



CHAPTER IV

PRELIMINARY STUDY THE EFFECT OF VULCANIZATION SYSTEM AND QUANTITY OF VULCANIZING AGENT ON MECHANICAL AND SWELLING PROPERTIES OF NATURAL RUBBER

4.1 Abstract

The effect of vulcanization system and the quantity of vulcanizing agent on mechanical and swelling properties of natural rubber is a preliminary study for optimizing the suitable vulcanization system and suitable amount of vulcanizing agent for making a thermoplastic vulcanizate (TPV) that used as rubber parts for automobile used in fuel system. The vulcanization systems, EV; DCP; and DBPH, were used in this study and the amount of vulcanizing agent, DBPH, were also observed. The compounded natural rubber of various vulcanization systems were prepared in an internal mixer at room temperature and the quantity of peroxide curing agent, DBPH, was also varied. The cure characteristic and parameters for vulcanizing compounded NR were studied. The mechanical properties, tensile strength and % elongation at break, were determined according to ASTM D412-06a or ISO 37 (Type 1). The swelling property was also observed at 25 and 100 °C for 24 hours according to ASTM D471-06 or ISO 2285 (Method A). In this study, biodiesel oil and gasohols 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.

4.2 Introduction

Thermoplastic vulcanizate (TPV) is a physical mix of two or more thermoplastic with a vulcanized or crosslink rubber. One important thing in making TPV is the vulcanization rubber phase. Good properties of vulcanized rubber phase contribute to the good properties of TPV [1-3]. To get the best properties, the vulcanization of rubber is studied. Natural rubber (NR) is used as a rubber phase for TPV in this study which is abundant in Thailand. It was mixed with chemicals into a compounded NR at various vulcanization systems and study the cure characteristic

to obtain the suitable condition to vulcanize compounded NR into a vulcanized NR. Then, the mechanical and oil swelling properties were determined.

4.3 Experimental

4.3.1 Materials

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.

4.3.2 Compounding of Natural Rubber

The compounded NR was derived from compounding NR (STR 5L grade) with chemicals for any vulcanization system in an internal mixer (Brabender[®] 815602 type, with N50 mixer, Germany). In efficient vulcanization system (EV system), the Acc:S ratio was 12, steric acid and zinc oxide (ZnO) were used as activators, N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS) was used as an accelerator, and sulfur was used as a vulcanizing agent. For the system involving peroxide, dicumyl peroxide (DCP) and 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (Luperox[®] 101 or DBPH) were used as peroxide vulcanizing agents. The formula of DBPH system was adopted from Magaraphan *et al.*, 2008 [4]. Calcium hydroxide (Ca(OH)₂) was used as activator. Triallyl Isocyanurate (TAIC[®]) was used as a coagent. The quantity of DBPH was also varied as 3, 5, and 7 phr. The mixing was performed at room temperature with a rotor speed of 80 rpm according to formulae and mixing schedule are given in Table 4.1.

Table 4.1 Compounding formulae and mixing schedule

Ingredients	EV system		DCP system		DBPH system [4]	
	Quantity (phr ^a)	Mixing time (min)	Quantity (phr ^a)	Mixing time (min)	Quantity (phr ^a)	Mixing time (min)
NR	100	5	100	5	100	4
Steric acid	1	1	-	-	0.25	1
ZnO	5	1	-	-	-	-
CBS	6	1	-	-	-	-
Sulfur	0.5	4	-	-	-	-
DCP	-	-	3	7	-	-
Ca(OH) ₂	-	-	-	-	3	1
TAIC	-	-	-	-	3	2
DBPH	-	-	-	-	3 ^b	4

^aphr = part per hundred part of rubber.

^bThe amount of DBPH was varied by 3, 5, and 7 phr in studying mechanical properties.

After mixing, the blend 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). Then, the sheet compounded NR was further compressed in a compression mold (Wabash MPI, V50H-18-CX model, USA) at the temperature of 150 °C for sulfur system and 180 °C for peroxide system with using 20 ton force of pressure for 10 min. The vulcanized NRs of various vulcanization systems were obtained.

4.3.3 Study of Mechanical Properties

The mechanical properties of vulcanized NRs in this study were the tensile strength, % elongation at break, and Young's modulus which 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.

4.3.4 Study of Swelling Properties

The Swelling test of vulcanized NR was determined for all vulcanization systems. The DBPH system was used at DBPH content of 3 phr. It was done at temperature of 25 °C and 100 °C for 24 hours 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 4.1:

$$\% \text{ Swelling} = \frac{(W_s - W_o)}{W_o} \times 100 \quad , \quad (4.1)$$

and the swelling index was also determined from equation 4.2:

$$\text{Swelling Index} = \frac{W_s}{W_o} \quad , \quad (4.2)$$

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

4.4 Results and Discussion

4.4.1 Preparation of Vulcanized Natural Rubber

The torque of compound NR in various vulcanization systems was monitored while compounding in the internal mixer. The high torque indicates the high viscosity of natural rubber and decreasing when it had masticated into shorter molecular chains. The adding of chemicals had oscillated the torque curve; but, the good mixing can be obtained from the plateau torque. The torque curve and the appearance of compounded NR from various vulcanization systems are shown in Figures 4.1-4.3.

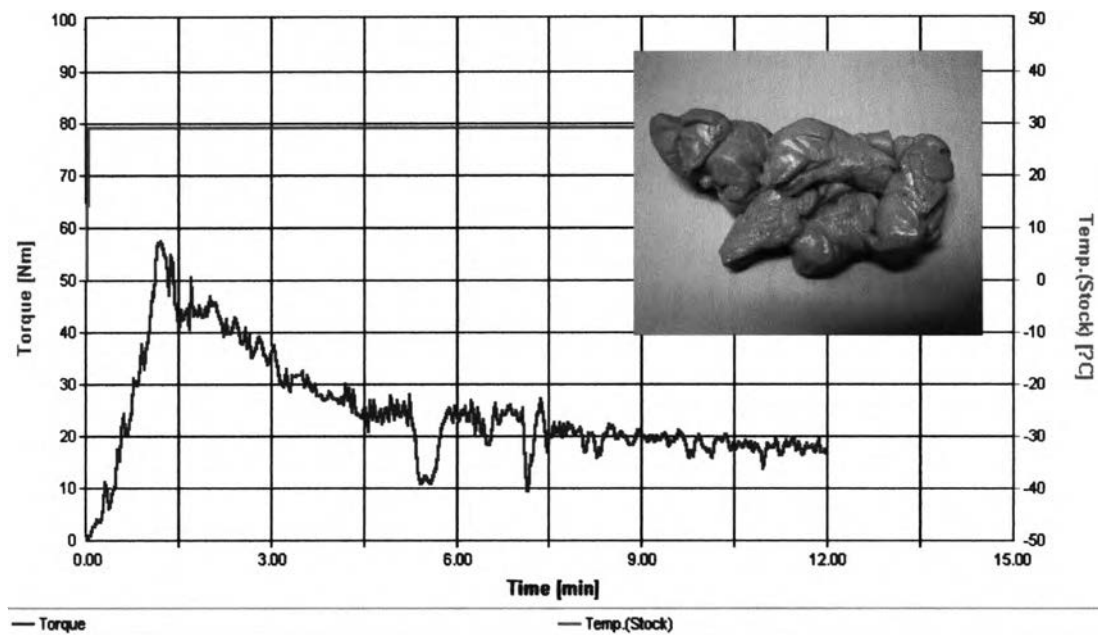


Figure 4.1 The torque curve and the appearance of compounded NR after compounding in EV system at room temperature.

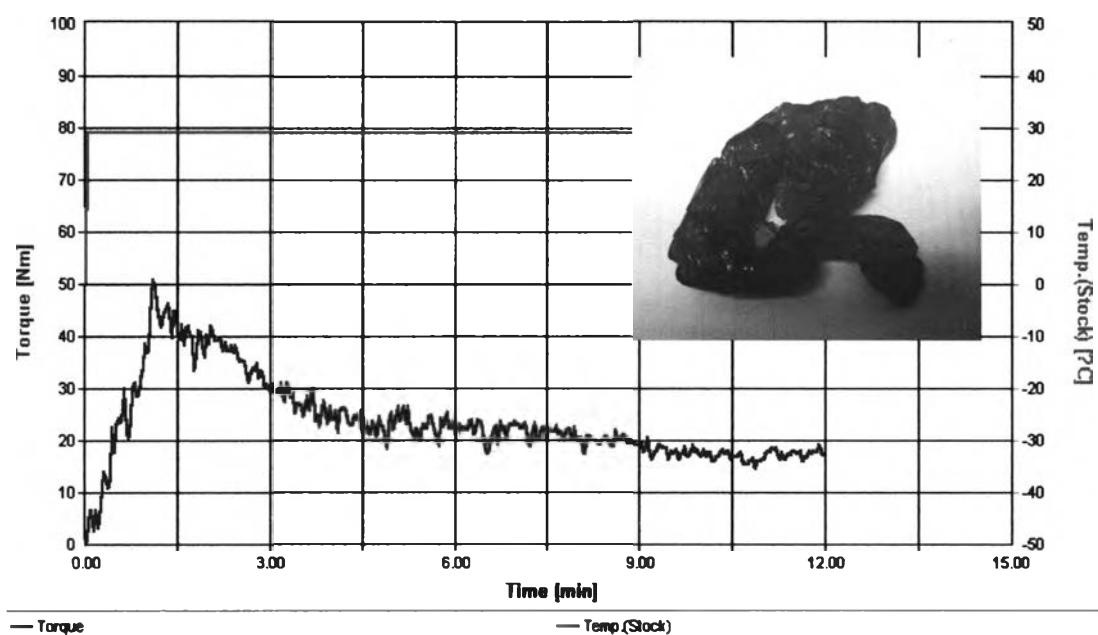


Figure 4.2 The torque curve and the appearance of compounded NR after compounding in DCP system at room temperature.

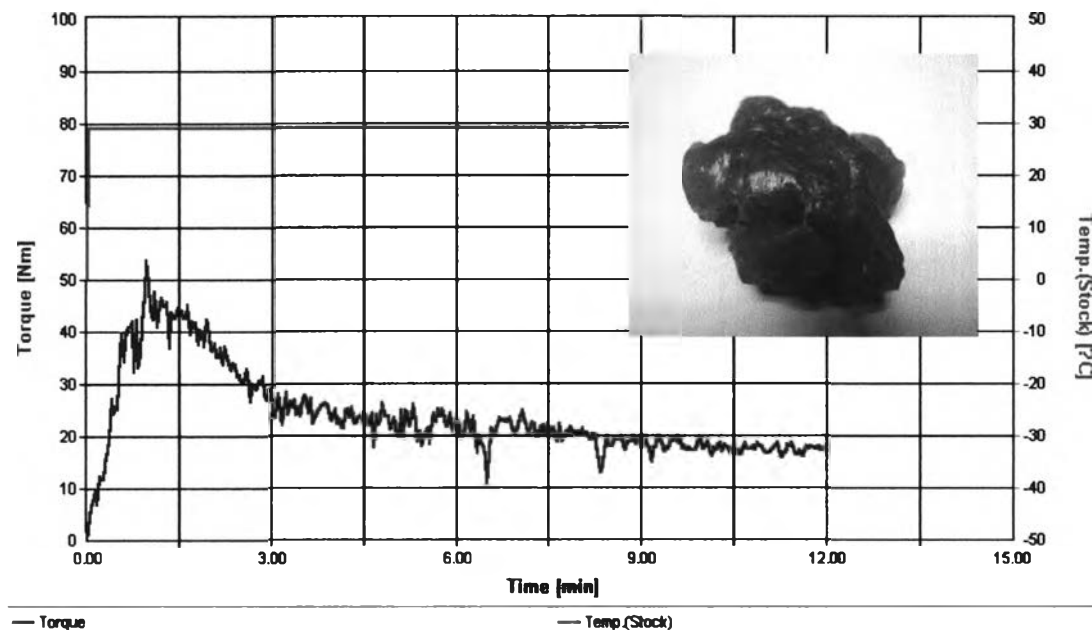


Figure 4.3 The torque curve and the appearance of compounded NR after compounding in DBPH system at room temperature.

4.4.2 Characterization of Cure Characteristic

The compounded NRs at various vulcanization systems without any cure or crosslinking were characterized for cure characteristic to obtain parameters, vulcanization temperature and time, for vulcanizing the compounded NR. Figures 4.4-4.6 and Tables 4.2-4.4 indicate cure characteristic curves (upper) and vulcanization parameters (lower) in different temperatures of the compounded NR vulcanized by EV, DCP, and DBPH system. It is found that they show plateau curves after fully crosslink for all systems revealing good thermal stability and the higher cure temperature gives the shorter vulcanization time. At the same temperature, the different vulcanization systems give the different vulcanization times because of the half life time of vulcanizing agents are different.

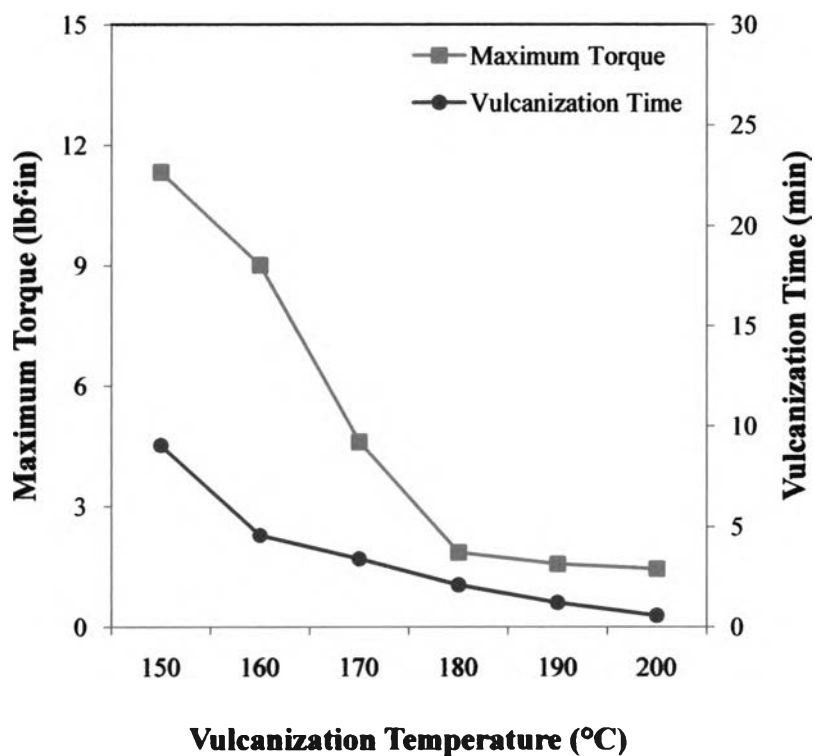
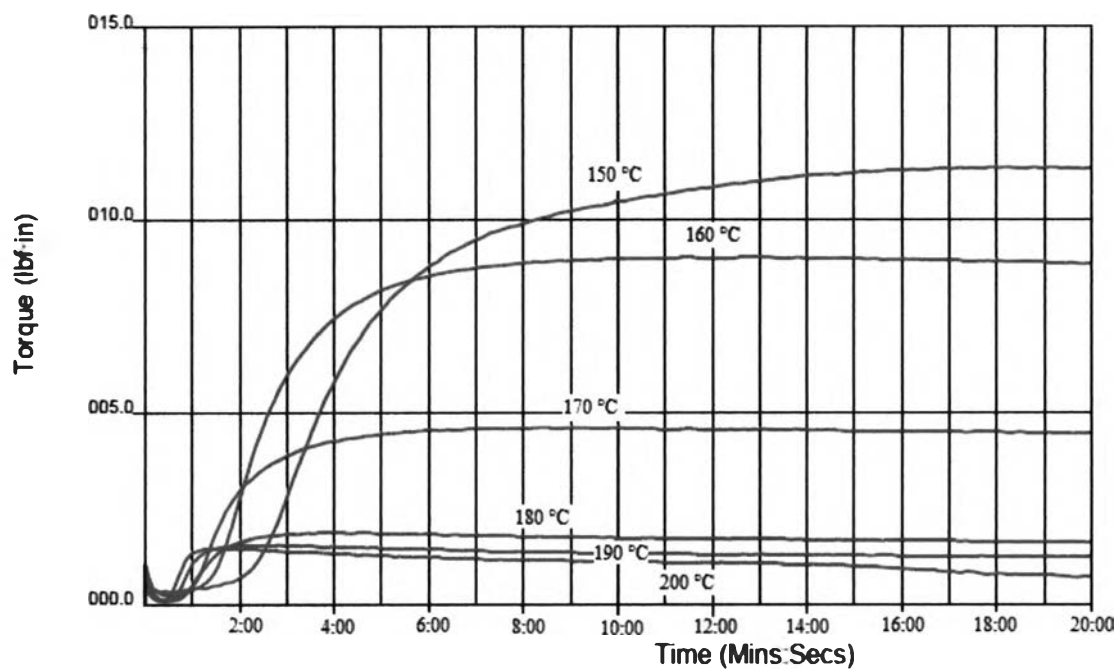


Figure 4.4 The cure characteristic and parameter curves for vulcanizing compounded NR in EV system.

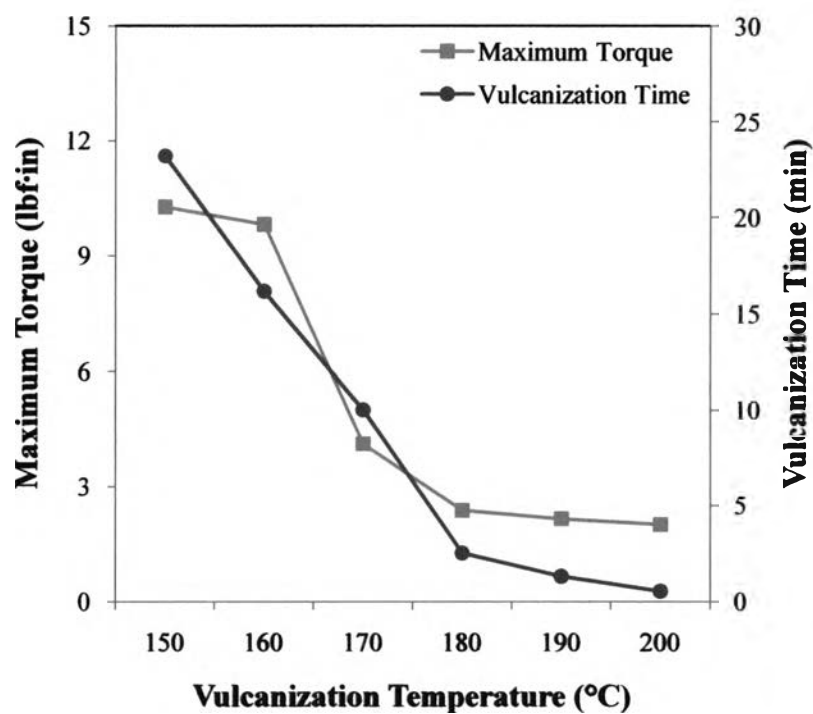
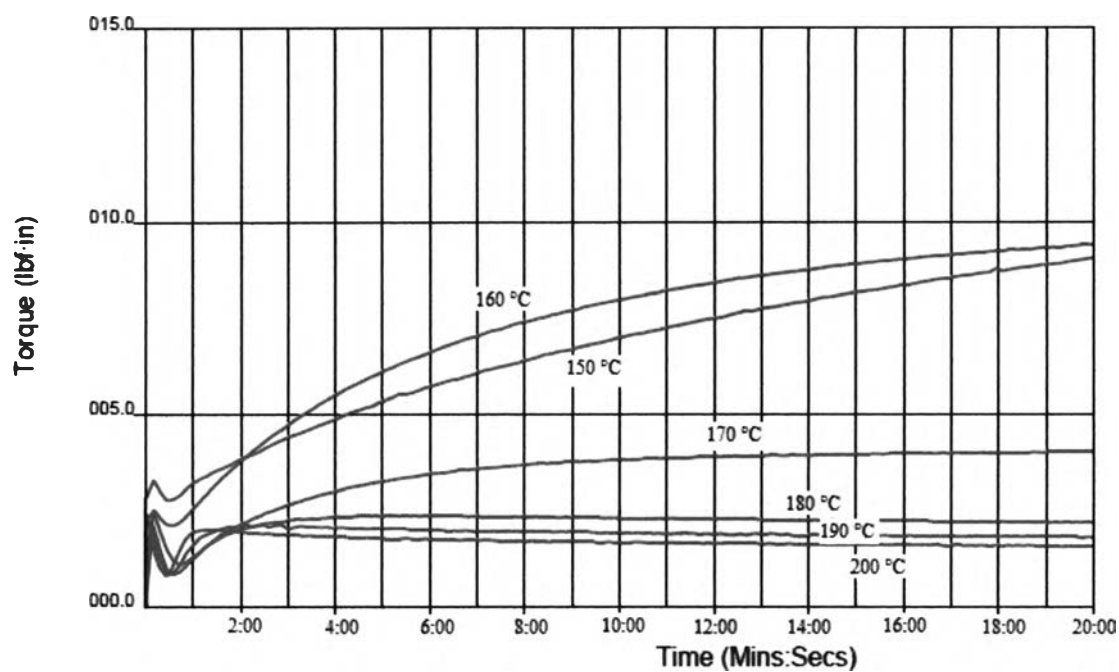


Figure 4.5 The cure characteristic and parameter curves for vulcanizing compounded NR in DCP system.

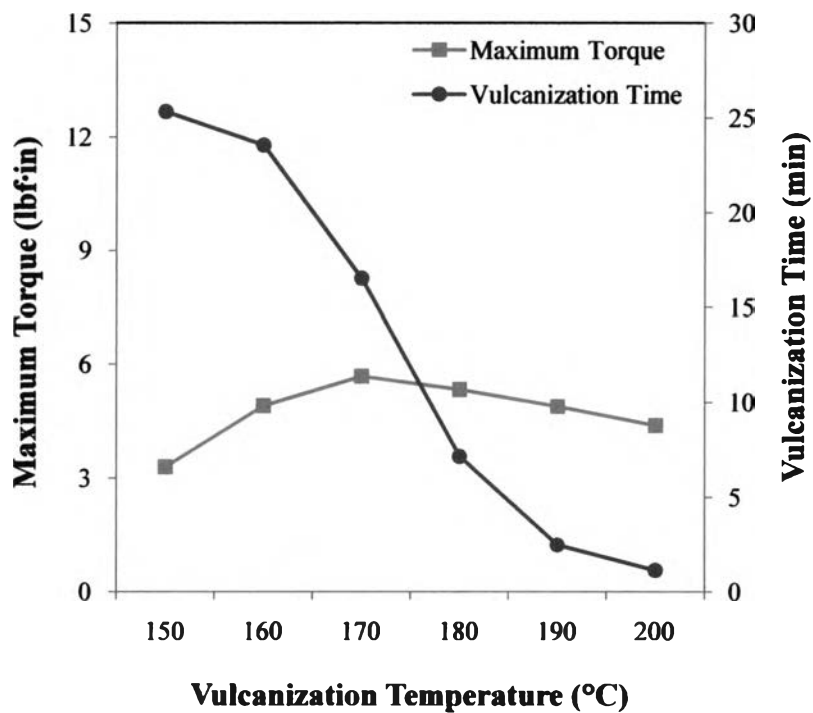
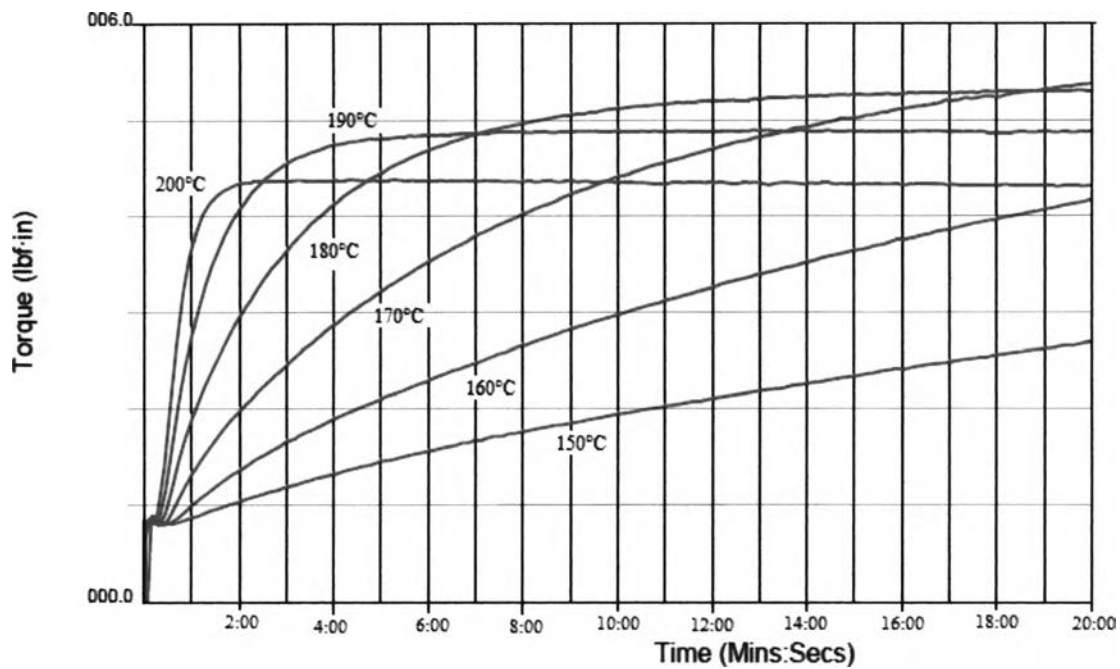


Figure 4.6 The cure characteristic and parameter curves for vulcanizing compounded NR in DBPH system.

For the temperature range of 150-170 °C, the EV and DCP systems indicate the higher maximum torque than the DBPH system; but, it indicates the opposite value at the temperature above 170 °C. The EV system has the highest maximum torque and DCP system is followed. The maximum torque of both systems is decreased when the temperature is increased from 150 to 170 °C, but is increased in the DBPH system. This is because the different crosslink temperatures affect to crosslink efficiency [5]. The temperature of 150 °C is near the crosslink temperature of sulfur, while 160 °C near DCP, and 170 °C near DBPH [6,7].

Considering the DBPH system, the maximum torques at 160 °C, 170 °C, and 180 °C are almost the same; but vulcanization times are largely different. Hence, the temperature of 180 °C is more practical for mass production in industry. The appearance of vulcanized NR is shown in Figure 4.7. The peroxide systems gave the clear sample compared with EV system [1] due to the absence of ZnO and the increasing of vulcanizing agent results in clearer specimens as shown in DBPH system and more brittleness than EV system.

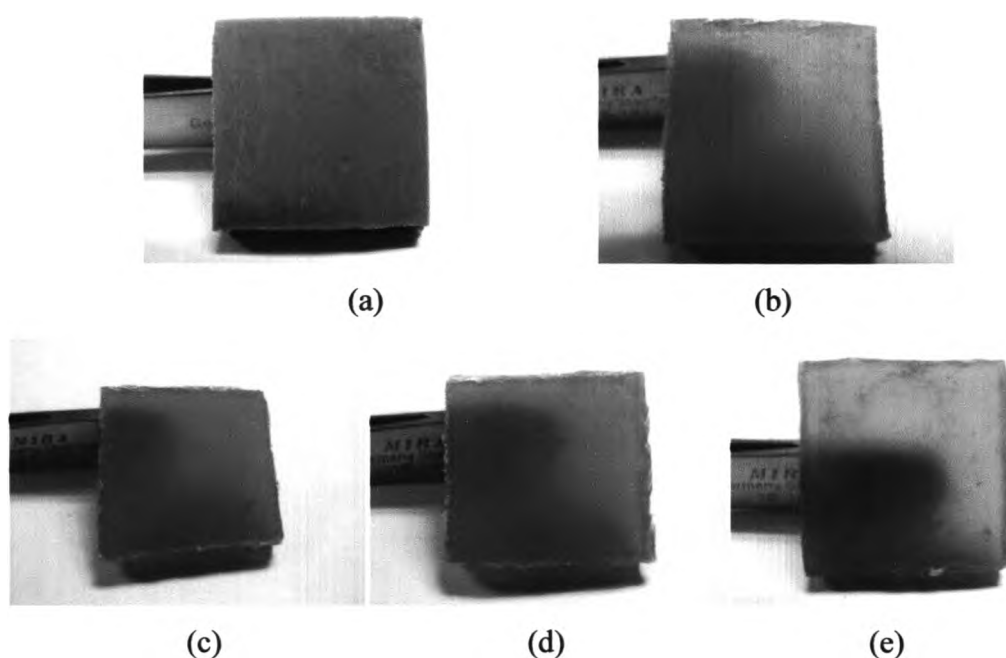


Figure 4.7 The appearance of vulcanized NR: (a) EV system, (b) DCP, (c) DBPH 3 phr, (d) DBPH 5 phr, and (e) DBPH 7 phr.

4.4.3 Mechanical Properties of Vulcanized NR

The Mechanical properties of vulcanized NR were determined including tensile strength, percent elongation at break, and Young's modulus. The results for all vulcanization systems are shown in Figures 4.8-4.10.

The tensile strength and percent elongation at break of vulcanized NR with peroxide cured systems are lower than EV system [8-10]. This can attribute to the influence of chemical bond formed. The flexible of C-S and S-S bonds are formed in the EV system while the peroxide systems can form only stiffer C-C bond [8-12]. Respond to the percent elongation at break, peroxide systems indicate the lower value because the stability of C-C bonds which is hardly to deform and need more force to pull it apart with a small extension. This resulting in the brittleness and higher Young's modulus occurred in peroxide system compared to EV system.

The DCP system indicates the poor mechanical properties than DBPH system due to the temperature in compression DCP is not match with typical crosslinking temperature of DCP, so this results in the small crosslink efficiency and low mechanical properties [5]. The different peroxides also have the different half life time at same temperature. So, it is reasonable that different crosslink density is achieved. Consider in DBPH system, the increasing amount of DBPH shows the increasing mechanical properties because the more crosslinking reaction is occurred [5, 13].

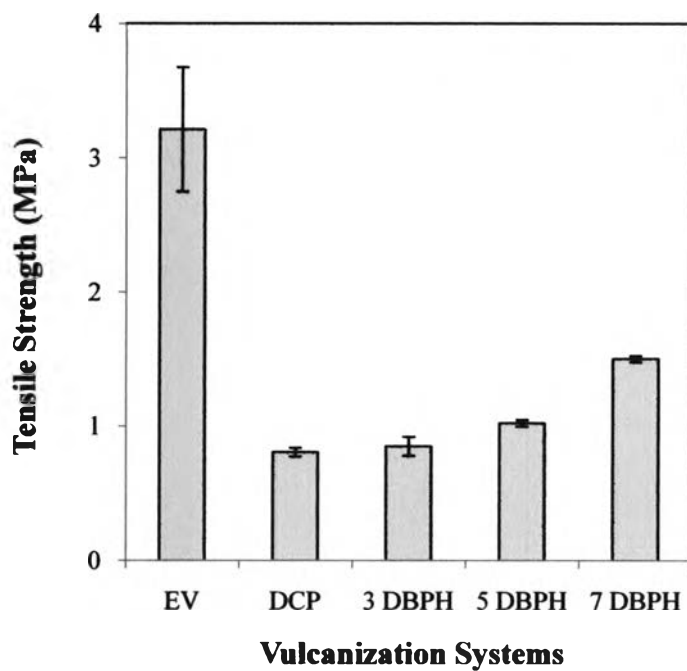


Figure 4.8 The tensile strength of vulcanized NR at various vulcanization systems.

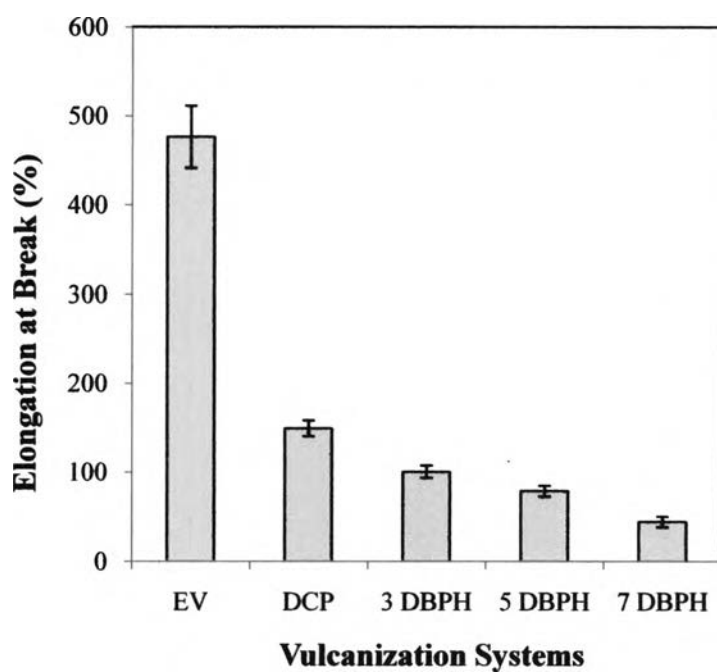


Figure 4.9 The percent elongation at break of vulcanized NR at various vulcanization systems.

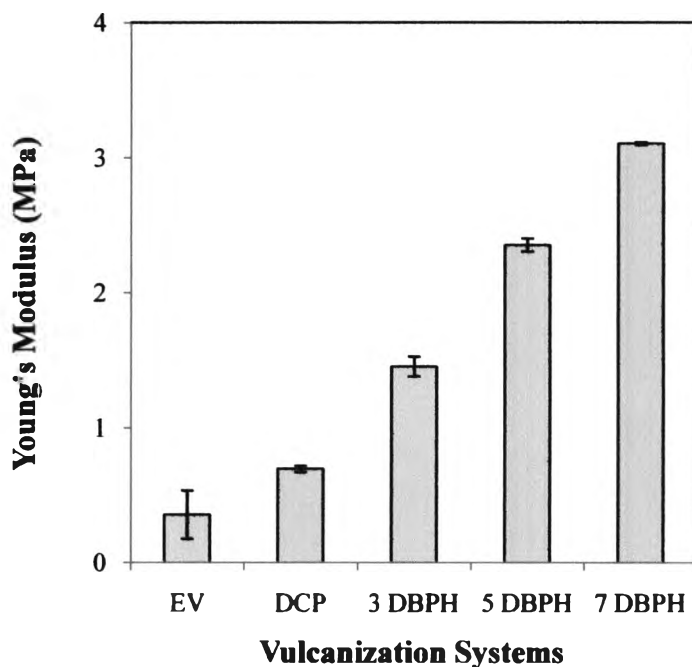


Figure 4.10 The Young's modulus of vulcanized NR at various vulcanization systems.

4.4.4 Oil Swelling of Vulcanized NR

The study of oil swelling was done on vulcanized NR with EV, DCP, DBPH 3 phr systems. The swelling percentage is calculated from the weight increment of immersed sample which is shown in Figure 4.11 for the testing temperature of 25 °C and Figure 4.12 for the temperature of 100 °C.

The swelling index was also determined to evaluate how many times the weight of immersed sample increases from the initial weight. The swelling index of sample tested at 25 °C and 100 °C are shown in Figures 4.13-4.14, respectively.

The gasohol E85 gives the lowest percent swelling because the very high ethanol content of 85% is much more than the content of gasoline which is 15%. The ability to contact oil of rubber is relatively low compared to each other; hence, the degree of swelling in Gasohol E85 is very low indicated in the lowest value at 25 and 100 °C which are around 10-13 %. The swelling index is equal to 1 that means the sample weight before and after immersion are the same for all vulcanization systems.

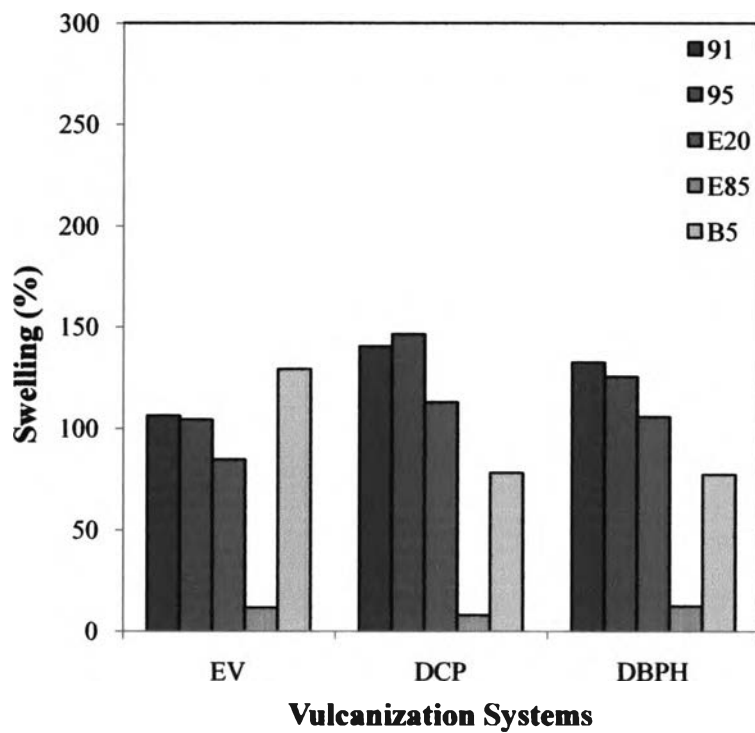


Figure 4.11 The percent swelling of vulcanized NR at 25 °C in different oil types.

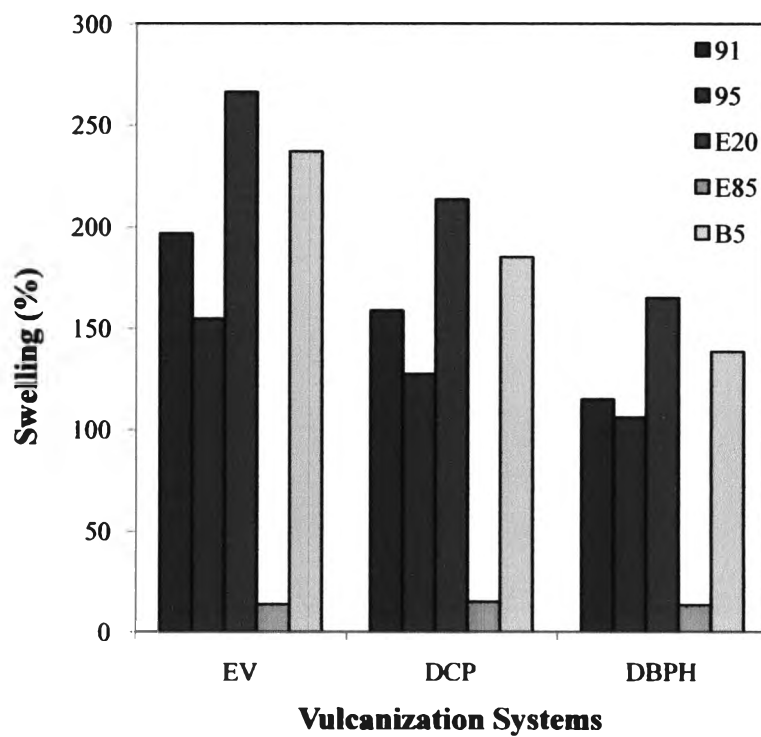


Figure 4.12 The percent swelling of vulcanized NR at 100 °C in different oil types.

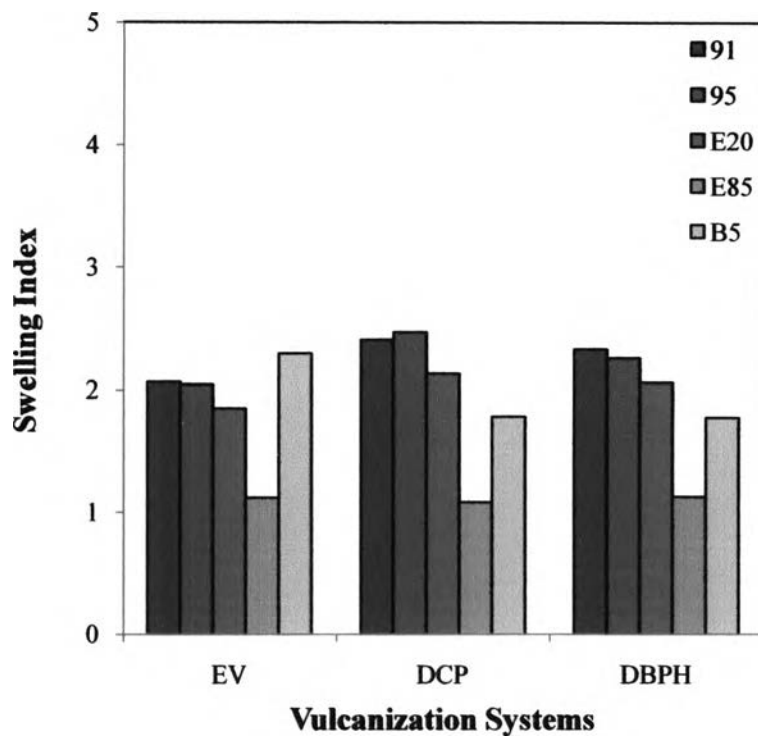


Figure 4.13 The swelling index of vulcanized NR at 25 °C in different oil types.

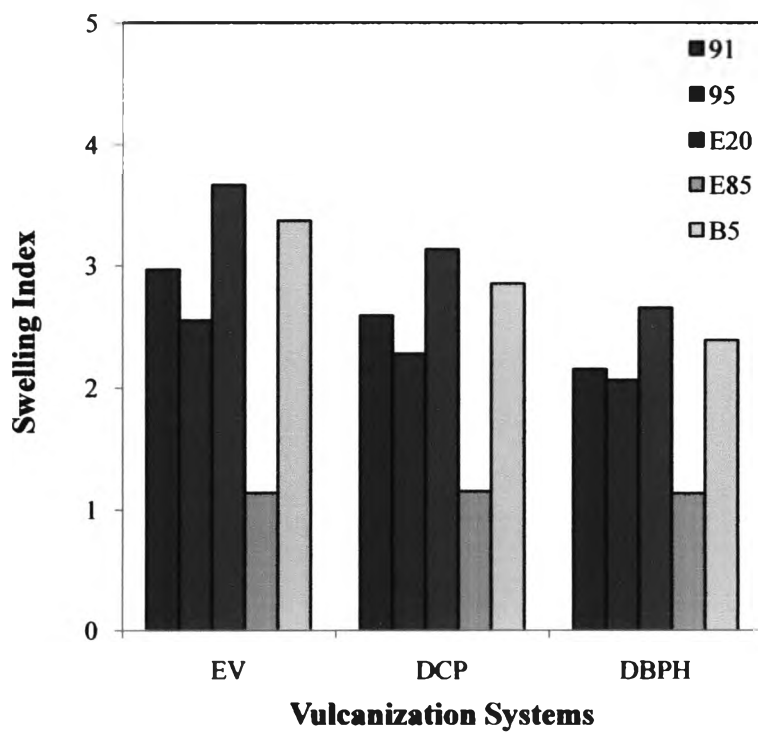


Figure 4.14 The percent swelling of vulcanized NR at 100 °C in different oil types.

The temperature of 25 °C give no obviously difference in degree of swelling. The percent swelling is around 100-150 % and the swelling index around 2-2.5 for all vulcanization systems that mean the type of vulcanization system has no significant effects on the swelling at 25 °C [9].

When the temperature was increased to 100 °C, the percent swelling was higher than that of 25 °C almost 1-1.5 times, especially, in EV system. The EV system, which has almost 250 % swelling and 3.5 swelling index, is more poor resistant to oil than DBPH peroxide systems, which has the lowest percent swelling of 150 % and swelling index of 2.5. The reasons because the different type of chemical bond formed in crosslinking process and the elevated temperature of 100 °C is resulted in the mobility of the polymer chain. Therefore, the flexible chemical bonds in EV system are more affected and show the highest swelling [5, 8-10, 12, 14]. Also, the DBPH system indicates the better degree of swelling at 100 °C than DCP, which indicates the intermediate value of percent swelling around 200 % and swelling index about 3. This because the low crosslink efficiency in DCP that the temperature in vulcanization in the experiment does not match [5] as mentioned earlier. In addition, the high temperature provides the ease of oil to penetrate through the samples [14].

4.5 Conclusion

In mixing process, the well-mix is obtained from the stable plateau curve of mixing torque.

From the cure characteristics; it can be concluded that to use the vulcanizing agent for properly working, the vulcanization temperature is important. Peroxide provides the higher vulcanization temperature than sulfur which works properly at 150 °C. DCP has efficiently vulcanized with the suitable time at 160 °C, and 180 °C for DBPH. All of the vulcanization systems give the plateau curve of cure characteristic after fully crosslink.

Peroxide cured systems provide the lower tensile strength and percent elongation at break than EV system, but the Young's modulus and swelling

properties are better. The increasing in vulcanizing agent gives the increasing in mechanical properties.

DCP has the crosslinking temperature at 160 °C which is not suitable for producing TPV with high performance thermoplastic, because it use high processing temperature due to the high melting point of thermoplastic and shear stress in dynamic vulcanization process generates very high heat. Thus DCP is not be used in further study.

4.6 Acknowledgements

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4.7 References

1. Akiba, M., and Hashim, A.S. (1997). Vulcanization and crosslinking in elastomers. Progress in Polymer Science, 22(3), 475-521.
2. Ibrahim, A., and Dahlan, M. (1998). Thermoplastic natural rubber blends. Progress in Polymer Science, 23(4), 665-706.
3. Koning, C., Duin, M.V., Pagnouille, C., and Jerome, R. (1998). Strategies for compatibilization of polymer blends. Progress in Polymer Science, 23(4), 707-757.
4. Magaraphan, R., and Yamoun, C. (2008). Dynamic vulcanization of fluoroelastomer and natural rubber. The 1st Thailand Natural Rubber Conference, 1, 152-163.

5. Thitihamwong, A., Nakason, C., Sahakaroa, K., and Noordermeer, J. (2007). Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends. Polymer Testing, 26(4), 537–546.
6. Varghese, S., Alex, R., and Kuriakose, B. (2004). Natural rubber-isotactic polypropylene thermoplastic blends. Journal of Applied Polymer Science, 92(4), 2063 – 2068.
7. Palys, L.H., and Callais, P.A. (2003). Understanding organic peroxides to obtain optimal crosslinking performance. Rubber World, December 1.
8. 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.
9. 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.
10. 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.
11. Loan, L.D. (1972). Peroxide crosslinking reactions of polymers. Pure and Applied Chemistry, 30(1-2), 173-180.
12. 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.
13. 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.

14. 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.