

CHAPTER VI

EFFECT OF EPOXIDIZED SOYBEAN OIL IN PEROXIDE CURED NR/PVDF/PHBV THERMOPLASTIC VULCANIZATE ON PROPERTIES OF RUBBER USED IN FUEL SYSTEM

6.1 Abstract

Rubber parts for resisting the swelling effects from gasohol were developed by making a thermoplastic vulcanizate (TPV), a blend of polymers; NR, PVDF, and PHBV; via the dynamic vulcanization technique. The amount of epoxidized soybean oil (ESO) was varied by 0, 1, 2, 5, 7, and 10 phr in DBPH vulcanized TPV. The mechanical properties included the tensile strength, percent elongation at break, and Young's modulus were determined according to ASTM D412-06a or ISO 37 (Type 1); and, the hardness were determined according to ASTM D2240. The oil resistance test was also done at 25 °C and 100 °C for 1 and 7 days according to ASTM D471-06 or ISO 2285 (Method A). In this study, biodiesel oil and gasohol with 10, 20, and 85 % ethanol were used as the test liquids and the increase in degree of swelling in percent by weight was calculated.

6.2 Introduction

Thermoplastic vulcanizate is an alternative material which has highly demand for automotive industry. For the properties such as oil resistance and thermal resistance are required for automotive rubber parts, especially those used in fuel transportation system. However, the rise in use of gasohol is so obvious with the aim to reduce global warming. This leads to the revolution of the rubber parts used in fuel system; the resistance to polar solvent has to be considered as well as the substitution of the synthetic rubbers. Thermoplastic vulcanizate (TPV) of high performance is developed as an alternative with a cheaper cost. Natural rubber (NR) and poly(vinylidene fluoride) (PVDF) are the good candidates for reducing cost [1-4]. Natural rubber, which has abundantly in Thailand, provides properties of elastomeric materials for using in rubber parts. PVDF provides properties such oil

and thermal resistances instead of fluoro rubber with the lower cost. It also becomes an environmental friendly in reducing the use of synthetic polymer by adding a biopolymer, Poly(hydroxybutyrate-co-hydroxyvalerate) or PHBV. All of them were blended together via dynamic vulcanization technique with the use of peroxide, DBPH, as a vulcanization system. This work aims to produce TPV and to study the effect of adding biocompatible materials, epoxidized soybean oil (ESO), on their mechanical properties and the swelling resistance to automobile oils, biodiesel and gasohol, which are the mainly used fuels in Thailand.

6.3 Experimental

6.3.1 Materials

Poly(vinylidene fluoride) or PVDF is an extrusion grade, SINOF[®] J100 PVDF, which purchased from Assembly Chemicals Co. (Nanjing, China). Poly(3-hydroxybutyrate-co-hydroxyvalerate) or PHBV is Y1000P grade which purchased from Thantawan Industry PCL (Bangkok, Thailand). Natural Rubber which is a STR 5L grade and sulfur were supplied by Banpan Research Laboratory Co., Ltd. 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (Luperox[®] 101 or DBPH) and dicumyl peroxide (DCP) were purchased from Sigma-Aldrich Co. N-cyclohexyl-2-benzothiazyl sulfenamide (CBS) and zinc oxide (ZnO) were supported by Inoue Rubber Thailand PCL. Steric acid and triallyl isocyanurate (TAIC[®]) were obtained from Neoplastomer Co., Ltd. Calcium hydroxide was purchased from Fluka Chemical Corp. Gasohol 91, 95, E20, E85 and biodiesel B5 were derived from PTT PCL.

6.3.2 Preparation of PVDF/PHBV Thermoplastic Blend

PVDF and PHBV were first mix together with a PVDF/PHBV composition of 80/20 by using a co-rotating twin-screw extruder (Labtech, LTE20-40 model, Thailand) to obtain a PVDF/PHBV blend. The temperature profile from the feed zone to die is 160, 170, 180, 180, 185, 190, 195, 200, 205, 210. The screw speed was used at 50 rpm with the pressure of 60 bar. The extrudate was cooled in the water bath (Labtech LW-100 model) and then cut into pellet by pelletizer (Labtech, LSC-108 model).

6.3.3 Characterization of Thermal Properties of PVDF/PHBV Blend

PVDF, PHBV and the PVDF/PHBV blend were characterized thermal properties by using a differential scanning calorimeter (DSC) (Perkin-Elmer, DSC 7) operated under a N₂ atmosphere with a flow rate of 10 ml/min. All samples were heated from -20 °C to 200 °C with the heating rate of 10 °C/min and held for 3 min to destroy a thermal history. Then, they were cooled down to -20 °C and re-heated to 200 °C again at the same rate. Their thermal properties were obtained. The crystallinity percentage (X_c) of PVDF and PHBV were calculated by equation 6.1:

$$X_c (\%) = \frac{\Delta H_{sample}^*}{\Delta H_{ref}^0} \times 100, \quad (6.1)$$

ΔH^* is the measured enthalpy of PVDF or PHBV. ΔH^0 is the enthalpy of melting per gram of 100 % crystalline, 109 J/g for PHBV [5], and 104.7 J/g for PVDF [6-7]. And the relative percent crystallinity of the blend was calculated from the combination of the enthalpy of melting per gram of 100 % crystalline (ΔH^0) of PVDF and PHBV at the composition of 80PVDF/20PHBV according to the equation 6.2:

$$X_{Blend}(\%) = \frac{\Delta H_{Blend}^*}{(0.8 \times \Delta H_{PVDF}^0) + (0.2 \times \Delta H_{PHBV}^0)} \times 100, \quad (6.2)$$

6.3.4 Preparation of Thermoplastic Vulcanizate

The thermoplastic vulcanizate was achieved by blending thermoplastic and elastomeric materials together via the dynamic vulcanization technique. NR was blended with PVDF and PHBV at the fixed composition of 50NR/40PVDF/10PHBV. NR was separately compounded with chemicals by using an internal mixer (Brabender[®] Plasticorder, 815602 type with N50 mixer, Germany) at room temperature. In this study, epoxidized soybean oil (ESO) was added in the mixing by varying at 0, 1, 2, 5, 7, and 10 phr (calculated from NR 100 phr). A half amount of ESO was added to compounded NR in the compounding process and another half was added when compounded NR was mixed with thermoplastic PVDF/PHBV blend. The formula and schedule for compounding NR is given in Table 6.1. The formula was adopted from Magaraphan, *et al.*, 2008 [8]. 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (DBPH or Luperox[®] 101) was used as a peroxide vulcanizing agent.

Table 6.1 Formula and mixing schedule for compounding NR

Ingredients	Quantity (phr ^a)	Mixing time (min)
NR	100	0-4
ESO	Varied ^b	4-6
Steric acid	0.125	6-7
Ca(OH) ₂	1.5	7-8
TAIC	1.5	8-10

^aphr = part per hundred part of rubber.

^bThe amount of ESO was varied by 0, 1, 2, 5, 7, and 10 phr which were calculated from NR 100 phr and were added in a half in compounding NR.

Mixing the above ingredients was performed at a rotor speed of 80 rpm at room temperature without adding curing agent. After that, the PVDF/PHBV blend was incorporated with compounded NR in the composition of 50/50 at 150 °C according to the mixing schedule as shown in Table 6.2. The composition of TPV contained 3 materials of NR/PVDF/PHBV is 50/40/10.

Table 6.2 Schedule for mixing compounded NR and thermoplastic blend

Ingredients	Quantity (phr ^a)	Mixing time (min)
PVDF/PHBV blend	50	0-5 or plateau torque reached
Compounded NR	50	5-8 or plateau torque reached
ESO	Varied ^b	8-10 or plateau torque reached
DBPH	3	10-11 or the torque started to increase

^aphr = part per hundred part of rubber.

^bThe amount of ESO was varied by 0, 1, 2, 5, 7, and 10 phr which were calculated from NR 100 phr and were added in a half in mixing the compounded NR with PVDF/PHBV blend.

The mixing was done until the vulcanization of NR was started to occur indicated in the plateau torque of well mixing was started to increase again to obtain the pre-vulcanized TPV. Next, it was then removed from the internal mixer and later mixed and masticated into the sheet form by using a two-roll mill (Labtech, LRM 110 model, Thailand). This pre-vulcanized TPV was fully vulcanized by further compressing in a compression mold (Wabash MPI, V50H-18-CX model, USA) at the temperature of 180 °C with the pressure of 20 ton force for 10 min. Then the TPV was cooled down.

6.3.5 Study of Thermal Properties of Thermoplastic Vulcanizates

Thermal properties of TPVs at various amount of ESO were characterized by using a differential scanning calorimeter (DSC) (Perkin-Elmer, DSC 7) operated under a N₂ atmosphere with a flow rate of 10 ml/min like PVDF/PHBV blend. All of samples were heated from 30 °C to 200 °C with the heating rate of 10 °C/min and held for 3 min to destroy a thermal history. Then, they were cooled down to 30 °C and re-heated again to 200 °C at the same rate. The melting temperature and cold crystallization temperature of ESO varied TPV were obtained from DSC thermograms. The crystallization was occurred from PVDF and PHBV phases, so percent crystallinity of TPVs were determined from equation 6.3:

$$X_{TPV}(\%) = \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \quad (6.3)$$

While, ΔH^* is the measured enthalpy of PVDF or PHBV. ΔH^0 is the enthalpy of melting per gram of 100 % crystalline, 109 J/g for PHBV [5], and 104.7 J/g for PVDF [6-7]. And percent crystallinity of the blend was calculated from the combination of the enthalpy of melting per gram of 100 % crystalline (ΔH^0) of PVDF and PHBV at the composition of 40PVDF/10PHBV.

6.3.6 Study of Mechanical Properties

The mechanical properties of TPVs studied in this work included the tensile strength, percent elongation at break, Young's modulus, and hardness. The first three properties were determined according to ASTM D412-06a or ISO 37 (Type 1) by using the universal testing machine (Instron, 4206-006 model) with a load cell of 5 kN and a crosshead speed at 500 mm/min. The hardness was

determined according to ASTM D2240 by using a shore A durometer (Zwick, type 7206).

6.3.7 Study of Oil Resistance

The oil resistance of TPV was study by measuring the degree of swelling in percent after immersing sample in various types of oil at temperature of 25 °C and 100 °C for 7 days according to ASTM D471–06 or ISO 2285 (Method A). In this study, biodiesel oil (B5) which contained 5 % biodiesel and gasohol 91, 95, E20, and E85 which contain 10, 20, and 85 % ethanol, respectively, were used as the test liquids. The increase in degree of swelling in percent by weight was calculated from equation 6.4:

$$\% \text{ Swelling} = \frac{(W_s - W_o)}{W_o} \times 100 \quad , \quad (6.4)$$

where the W_s refer to a swelling weight, and the W_o refer to an original weight.

6.4 Results and Discussion

6.4.1 Thermal Properties of PVDF/PHBV Blend

The DSC thermograms of PVDF, PHBV, and PVDF/PHBV blend are shown in Figures 6.1-6.2 and their thermal properties are shown in Table 6.3.

Table 6.3 Melting temperature, crystallization temperature, and percent crystallinity of PVDF, PHBV, and the blend

Materials	T_m (°C)	T_c (°C)	ΔH^* (J/g)	Crystallinity (%)
PVDF	160.4	134.0	34.4	33
PHBV	161.5	116.3	98.7	91
PVDF/PHBV Blend	158.4	133.5	57.9	55

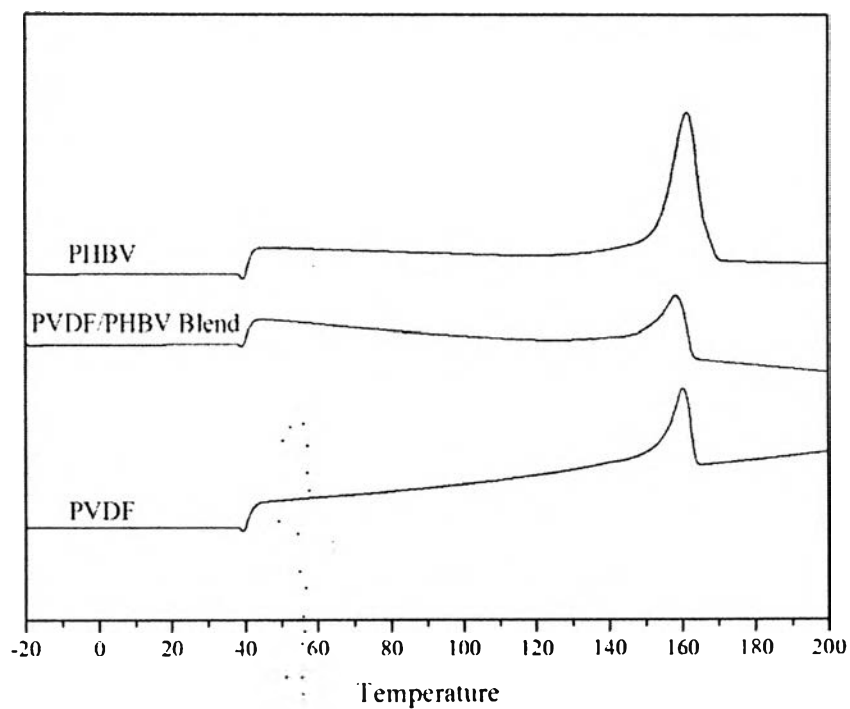


Figure 6.1 The heating curves of DSC thermogram.

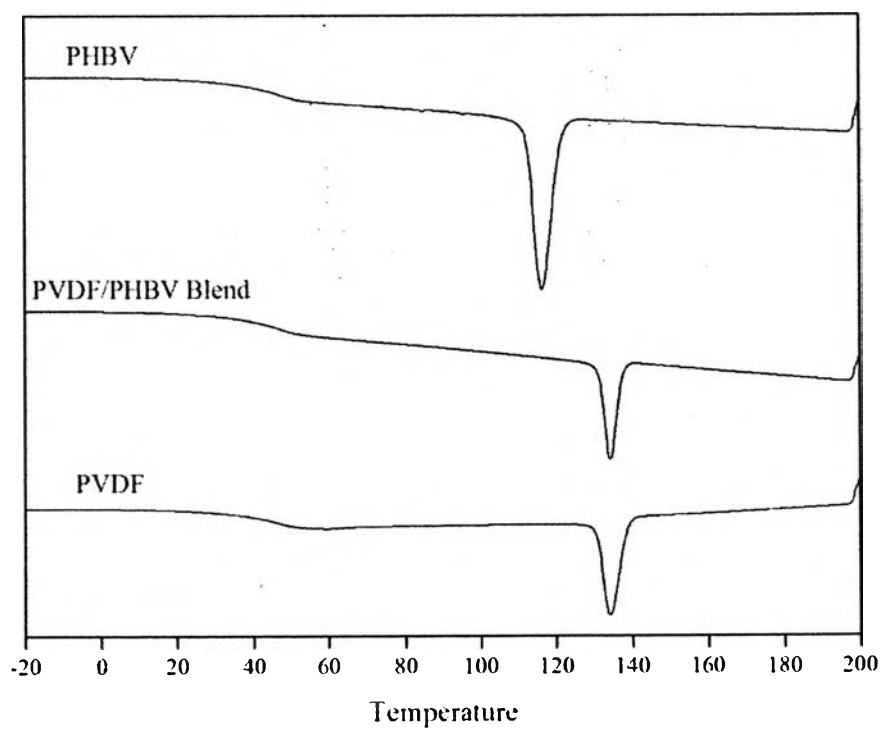


Figure 6.2 The cooling curves of DSC thermogram.

From the result, the neat PHBV has the lower crystallization temperature than neat PVDF, it is hidden with that of PVDF and cannot exhibit as a separated crystallization peak as same as melting peak. Their melting temperature is close to each other which indicated only one melting peak of PVDF/PHBV blend. The melting peak of PHBV is dominated by PVDF and the melting peak of PVDF in the blend was shifted to the lower temperature of 158.0 when added PHBV, this indicates the miscibility of PVDF and PHBV [9].

6.4.2 Preparation of Thermoplastic Vulcanizate

The thermoplastic vulcanizates with the NR/PVDF/PHBV composition of 50/40/10 (TPV) vulcanized by DBPH at 180 °C with various amounts of ESO were characterized for cure characteristics and vulcanization parameters before molding in a compression mold by using Moving Die Rheometer (MDR) (TECHPRO, rheoTECH MD+ model). The results are shown in Figure 6.3.

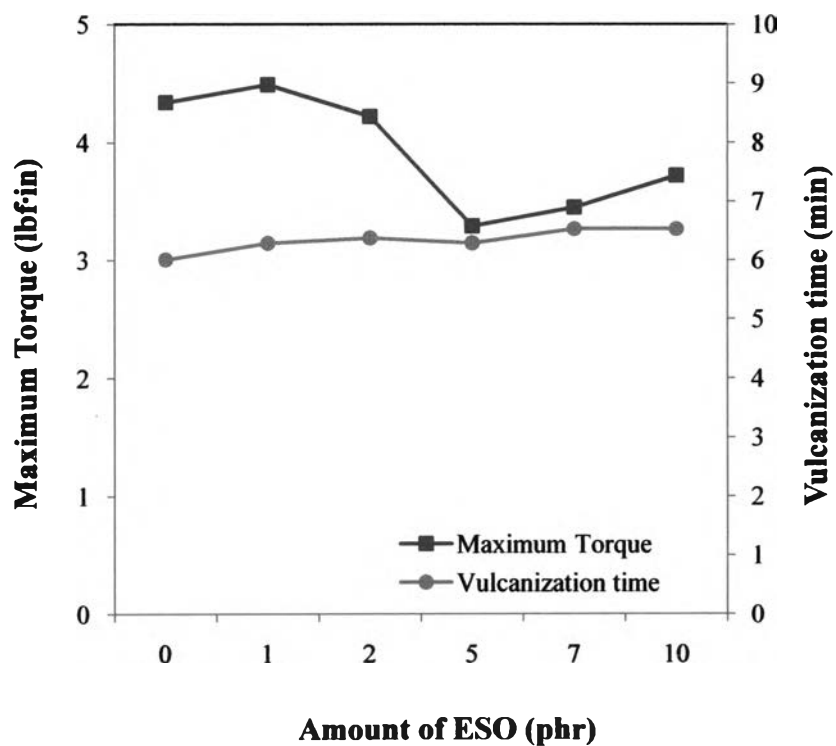
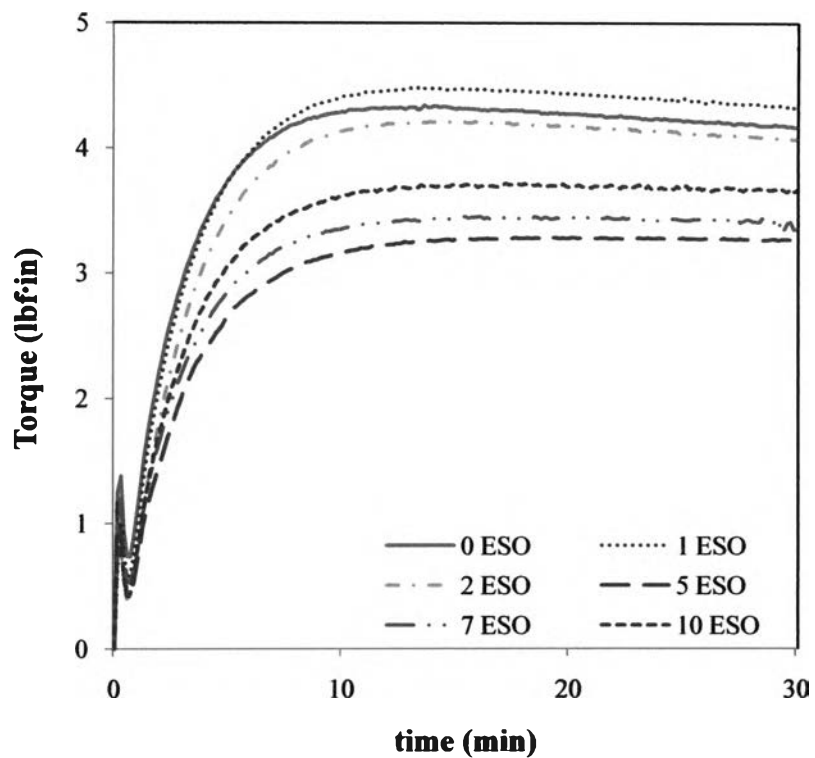


Figure 6.3 The cure characteristic and parameter curves for vulcanizing TPV at 180 °C in different amount of ESO.

All TPVs with different amount of ESO gave the same vulcanization time about 6 minutes, but the maximum torques were different. At the low amount of ESO, 0-2 phr, indicate the higher torques than those of higher amount of ESO, 5-10 phr. The obtained TPVs with high content of ESO provide the more compatibility in vulcanized TPV as shown in Figure 6.4. The TPV becomes more compatible with increasing ESO content and the rough texture was disappeared at high ESO level.

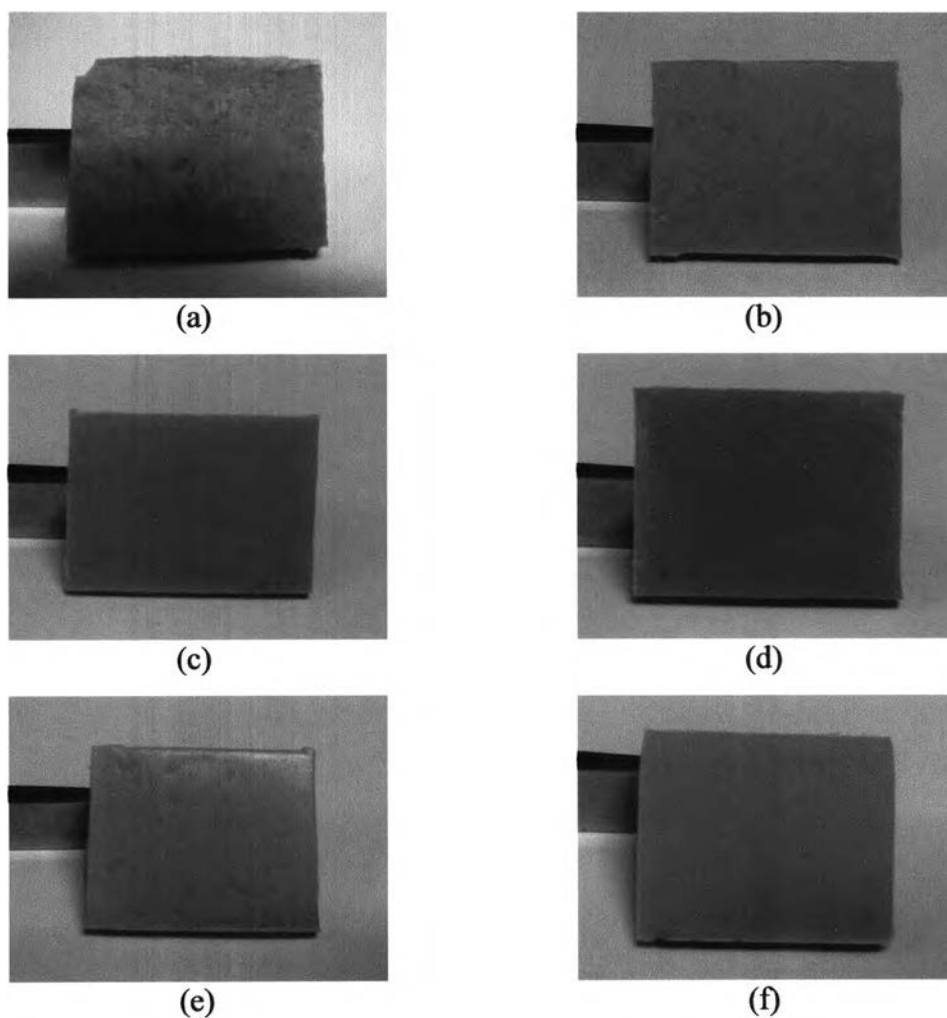


Figure 6.4 The appearance of fully vulcanized TPVs at various amount of ESO: (a) 0 phr, (b) 1 phr, (c) 2 phr, (d) 5 phr, (e) 7 phr, and (f) 10 phr.

6.4.3 Study of Thermal Properties of Thermoplastic Vulcanizate

The thermal properties of TPVs were characterized by varying the amount of ESO added to TPVs. The result is shown in Table 6.4 and DSC thermograms for all samples are shown in Figures 6.5-6.6.

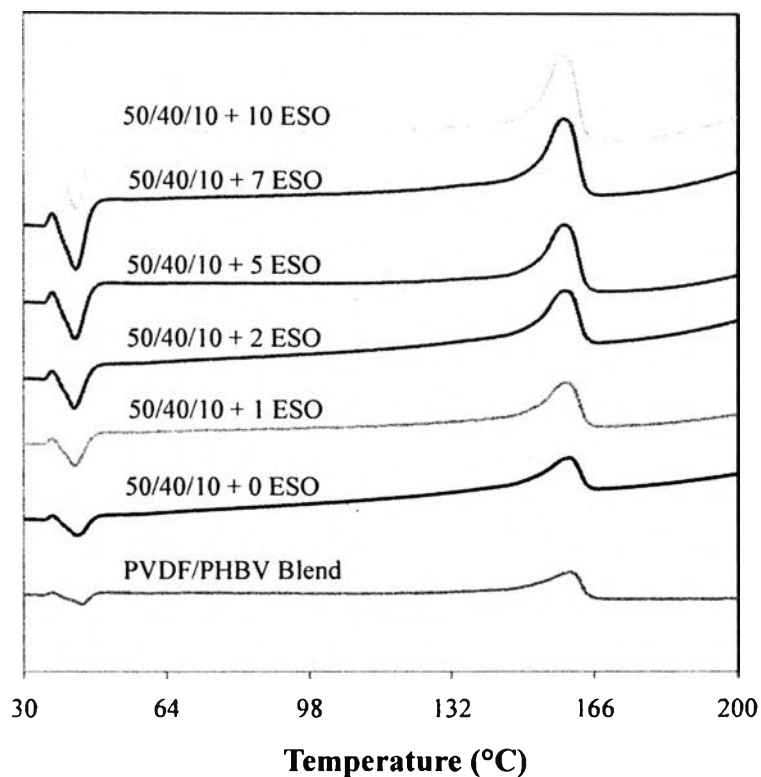


Figure 6.5 The heating curves of DSC thermogram from TPVs at various amount of ESO.

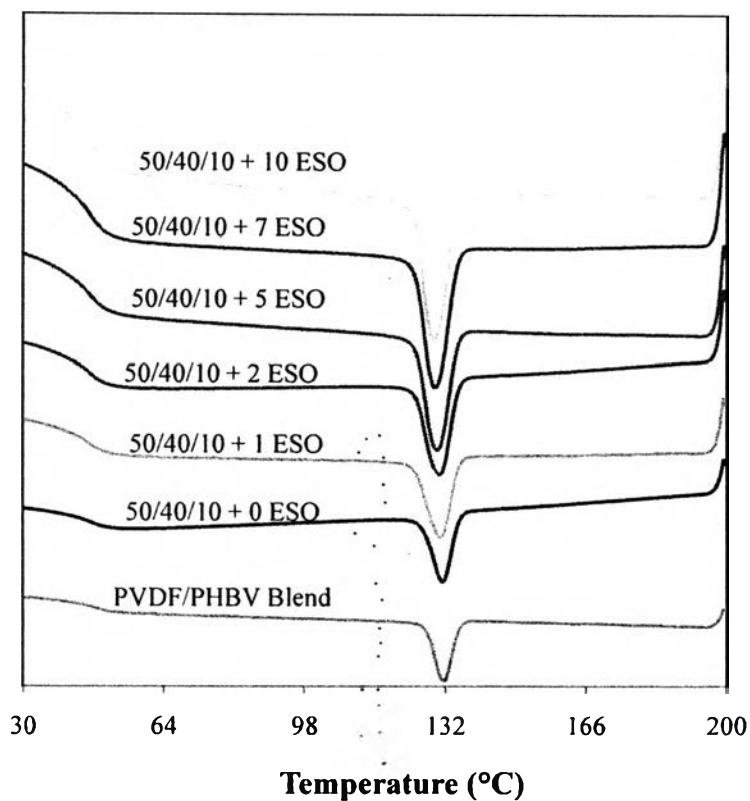


Figure 6.6 The cooling curves of DSC thermogram from TPVs at various amount of ESO.

Table 6.4 The thermal properties of TPVs at various amount of ESO

Materials	T_m (°C)	T_c (°C)	ΔH (J/g)	Crystallinity (%)
PVDF/PHBV Blend	158.4	133.5	57.9	55
50/40/10 with 0 ESO	158.7	129.0	16.9	32
50/40/10 with 1 ESO	158.5	128.6	15.2	29
50/40/10 with 2 ESO	158.2	129.1	15.4	30
50/40/10 with 5 ESO	158.7	129.6	15.5	30
50/40/10 with 7 ESO	158.2	128.3	15.7	30
50/40/10 with 10 ESO	157.5	128.1	14.3	27

From the results, the melting temperatures show the same value around 158 °C which from the melting point of the PVDF/PHBV blend. Until the

TPV with ESO content of 10 phr, the melting temperature further decreased that refers to the miscibility of the materials [9] and ESO can impart the compatibility of materials obviously over 10 phr. The melt crystallization temperatures are decreased when NR and ESO were added to TPV suggesting their effects to retard crystallization of PVDF and PHBV, especially at high content of ESO (10 phr). So ESO is miscible and can plasticize TPV [9-10]. The enthalpy of melting of TPV has large decrease when NR and ESO were added resulting in the decreasing of relative percent crystallinity of TPV with almost a half decrease. That means the vulcanized NR and PVDF obstructed the melt crystallization of TPV and make the percent crystallinity dropped and largely dropped at high ESO content of 10 phr, due to the unreact segmental chain in the structure of ESO disturbed the crystallization and become a plasticizer [9-20].

6.4.4 Mechanical Properties of Thermoplastic Vulcanizate

Figures 6.7-6.10 show that the tensile strength, percent elongation at break, Young's modulus, and hardness of TPV of various amount of ESO.

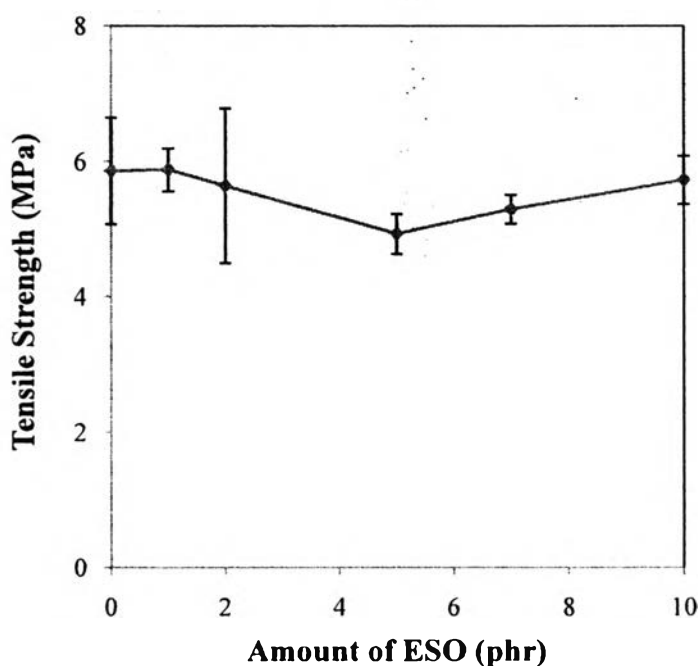


Figure 6.7 The tensile strength of TPVs at various amount of ESO.

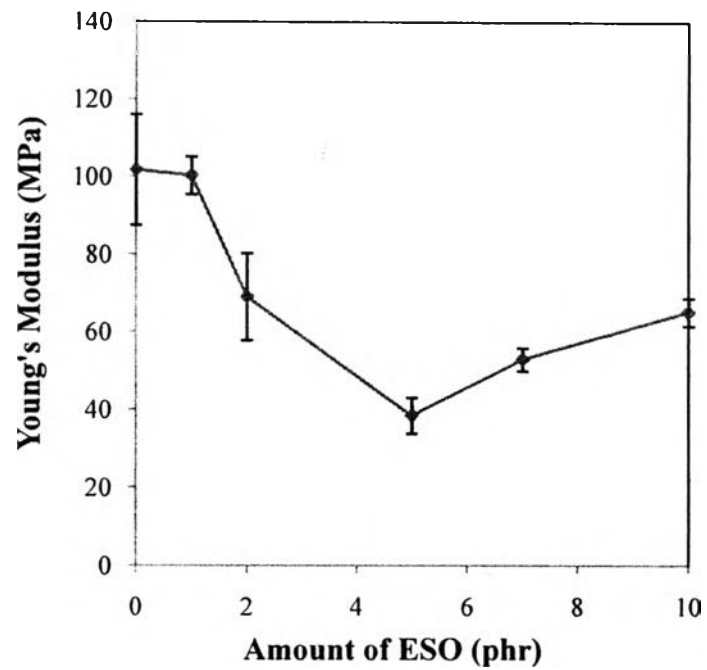


Figure 6.8 The Young's modulus of TPVs at various amount of ESO.

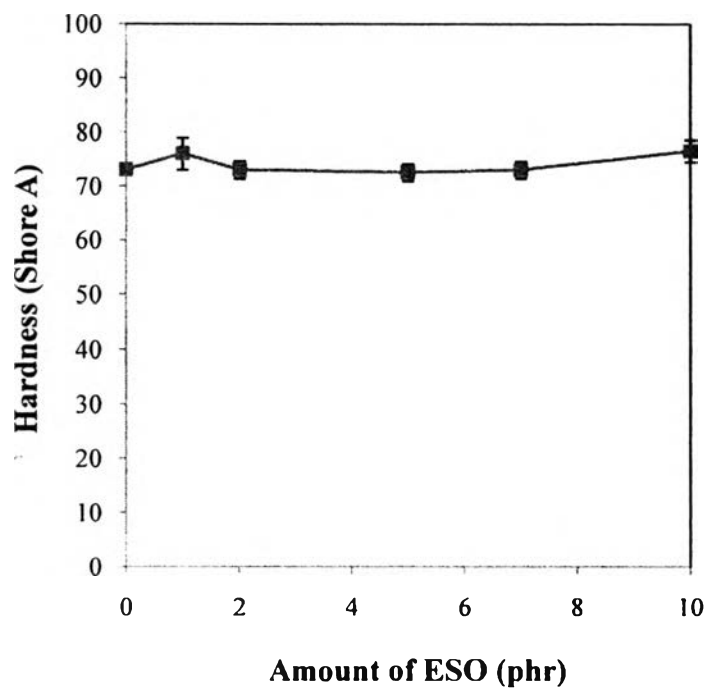


Figure 6.9 The hardness of TPVs at various amount of ESO.

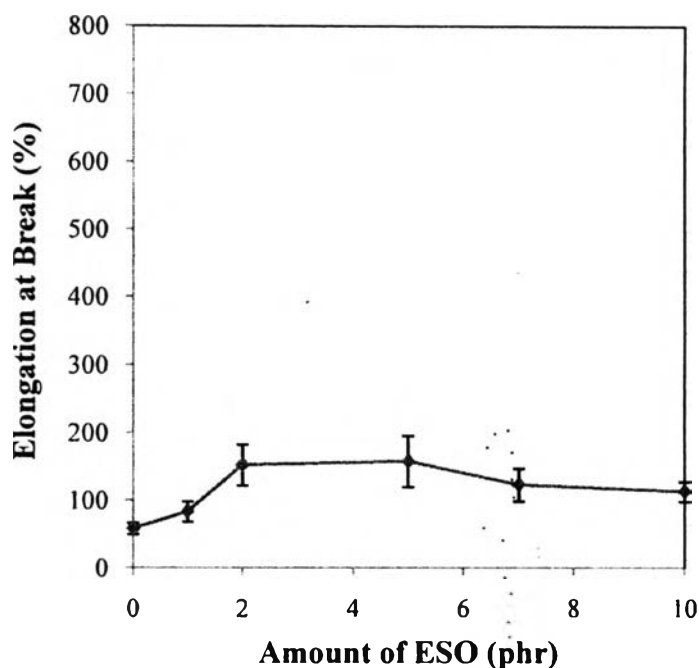


Figure 6.10 The percent elongation at break of TPVs at various amount of ESO.

At the small amount of ESO, 0-5 phr, the tensile strength, Young's modulus, and hardness were decreased with the increasing ESO content while percent elongation at break was increased. It means the toughness and flexibility of the TPV are improved, because the low reactivity of ESO which leads to retard the crosslinking reaction [11]. But, the temperature does not change in this study and the crosslink density was decreased attributed to the decreasing of maximum torque in cure characteristic. So, the ESO acts as a plasticizer which reduces the viscosity, tensile strength, Young's modulus, and hardness, also increases the elongation at break percentage [10-11, 21-23].

In contrast, when the level of ESO is higher, 5-10 phr, the tensile strength, Young's modulus, and hardness become increasing with increasing the higher amount of ESO and percent elongation at break goes down. This is because higher content provides more chance for ESO to behave like a compatibilizer and plasticizer at the same time. As the compatibilizer, ESO helps to improve the compatibility of all materials in TPV components which contribute to the increase in viscosity, tensile strength, Young's modulus, hardness, and the decrease in percent

elongation at break which correspond to the results of cure characteristic and thermal properties [10-11, 21-23] and the compatible ESO also gives the well dispersed of rubber phase in TPV sample as seen in Figure 6.11 with the size of rubber particle around 1-1.5 micron. The remained ESO acts as a plasticizer.

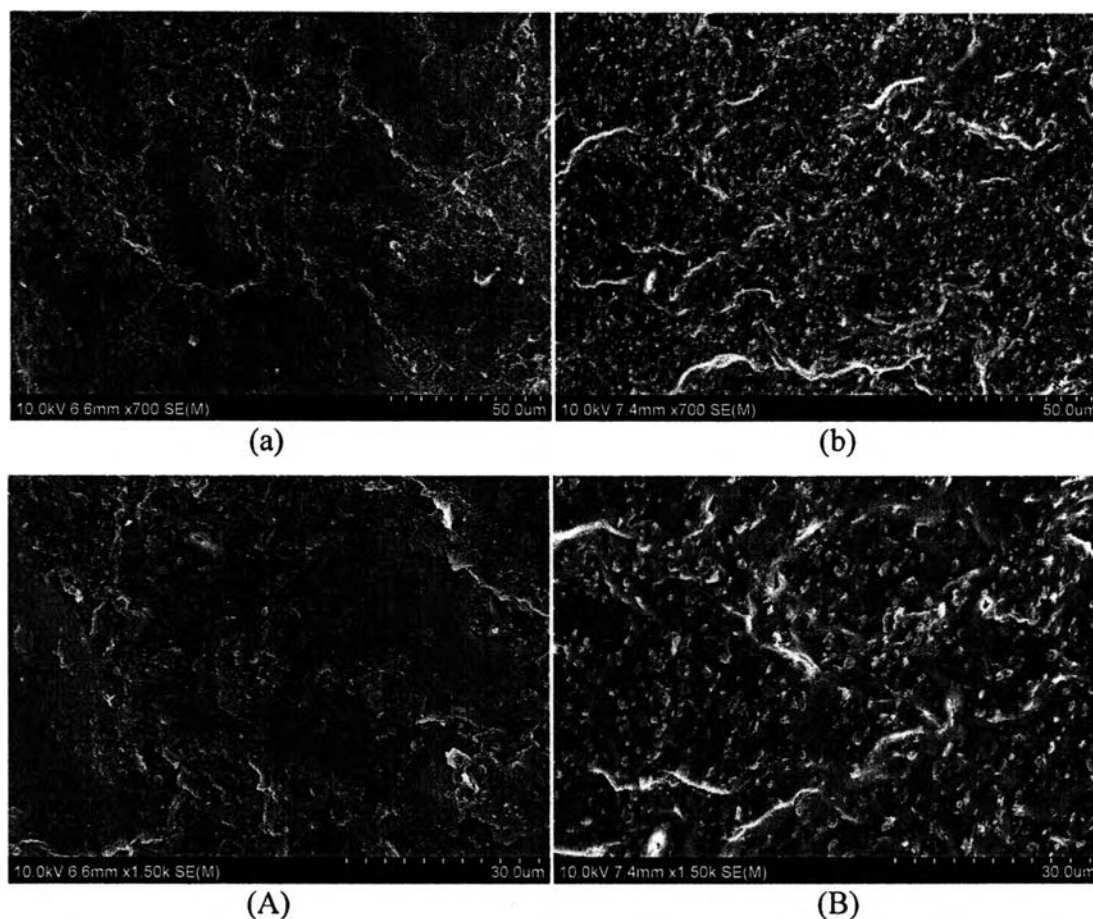


Figure 6.11 The morphology of TPVs at various amount of ESO: (a) ESO 0 phr, (b) ESO 10 phr with 700x magnification; (A) ESO 0 phr, (B) ESO 10 phr with 1,500x magnification.

5.4.3 Oil resistance of Thermoplastic Vulcanizate

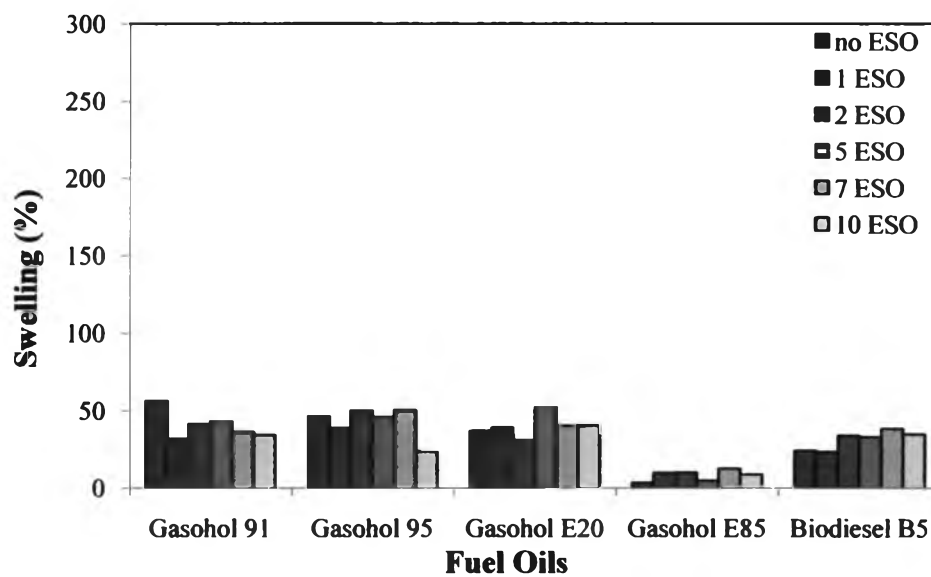


Figure 6.12 The percent swelling of TPVs at various amount of ESO at 25 °C in different oil types for 1 day.

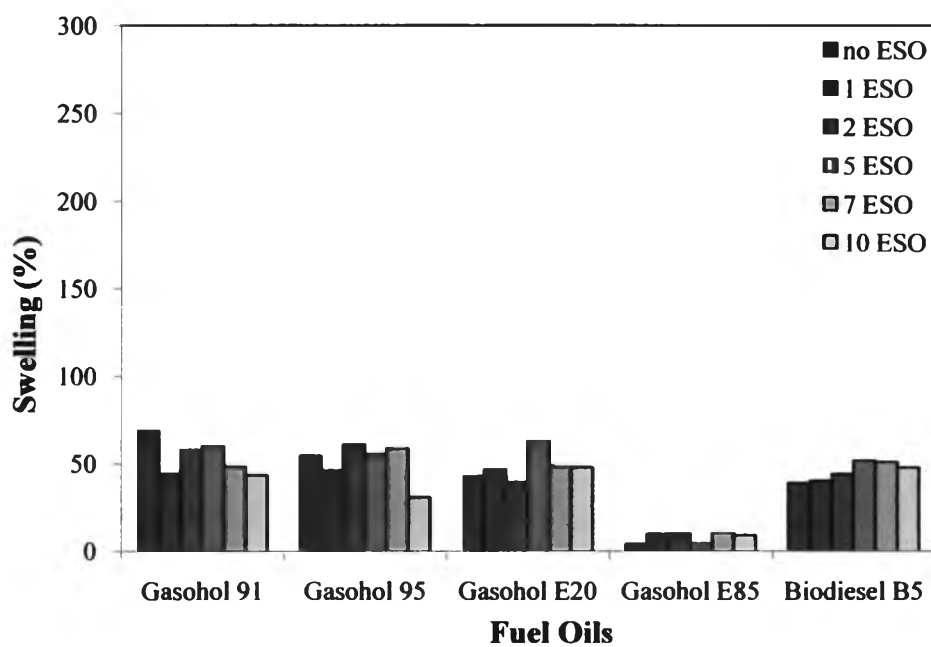


Figure 6.13 The percent swelling of TPVs at various amount of ESO at 25 °C in different oil types for 7 days.

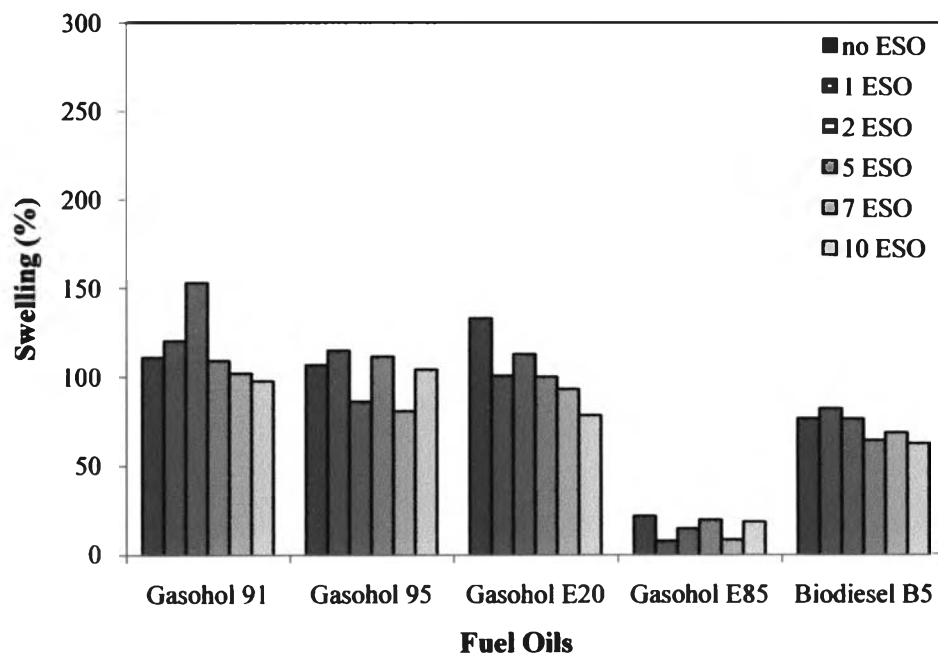


Figure 6.14 The percent swelling of TPVs at various amount of ESO at 100 °C in different oil types for 1 day.

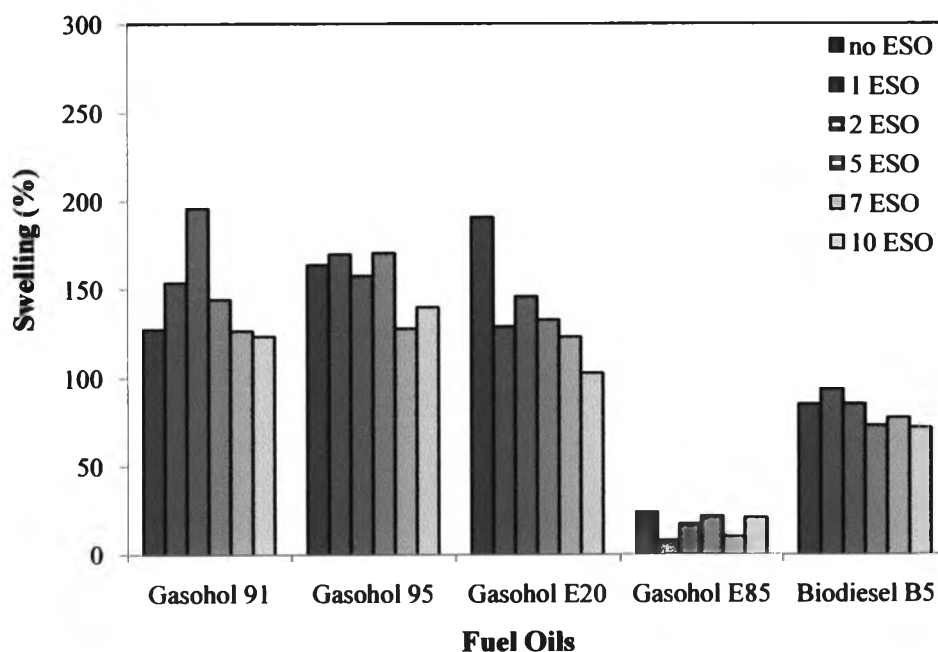


Figure 6.15 The percent swelling of TPVs at various amount of ESO at 100 °C in different oil types for 7 days.

The resistance to swelling of TPVs at various amount of ESO from different oil types was done at 25 °C and 100 °C for 7 days. The results shown in Figures 6.12-6.15 indicate that percent swelling of TPVs has the same trend for all amount of ESO. The percent swelling indicated the lowest value in gasohol E85 (85 % ethanol) and the highest value in gasohol 91 and 95 which have 10 % ethanol for all TPVs due to different amount of gasoline in different fuel oil which gasohol E85 has the lowest oil content of 15 % in 85 % ethanol exhibit the lowest degree of swelling. At the temperature of 25 °C, the swelling percentage after 7 days had the same value as 1 day around 50-55 % with the swelling index of 1.3 and 1.5, respectively. But, when the temperature was increased to 100 °C, the swelling percentage is increased to 125-150 % with the swelling index of 1.5-2.0 for 1 day. And also increase to 150-200 % swelling or 2.0-2.5 swelling index for 7 days. This means the increasing of heat and time leads to increase swelling of TPV [24] which 100 °C indicates 3 times higher of percent swelling than 25 °C.

It can be note that the degree of swelling of TPV is near the commercial rubber parts, vulcanized FKM [8] and the higher ESO content gives the lower degree of swelling because the ESO imparts compatibility of materials even in PHBV with the dispersion factor of solubility parameter are almost the same [10-11, 21-23] and provides the well dispersion of rubber phase which small rubber particles of 1-1.5 micron disperse in the thermoplastic phase (PVDF/PHBV blend). This lets the rubber particles not contacted to fuel oils directly. The incorporated of PHBV which does not dissolve in ethanol, PVDF which is the well known for chemical resistance, and the rubber particle surrounded by both polymers, improve the swelling property significantly.

6.5 Conclusion

PHBV can be miscible with PVDF. The incorporation of vulcanized NR and PVDF largely decreases the melt crystallization temperature and the relative percent crystallinity. The increasing ESO content gives the miscibility of materials by decreasing the melting temperature of PVDF and the relative crystallinity obviously at 10 phr.

The small amount of ESO behaves like a plasticizer which reduces the viscosity and mechanical properties; i.e., the processability and flexibility become better. But, at the higher content, ESO behaved like a compatibilizer which increases the mechanical properties and improves swelling resistance and morphology.

6.6 Acknowledgements

This work is funded by National Research Council of Thailand (NRCT); Polymer Processing and Polymer Nanomaterials Research Unit, the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand; and, the Petroleum and Petrochemical College.

The author would like to acknowledge Mr. Chatchai Simasatitkul from Banpan Research Laboratory Co., Ltd.; Mr. Amorn Ajinsamajan and Mr. Chayawat Pongkalab from Inoue Rubber (Thailand) Pcl. for the materials and all support of this project.

6.7 References

1. Scharnowski, D. (2005). Characterisation of the influence of cooling rates on structure and properties of dynamic vulcanizates. Dissertation: Halle (Saale), Martin-Luther-Universität, Halle-Wittenberg, Germany. 1-134.
2. Holden, G., Kricheldorf, H.R., and Quirk, R.P. (Eds.). (2004). Thermoplastic Elastomers. Munich: Hanser Verlag, 143-146.
3. Abdou-Sabet, S., Puydak, R.C., and Rader, C.P. (1996). Dynamically vulcanized thermoplastic elastomers. *Rubber Chemistry and Technology*, 69, 476-494.
4. Jürdens, K. (2002). The pan-European strategic market study TPE 2000. TPE in der Prozesskette, VDI-Gesellschaft Kunststofftechnik, VDI-Verlag, Düsseldorf.
5. Javadi, A., Srithep, Y., Pilla, S., Lee, J., Gong, S., and Turng, L.S. (2010). Processing and characterization of solid and microcellular

- PHBV/coir fiber composites. Materials Science and Engineering: C, 30(5), 749–757.
6. Hietala, S., Holmberg, S., Karjalainen, M., Näsman, J., Paronen, M., Serimaa, R., Sundholm, F., and Vahvaselkä, S. (1997). Structural investigation of radiation grafted and sulfonated poly(vinylidene fluoride), PVDF, membranes. Journal of Materials Chemistry, 7(5), 721–726.
 7. Marega, C. and Marigo, A. (2003). Influence of annealing and chain defects on the melting behaviour of poly(vinylidene fluoride). European Polymer Journal, 39(8), 1713-1720.
 8. Magaraphan, R., and Yamoun, C. (2008). Dynamic vulcanization of fluoroelastomer and natural rubber. The 1st Thailand Natural Rubber Conference, 1, 152-163.
 9. Qiu, Z., Fujinami, S., Komura, M., Nakajima, K., Ikehara, T., and Nishi, T. (2004). Spherulitic morphology and growth of poly(vinylidene fluoride)/poly(3-hydroxybutyrate-co-hydroxyvalerate) blends by optical microscopy. Polymer, 45(13), 4355–4360.
 10. Ali, F., Chang, Y.W., Kang, S.C., and Yoon, J.Y. (2009). Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends. Polymer Bulletin, 62(1), 91–98.
 11. Park, S.J., Jin, F.L., and Lee, J.R. (2004). Thermal and mechanical properties of tetrafunctional epoxy resin toughened with epoxidized soybean oil. Materials Science and Engineering A, 374(1-2), 109-114.
 12. Akiba, M., and Hashim, A.S. (1997). Vulcanization and crosslinking in elastomers. Progress in Polymer Science, 22(3), 475-521.
 13. Hagen, R., Salmén, L., and Stenberg, B. (1996). Effects of the type of crosslink on viscoelastic properties of natural rubber. Journal of Polymer Science Part B: Polymer Physics, 34(12), 1997-2006.
 14. Unnikirishnan G., and Thomas, S. (1997). Sorption and diffusion of aliphatic hydrocarbons into crosslinked natural rubber. Journal of Polymer Science Part B: Polymer Physics, 35(5), 725-734.

15. Li, Y., Oono, Y., Kadowaki, Y., Inoue, T., Nakayama, K., and Shimizu, H. (2006). A novel thermoplastic elastomer by reaction-induced phase decomposition from a miscible polymer blend. Macromolecules, 39(12), 4195-4201.
16. Taguet, A., Ameduri, B., and Boutevin, B. (2005). Crosslinking of vinylidene fluoride-containing fluoropolymers. Advances in Polymer Science, 184, 127–211.
17. Nakason, C., Nuansomsri, K., Kaesaman, A., and Kiatkamjornwong, S. (2006). Dynamic vulcanization of natural rubber/high-density polyethylene blends: Effect of compatibilization, blend ratio and curing system. Polymer Testing, 25(6), 782–796.
18. Nakason, C., Wannavilai, P., and Kaesaman A. (2006). Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. Polymer Testing, 25(1), 34–41.
19. Nakason, C., Worlee, A., and Salaeh, S. (2008). Effect of vulcanization systems on properties and recyclability of dynamically cured epoxidized natural rubber/ polypropylene blends. Polymer Testing, 27(7), 858–869.
20. Loan, L.D. (1972). Peroxide crosslinking reactions of polymers. Pure and Applied Chemistry, 30(1-2), 173-180.
21. Choi, J.S., and Park, W.H. (2004). Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate). Polymer Testing, 23(4), 455–460.
22. Ismail, H., and Hairunezam, H.M. (2001). The effect of a compatibilizer on curing characteristics, mechanical properties and oil resistance of styrene butadiene rubber/epoxidized natural rubber blends. European Polymer Journal, 37(1), 39-44.
23. Choi, J.S., and Park, W.H. (2003). Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) plasticized by biodegradable soybean oils. Macromolecular Symposia, 197(1), 65-76.

24. Ismail, H., and Suzaimah, S. (2000). Styrene butadiene rubber/epoxidized natural rubber blends: dynamic properties, curing characteristics and swelling studies. Polymer Testing, 19(8), 879–888.