



CHAPTER V

EFFECT OF VULCANIZING AGENT OF NR/PVDF THERMOPLASTIC VULCANIZATE ON PROPERTIES OF RUBBER USED IN FUEL SYSTEM

5.1 Abstract

Rubber parts for resisting the swelling effects from gasohol were developed by designing a new material which is thermoplastic vulcanizate (TPV), a blend of polymers (NR and PVDF) via the dynamic vulcanization technique. The CV, EV, and peroxide system were used as vulcanization system. The amount of peroxide curing agent was varied by 1, 3, 5, and 7 phr. The mechanical properties were studied before and after aging at 100 °C for 22 hours according to ASTM D573–04. The tensile strength and percent elongation at break were determined according to ASTM D412–06a or ISO 37 (Type 1), the tear strength was determined according to ASTM D624–00 or ISO 34, and the hardness was determined according to ASTM D2240. The oil resistance test was also done at 25 °C for 24 hours 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.

5.2 Introduction

Some 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. To achieve this aim, the new thermoplastic vulcanizate (TPV) of high performance is developed as an alternative with a cheaper cost [1-4]. For making this novel thermoplastic vulcanizate, natural rubber (NR) and poly(vinylidene fluoride) (PVDF) are the good candidates for reducing cost. Natural rubber provides properties of elastomeric materials for use in rubber parts.

Poly(vinylidene fluoride) provides properties such as oil and thermal resistances instead of fluoro rubber. Both of them were blended together via dynamic vulcanization technique, the process of vulcanizing an elastomer phase during its melt mixing with the molten plastic, to obtain thermoplastic vulcanizates (TPV). This work aims to produce TPV and to study their mechanical properties and the swelling resistance to automobile oils that are biodiesel and gasohol, the mainly used fuels in Thailand.

5.3 Experimental

5.3.1 Materials

Poly(vinylidene fluoride) or PVDF is an extrusion grade, SINO[®] J100 PVDF, which purchased from Assembly Chemicals Co. (Nanjing, China). 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.

5.3.2 Preparation of NR/PVDF Thermoplastic Vulcanizates

The thermoplastic vulcanizate was achieved by blending thermoplastic and elastomeric materials together via the dynamic vulcanization technique. NR was blend with PVDF at the fixed composition of 50/50 in an internal mixer (Brabender[®] 815602 type with N50 mixer, Germany) at various vulcanization systems. For the system involving sulfur (the formulae was adopted from Boochathum *et al.*, 2001 [5]), the Acc:S ratio were used at 0.5 and 2.0 for the CV and EV systems, respectively. In peroxide system (the formulae was adopted from Magaraphan *et al.*, 2008 [6], 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (Luperox[®] 101 or DBPH) was used as a peroxide vulcanizing agent and the quantity of DBPH was varied at 1, 3, 5, and 7 phr. Mixing was performed at a rotor speed of

80 rpm at 150 °C according to the formulae and mixing schedule given in Table 5.1. Mixing was done until the vulcanization of NR was started to occur as indicated by the increasing torque curve. 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) and obtained a pre-vulcanized TPV. This pre-vulcanized TPV was a fully vulcanized by further compressing in a compression mold (Wabash MPI, V50H-18-CX model, USA) with the pressure of 20 ton force at the temperature of 150 °C in sulfur system and 180 °C in peroxide system for 10 min. Then cooled down and the TPV was obtained.

Table 5.1 Compounding formulae and mixing schedule

Ingredients	CV system		EV system		Peroxide system	
	Quantity (phr ^a)	Mixing time (min)	Quantity (phr ^a)	Mixing time (min)	Quantity (phr ^a)	Mixing time (min)
PVDF	50	5	50	5	50	5
NR	50	5	50	5	50	5
Steric acid	2	1	2	1	0.125	1
ZnO	3.5	1	3.5	1	-	-
CBS	0.9	2	3	2	-	-
Sulfur	1.8	2	1.5	2	-	-
Ca(OH) ₂	-	-	-	-	1.5	1
TAIC	-	-	-	-	1.5	2
DBPH	-	-	-	-	Varied ^b	1

^aphr = part per hundred part of rubber.

^bThe amount of DBPH was varied by 1, 3, 5, and 7 phr, which were calculated from NR 100 phr.

5.3.3 Study of Mechanical Properties

The mechanical properties of TPVs were done before and after aging at 100 °C for 22 h in air oven followed the ASTM D573-04. The mechanical properties of TPVs included the tensile strength, percent elongation at break, tear strength, and hardness. The tensile strength and percent elongation at break were determined according to ASTM D412–06a or ISO 37 (Type 1) and the tear strength was determined according to ASTM D624–00 or ISO 34 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).

5.3.4 Study of Oil Resistance on Thermoplastic Vulcanizates

The oil resistance test of TPVs was done at the temperature of 25 °C for 24 hours according to ASTM D471–06 and 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 5.1:

$$\% \text{ Swelling} = \frac{(W_s - W_o)}{W_o} \times 100 \quad , \quad (5.1)$$

and the swelling index was also determined from equation 5.2:

$$\text{Swelling Index} = \frac{W_s}{W_o} \quad , \quad (5.2)$$

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

5.4 Results and Discussion

5.4.1 Preparation of Thermoplastic Vulcanizate

The vulcanizing times of compounded NR were first determined before compress in a compression mold by using Moving Die Rheometer (MDR) (TECHPRO, rheoTECH MD+ model).

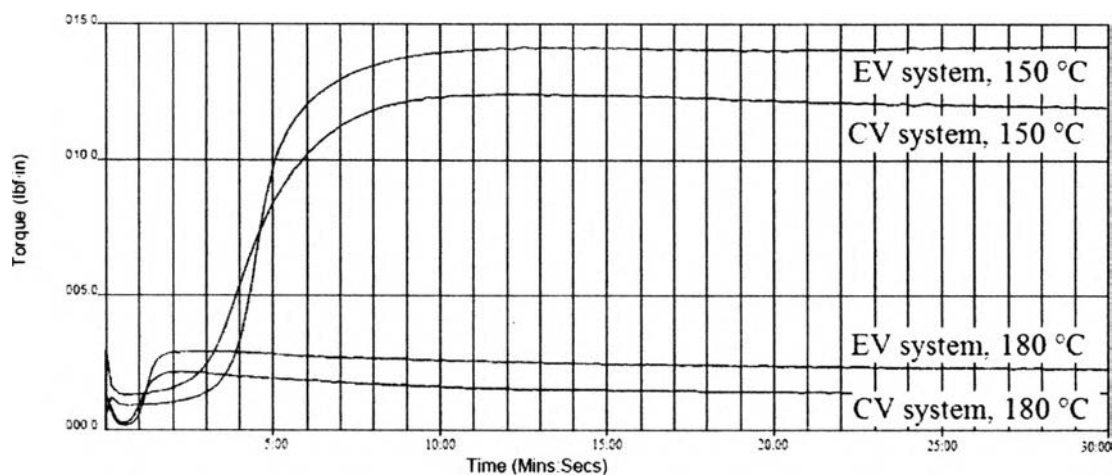


Figure 5.1 The cure characteristics of compounded NR by CV and EV systems.

Figure 5.1 indicates cure characteristics of the compounded NR vulcanized by sulfur at the temperatures of 150 and 180 °C for 30 min. It is found that sulfur works properly at 150 °C rather than 180 °C indicated in the higher torque, but the vulcanization time at 180 °C is shorter. This is because the crosslinking temperature or vulcanization temperature of 150 °C is closed to the vulcanization temperature of sulfur [7]. The plateau was given after fully crosslink and the EV system gave higher torque than CV system for both temperatures [8-10] because the CV system giving more polysulfidic and cyclic sulfide crosslink structure.

For DBPH system, the cure characteristics of a compounded NR vulcanized by 3 phr of DBPH at various temperatures are indicated in Figure 5.2. It is found that the plateau torque curves are achieved after fully crosslink and the higher vulcanization temperature gives the shorter vulcanization time. The maximum torque is increased when the temperature increase from 150 to 180 °C and decreased after the temperature is raised over 180 °C to 200 °C because the different half life time in different temperature of DBPH. It means that the temperature around 180 °C is near the typical crosslinking temperature of DBPH which has high crosslink efficiency indicated in high torque with not too long vulcanization time in this temperature range [7].

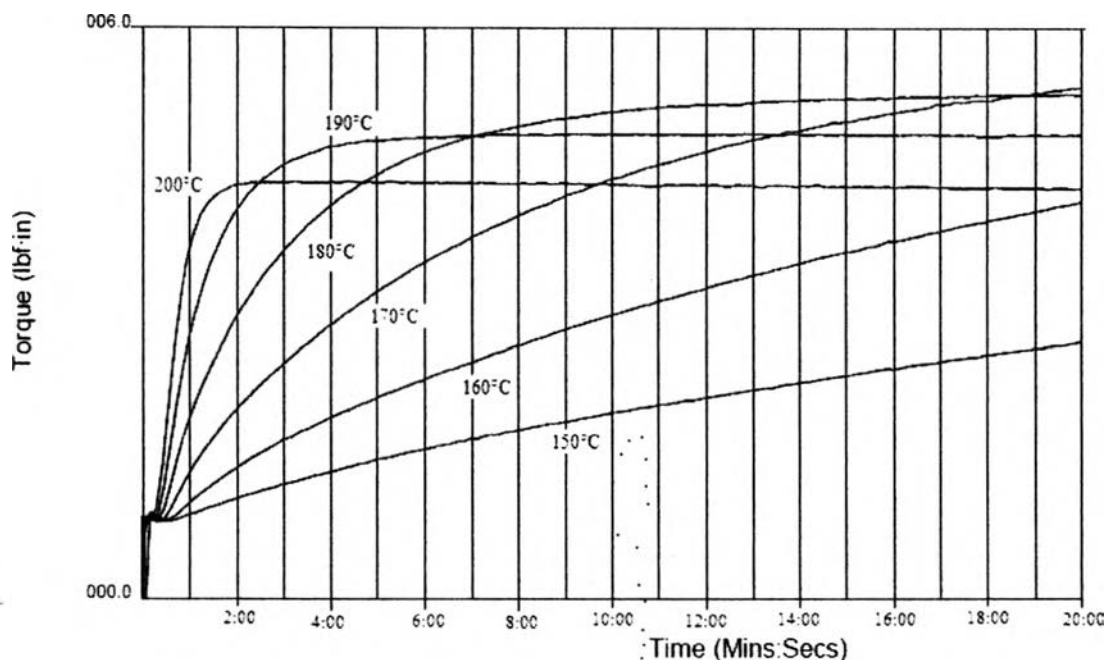


Figure 5.2 The cure characteristic of compounded NR by peroxide DBPH of 3 phr.

From both cure characteristics, it can conclude that to use the vulcanizing agent at properly working, it should be consider the crosslinking temperature, crosslink efficiency, and time with the type of vulcanizing agent, significantly. So, the temperature of 150 °C and 180 °C is the vulcanization temperatures of sulfur and DBPH system. Both of these temperatures were further used to vulcanize thermoplastic vulcanizates with sulfur and DBPH cured systems. The thermoplastic vulcanizate with the NR/PVDF composition of 50/50 (TPV) vulcanized by DBPH system at 180 °C was also characterized for the cure characteristic by varying the amount of DBPH vulcanizing agent, and the results are shown in Figure 5.3.

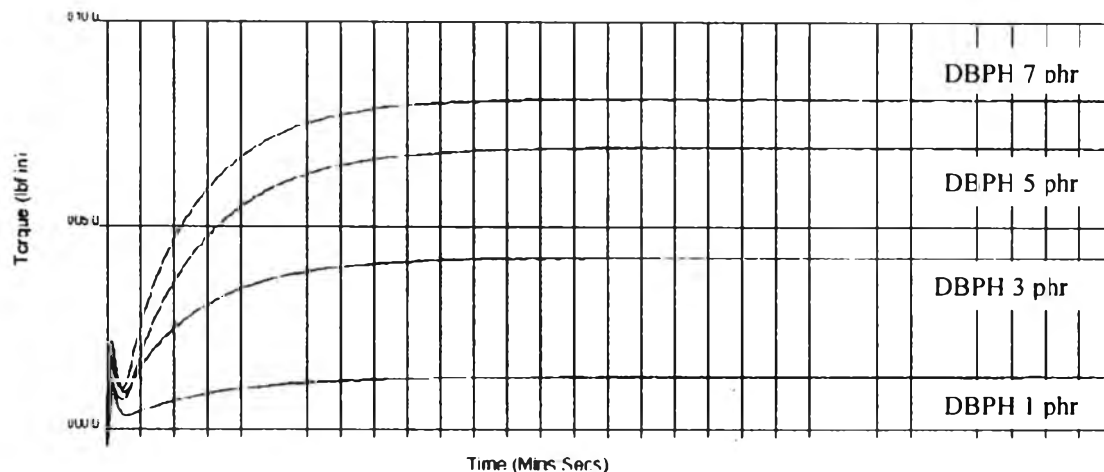


Figure 5.3 The cure characteristics at 180 °C of TPV with various amounts of DBPH.

The result shows that the mixing torque is higher and the vulcanization time becomes shorter when the amount of DBPH is increased, similar to the results done by Li, *et al.* (2006) [11]. This because the more initiators are created result to the crosslinking reaction more occurs and faster than the low initiator. The appearance of TPV at various vulcanization systems is shown in Figure 5.4. The sulfur systems show the poor compatibility of NR and PVDF indicated the small white cluster of PVDF embed in vulcanized NR phase. The DBPH systems give the better compatibility than those of sulfur systems demonstrated in the low dispersive or non-appearance of PVDF separated from TPV. The reason of crosslinking PVDF can be answered, the DBPH incorporated with TAIC can initiate the crosslinking in PVDF [12].

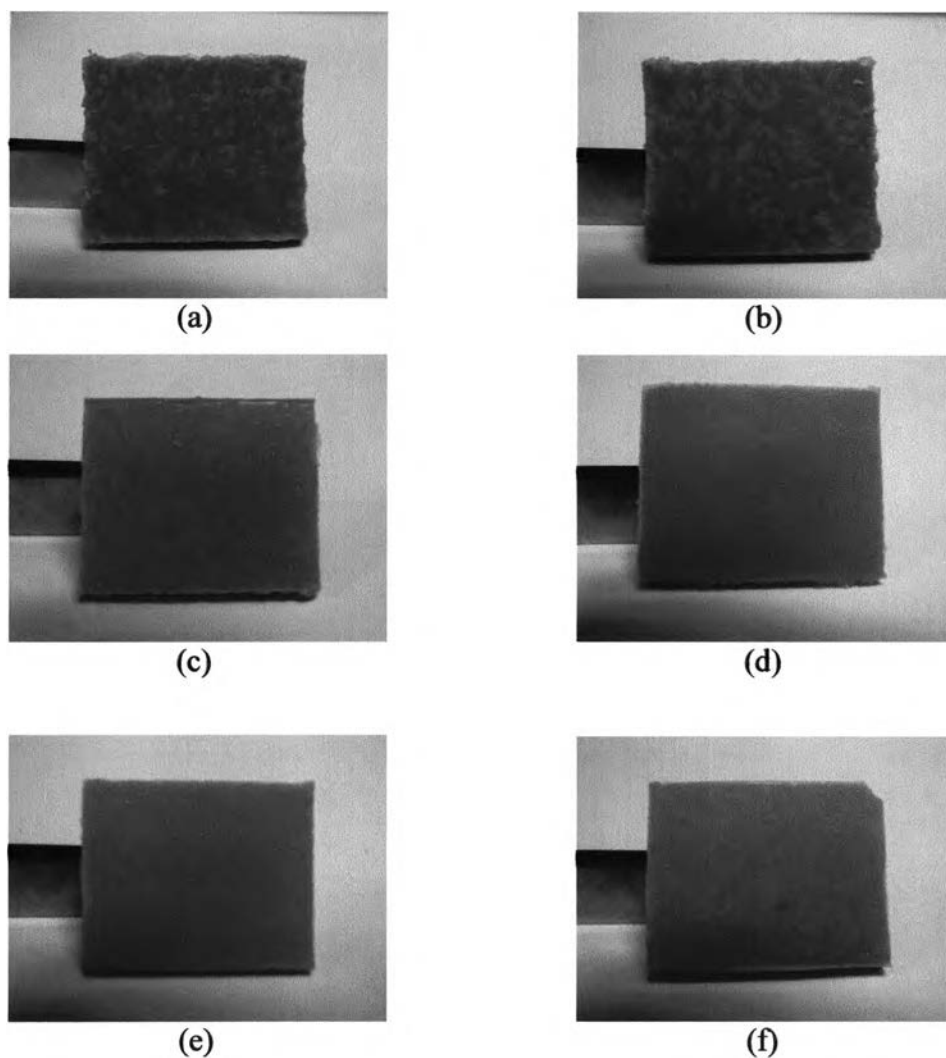


Figure 5.4 The appearance of fully vulcanized TPV after compression: (a) CV system, (b) EV system, (c) 1 DBPH system, (d) 3 DBPH system, (e) 5 DBPH system, (f) 7 DBPH system.

5.4.2 Mechanical Properties of Thermoplastic Vulcanizate

Figure 5.5 shows the tensile strength given from DBPH systems are higher than sulfur systems (CV and EV systems) and increase with the increasing amount of DBPH. The reasons are the stronger C-C linkages are formed only in DBPH system instead of the more flexible C-S and S-S in sulfur systems [11, 13-16], and the crosslinking reaction of PVDF is also taken place [12]. But, the 1 DBPH system is exceptional because of the very small amount of DBPH vulcanizing agent

(1 phr) which is not enough to generate the 3D network structure all over the bulk TPV in vulcanization process resulted in very low crosslink density. The CV system gives the lower tensile strength than the EV system because of the higher polysulfidic and cyclic sulfide linkages are formed [8-10] that conform to the result of cure characteristic.

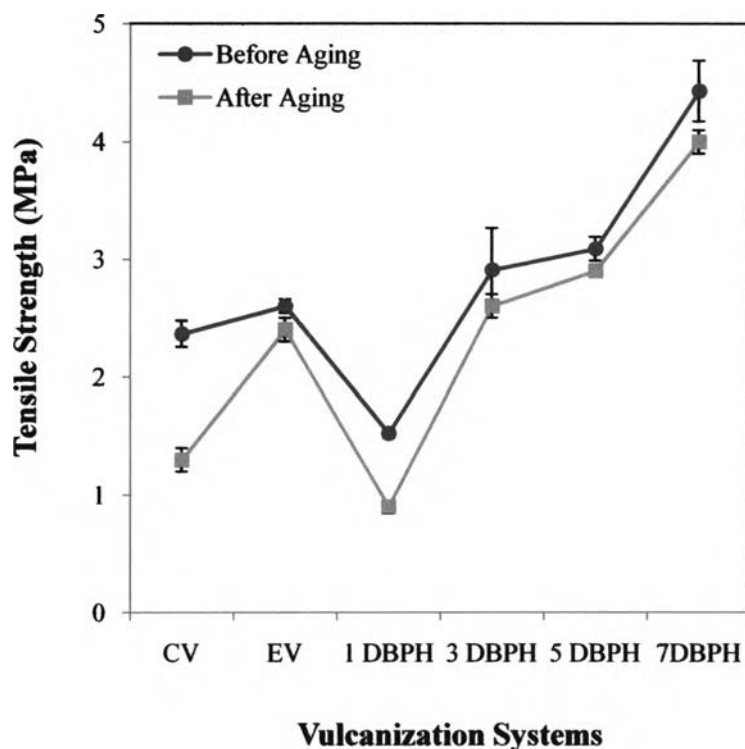


Figure 5.5 The tensile strength of TPVs before and after aging at various vulcanization systems.

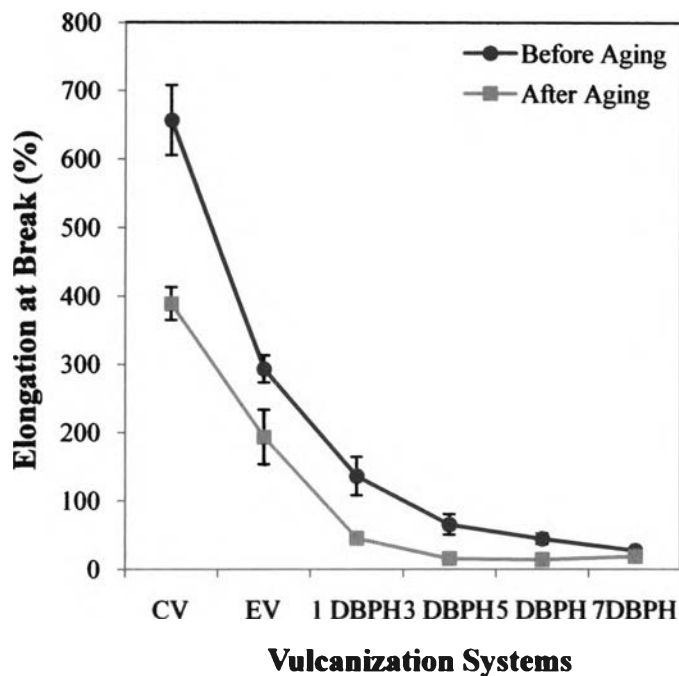


Figure 5.6 The percent elongation at break of TPVs before and after aging at various vulcanization systems.

The percent elongation at break before and after aging in Figure 5.6 indicates the trend opposite from tensile strength. The CV system, which contains many of the most flexible S-S bonds than C-S in EV system, indicated the highest percent elongation at break. And, both of these linkages are more flexible than C-C linkage incorporated with crosslinked PVDF in DBPH system indicated in the higher percent elongation at break and tear strength of CV and EV systems than DBPH system that also shown Figure 5.7 [8-16].

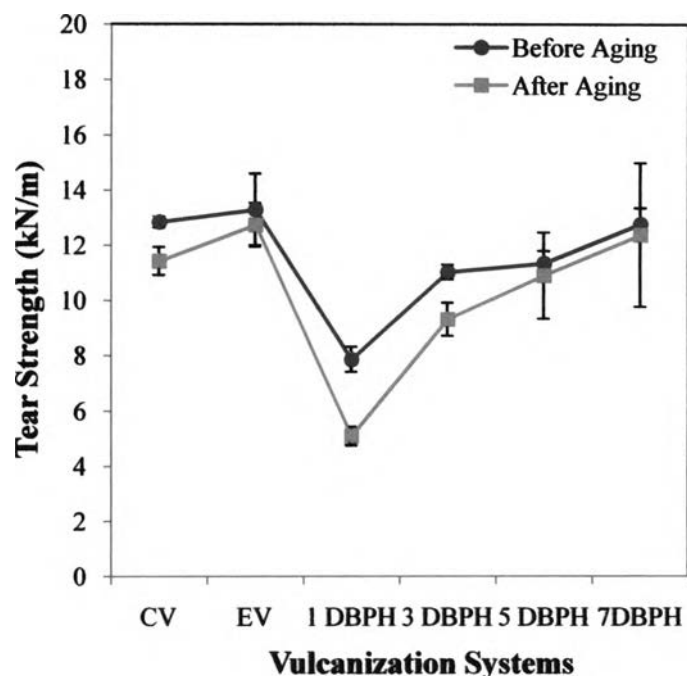


Figure 5.7 The tear strength of TPVs before and after aging at various vulcanization systems.

Consider the tear strength; it is well known that the increasing curing agent increase the crosslink density, this concord with the result indicated in Figure 5.7 that the tear strength increases with DBPH content due to the more crosslinking reaction of NR and PVDF are occurred [11-12]. Although the C-C bond is stronger than C-S and S-S bonds, the tear strength of DBPH cured system does not higher than sulfur cured systems. This can be explained that there is no crosslinked PVDF occur in sulfur cured system, consequently no compatibility between NR and PVDF as seen the phase separation in TPV. The small pieces of PVDF with any shape distributed in the NR phase become the objects obstructed the propagation of the crack in tear test. Hence, the crack cannot propagate easily, it needs more force to create new propagation path and thus the tear strength is high as indicated in the drawing in Figure 5.8.

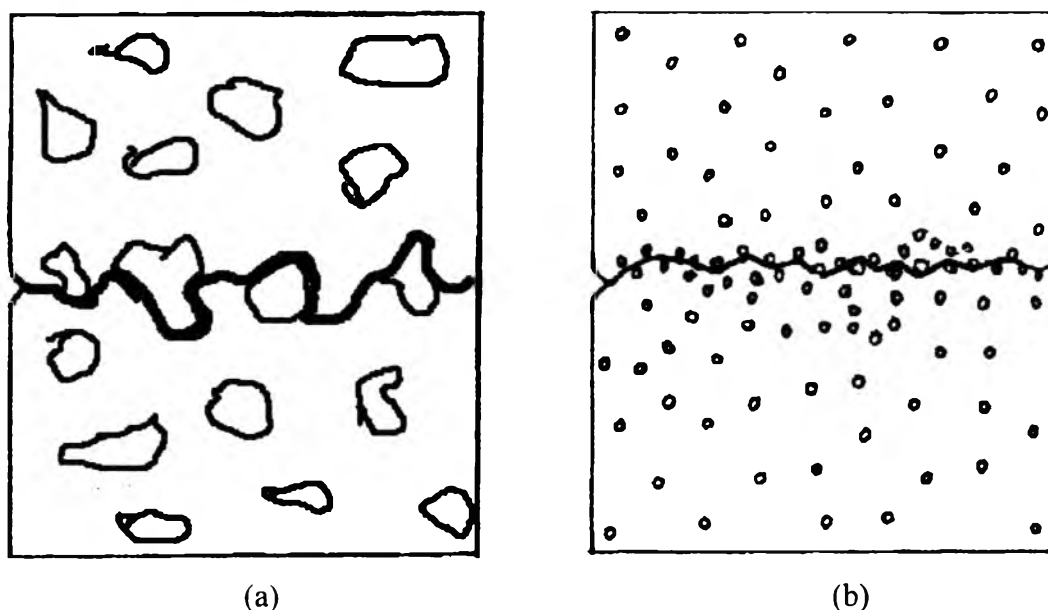


Figure 5.8 The drawing of crack propagation in TPV at different vulcanization systems: (a) sulfur system, and (b) peroxide systems.

Moreover, the DBPH system shows the very low percent elongation at break and tears strength due to the low degree of crosslink in NR phase. Because some of DBPH diffuse to PVDF phase to crosslink and the structure of crosslinked PVDF is more rigid that gives the rigidity and the brittleness to the whole TPV.

All mechanical properties of TPV before and after aging indicate the same trend, but the TPVs after aging give the lower than before aging majorly causes from NR phase which cannot resist to heat like PVDF. The CV system shows the very large decrease in mechanical properties after aging than EV system because the different amount of polysulfidic structure. It does not like to withstand the decomposition when it is thermally fugitive and disulfurized into the shorter structure of sulfur linkage compared to the monosulfidic structure in EV system [5, 8]. The C-C structure in peroxide system is exactly resist to heat than those in sulfur due to the higher bond dissociation energy. But, the change in mechanical properties after aging is depended on the crosslink density which refes to the DBPH content. The very low DBPH content provides the small crosslink density which is not enough to resist to heat, but the higher DBPH content gives the higher crosslink density.

5.4.3 Oil resistance of Thermoplastic Vulcanizate

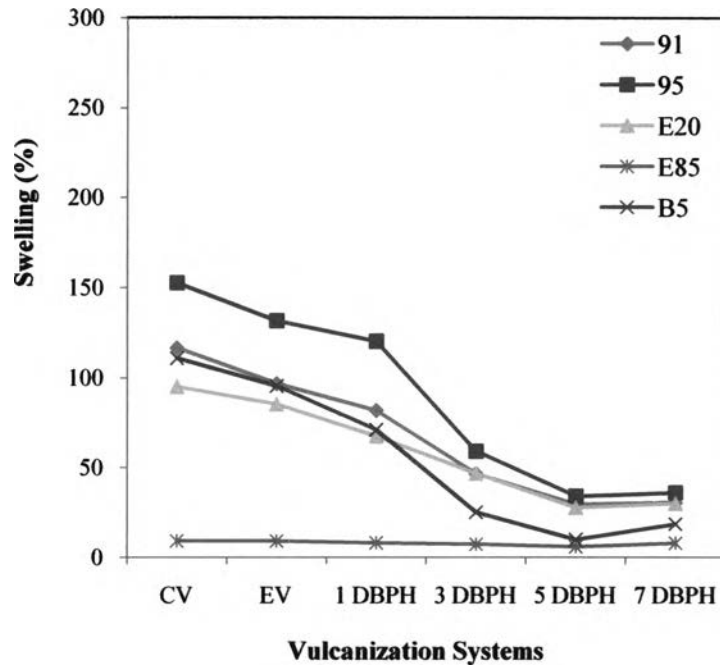


Figure 5.9 The percent swelling of TPVs at 25 °C in various oil types.

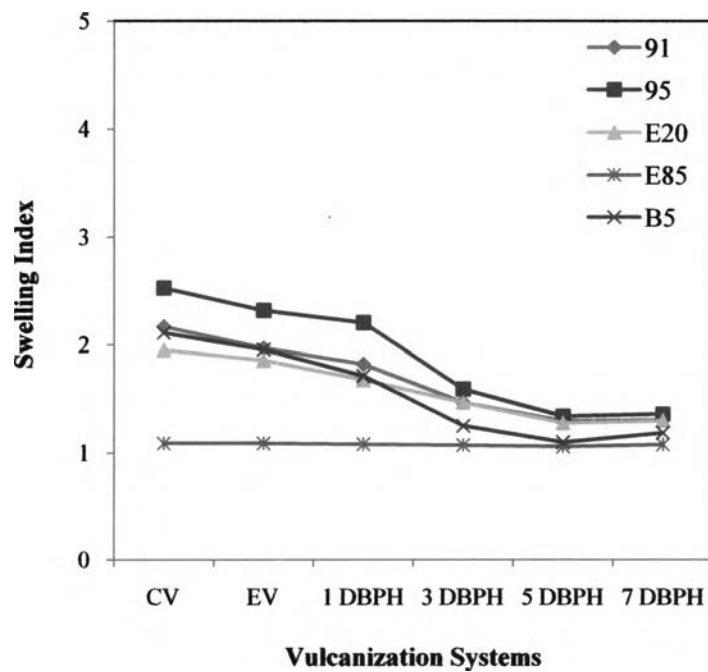


Figure 5.10 The swelling index of TPVs at 25 °C in various oil types.

The resistance to swelling of TPVs from various oil types is done at 25 °C with various vulcanization systems which the result shows in Figures 5.9-5.10. From the result, the percent swelling of TPVs has the same trend in each oil type for all vulcanization systems. It means that even different vulcanization system, the percent swelling looked the same for each oil type. The percent swelling indicated the lowest value in gasohol E85 (85 % ethanol) because of the very low oil or gasoline content which is only 15 % can contact to TPV. The gasohol E85 exhibits the swelling index of 1 that means there is very low or no oil penetrated into TPV due to the weight before and after immersion are the same.

The TPV cured by sulfur systems give high percent swelling of 130-150 % and the swelling index around 2.5 times of original weight due to the nature of linkages which are weaker than the others from DBPH peroxide system and the phase separation [11-16] indicated in the white spots in the immersed sample shown in Figure 5.11. The appearances of samples cured by system of CV, EV, 1 DBPH, 3 DBPH, 5 DBPH, and 7 DBPH indicate from left to right, respectively, in different fuel oil types. The white spots are reduced when increase DBPH content because PVDF has crosslink with NR by peroxide initiation incorporated of coagent [11-12]. The nature of bond and the crosslinked PVDF in peroxide system let the TPV has more resistance to swell in oil indicated in the low degree of percent swelling of 50 % and the swelling index of 1.5 in the system of 3, 5 and 7 DBPH [9, 11-16].

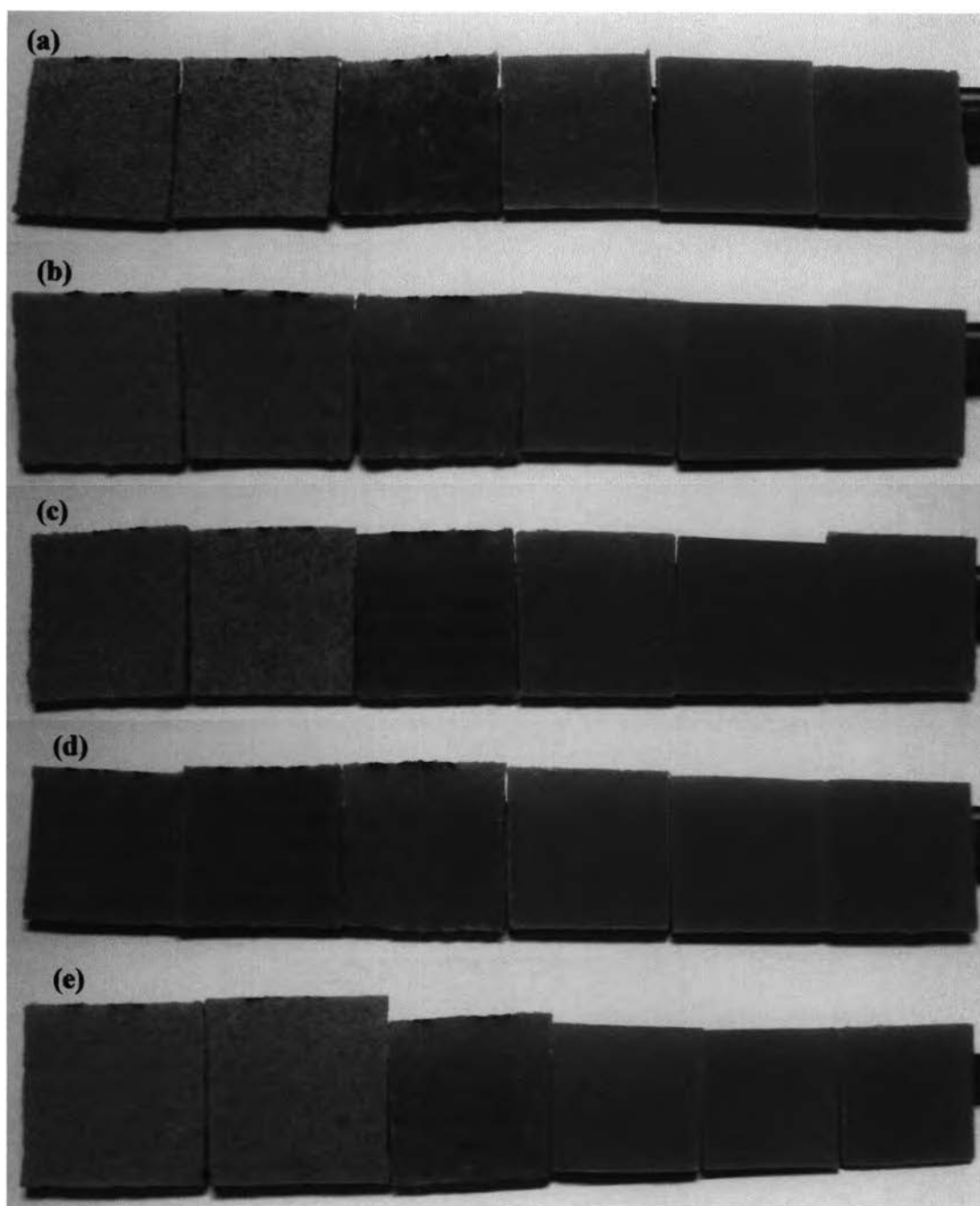


Figure 5.11 Immersed Samples of oils at various vulcanization system which were CV, EV, 1 DBPH, 3 DBPH, 5 DBPH, and 7 DBPH from left to right, respectively. The immersion was done at 25 °C for 24 h: (a) gasohol 91, (b) gasohol 95, (c) gasohol E20, (d) gasohol E85, and (e) biodiesel.

5.5 Conclusion

The vulcanization temperature of 150 °C is preferable to vulcanized TPV in sulfur systems; but, 180 °C is suitable for DBPH systems.

The nature of linkage bonds in each vulcanization system effects to the properties of materials directly.

Peroxide vulcanizing agent can initiate crosslinking reaction in thermoplastic and rubber.

The incompatibility of PVDF and NR in Sulfur systems makes PVDF formed small irregular shape particles in vulcanized NR phase that against the propagation of cracks.

The increase in amount of peroxide curing agent, DBPH, increase the crosslink density that effects to the improvement of mechanical properties, swelling resistance, thermal stability and also compatibility of thermoplastic and rubber phase of TPV. Mechanical properties increase with increasing content of DBPH and reducing in % Swelling.

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