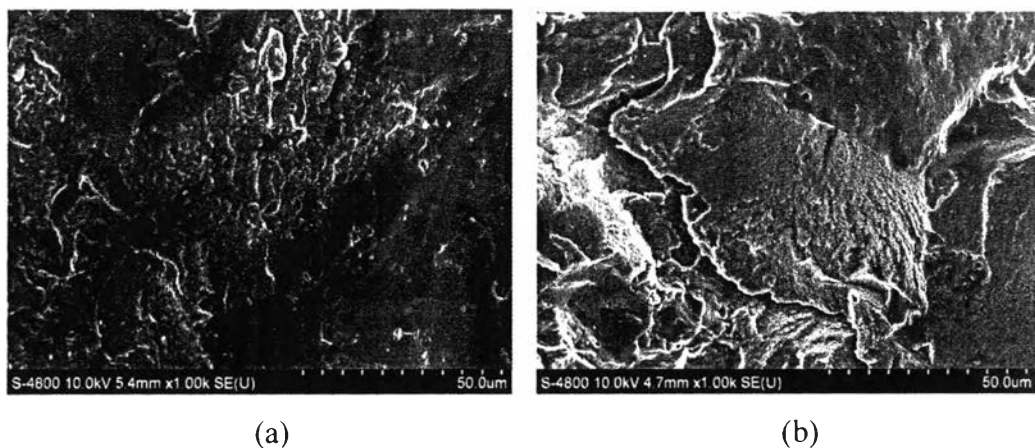


Figure 6.14 The SEM morphology with 1000x magnification; (a) NBR/PVDF/PLA and (b) ENR/PVDF/PLA.

6.5 Conclusion

The TPV of ENR/PVDF was compared to NBR/PVDF which NBR used as a benchmark. The effects of rubber types and PLA contents on cure characteristics,

mechanical, oil resistant and morphological properties have been studied. The results showed that NBR compound gave higher cure rate index and maximum torque than ENR. The NBR/PVDF with and without PLA showed higher tensile and tear strengths and hardness than ENR/PVDF system. The SEM morphology revealed the better interfacial adhesion between NBR and PVDF than that of ENR and PVDF.

6.6 Acknowledgements

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6.7 References

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