DEVELOPMENT OF ZERO-WASTE PACKAGE FOR ASPHALT FROM NATURAL RUBBER / ETHYLENE VINYL ACETATE COPOLYMER THERMOPLASTIC VULCANIZATES

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การพัฒนาบรรจุภัณฑ์ยางมะตอยที่ไม่มีของเสียจากเทอร์โมพลาสติกวัลคาไนเซตของยางธรรมชาติ/เอทีลีนไวนิลอะซิเตตโคพอลิเมอร์

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
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นภพรรณ คุณานุสนธิ์ : การพัฒนาบรรจุภัณฑ์ยางมะตอยที่ไม่มีของเสียจากเทอร์โมพลาสติกวัลคาไนเซต ของยางธรรมชาติ/เอทีลีนไวนิลอะซิเตดโคพอลิเมอร์. (DEVELOPMENT OF ZERO-WASTE PACKAGE FOR ASPHALT FROM NATURAL RUBBER / ETHYLENE VINYL ACETATE COPOLYMER THERMOPLASTIC VULCANIZATES) อ.ที่ปรึกษาหลัก : รศ. ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาร่วม : รศ. ดร.บุญชัย แสงเพชรงาม

การขนส่งยางมะตอยในปัจจุบันนิยมส่งแบบของเหลวซึ่งจำเป็นต้องให้ความร้อนตลอดระยะเวลาที่ขนส่งซึ่งสิ้นเปลืองพลังงาน และจำเป็นต้องใช้รถบรรทุกพิเศษในการขนส่ง การขนส่งในลักษณะก้อนแข็งที่มีบรรจุภัณฑ์ห่อหุ้มนอกจากจะมีข้อดีกว่าในเรื่องการประหยัดพลังงาน ยังสามารถใช้รถบรรทุกธรรมดาขนส่งได้ จุดประสงค์ของงานวิจัยนี้ คือ การพัฒนาบรรจุภัณฑ์ที่ทนร้อนขณะบรรจุและสามารถหลอมผสมไปกับยางมะตอยได้โดยไม่ก่อให้เกิดขยะและไม่ทำให้สมบัติของยางมะตอยเสียไป โดยงานวิจัยนี้แบ่งเป็น 2 ส่วน คือ (1) การพัฒนาบรรจุภัณฑ์จากเทอร์โมพลาสติกวัลคาไนเซต (thermoplastic vulcanizate, TPV) ของยางธรรมชาติ (natural rubber, NR) ร่วมกับเอทีลีนไวนิลอะซิเตดโคพอลิเมอร์ (ethylene vinyl acetate copolymer, EVA) จากนั้น (2) จะนำ TPV ที่ได้ไปทดสอบบรรจุยางมะตอยและนำไปหลอมผสมกับยางมะตอย พร้อมกับทดสอบสมบัติของยางมะตอย และศึกษาการปรับปรุงสมบัติยางมะตอยด้วย TPV ที่มีระดับการเชื่อมขวาง (degree of crosslink) ที่แตกต่างกัน โดยในส่วนที่ 1 เป็นการศึกษาวิธีการผสม TPV ที่แบ่งเป็น 2 ขั้นตอน คือ การเชื่อมขวางแบบพลวัต (dynamic vulcanization, DV) และการผสมภายหลัง (further blending, FB) กำหนดอัตราส่วนโดยน้ำหนักของ EVA:NR เท่ากับ 50:50 เลือกใช้สารเชื่อมขวางเป็นไดคิลมิลเพอร์ออกไซด์ (dicumyl peroxide, DCP) ที่ปริมาณ 2 ส่วนใน 100 ส่วนของเรซิน (part per hundred resin, phr) และสารป้องกันการเสื่อมสภาพ (thermal stabilizer, TS) ปริมาณ 1 phr โดยศึกษาวิธีผสม 3 วิธี ได้แก่ NR-DV คือ DV เฉพาะ NR และ FB EVA กับ TS, Split-DV คือ DV EVA บางส่วนกับ NR และ FB EVA ส่วนที่เหลือ กับ TS, และ All-DV คือ DV EVA ทั้งหมดกับ NR และ FB เฉพาะ พบว่าวิธีการผสมส่งผลต่อสมบัติของ TPV โดยวิธี NR-DV ให้ชิ้นงานที่ไม่เป็นเนื้อเดียวกันเนื่องจากการมี NR เชื่อมขวางกันเองมากไป ไม่สามารถนำไปใช้งานต่อได้ ส่วน All-DV มีสมบัติเชิงกลด้อยกว่า Split-DV เนื่องมาจากการเกิดการเชื่อมขวางกันเองของ EVA มากเกินไป จึงนำวิธีผสม Split-DV ไปเตรียมชิ้นงานสำหรับการทดสอบบรรจุภัณฑ์ยางมะตอย โดยปรับระดับการเชื่อมขวางของ TPV โดยการปรับปริมาณ DCP ตั้งแต่ 0 – 1.5 phr โดยผสม TPV กับยางมะตอยที่อัตราส่วนร้อยละ 5 โดยน้ำหนักเพื่อทำยางมะตอยที่ดัดแปรด้วยพอลิเมอร์ (polymer modified asphalt, PMA) พบว่าปริมาณการเชื่อมขวางส่งผลต่อสมบัติของ PMA โดยเมื่อมีการเชื่อมขวางมากจะทำให้ยางมะตอยที่ได้มีความทนทานมากขึ้น แต่จะมีความหนืดเมื่อหลอมเหลวน้อยกว่าการเติม TPV ที่ไม่เชื่อมขวาง เนื่องมาจากการต้านการไหลของสายโซ่พอลิเมอร์ที่เกิดการเกี่ยวพันกัน (entanglement) มีผลในการต้านการไหลมากกว่าอนุภาคยางเชื่อมขวางที่แขวนลอยในยางมะตอย

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Nappaphan Kunanusont : DEVELOPMENT OF ZERO-WASTE PACKAGE FOR ASPHALT FROM NATURAL RUBBER / ETHYLENE VINYL ACETATE COPOLYMER THERMOPLASTIC VULCANIZATES. Advisor: Assoc. Prof. Anongnat Somwangthanaroj, Ph.D. Co-advisor: Assoc. Prof. Boonchai Sangpetngam, Ph.D.

Asphalt is normally delivered in liquid form which was heated all the time. It consumes more energy and need the special truck to deliver it. An alternative way to deliver the asphalt in form of solid covered with package can reduce energy consumption and normal truck can be used to deliver. The objective of this research was to develop the zero-waste package for asphalt that was no waste after use and not harmful to asphalt properties. The research consists of two parts which are (1) development of package from natural rubber (NR) and ethylene vinyl acetate copolymer (EVA) thermoplastic vulcanizates (TPV), and (2) Test of asphalt package prepared from the TPV and studied on asphalt modification by incorporating TPV with various degree of crosslink. For the first part, the mixing method consists of two steps: dynamic vulcanization (DV) and further blending (FB). The weight ratio of EVA/NR was fixed at 50/50 wt/wt. Dicumyl peroxide (DCP) was used as a crosslinking agent and was fixed at 2 phr. Thermal stabilizers (TS) were fixed at 1 phr. Three mixing methods were compared: NR-DV which NR was only DV and then FB with EVA and thermal stabilizers (TS), Split-DV which NR and some EVA were DV and then FB with the rest of EVA and TS, and All-DV which NR and EVA was DV and then FB with TS. It was found that mixing method affected properties of TPV. NR-DV sample showed a heterogeneous texture because there was only crosslinked NR, this sample cannot be used. Mechanical properties of All-DV sample were inferior to those of Split-DV sample because of self-crosslinked EVA. The Split-DV method was selected to prepare the polymer modified asphalt (PMA). The TPV with different degree of crosslink were prepared by varying the DCP content from 0 to 1.5 phr. The TPV content was fixed at 5 wt%. It was found that the degree of crosslink affected the properties of PMA. The more degree of crosslink of TPV improved the physical properties of PMA with less viscosity when compared with the asphalt modified with non-crosslink TPV. It might be due to the long-chain polymer contained in non-crosslink TPV which has more entanglement of chain than the short-chain polymer or crosslinked rubber particles.

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Figure A.1 Shear storage modulus (G') at 190 °C versus time of neat NR and neat EVA contained 1 and 5 phr DCP 123

Figure B.1 Vulcanized sample from the internal mixer of 30 cm^3 (left) EVA25/NR50/DCP2 (right) EVA25/NR50/DCP3 130

Figure B.2 Vulcanized sample from the internal mixer of 60 cm^3 (left) EVA25/NR50/DCP1.5 (right) EVA25/NR50/DCP2 130

CHAPTER I

INTRODUCTION

1.1 General Introduction

Asphalt is a mixture of hydrocarbons and is commercially obtained from petroleum refinery process. It is solid at room temperature while it becomes liquid and can be pumped when its temperature is higher than 120 °C [1, 2]. The asphalt is widely used as a binder in paving (road construction), roofing (asphalt shingles) and sealing application. Normally, the asphalt is mixed with aggregates at temperature around 160 – 180 °C. This asphalt is called a hot-mix asphalt. But, due to the environmental issue, there is demand for lower organic compound emission during mixing of asphalt and aggregates. This can be done by lowering the mixing temperature of asphalt and aggregates to be around 130 °C [3-5]. Therefore, a warm-mix asphalt is interesting.

In general, the temperature of asphalt obtained from the refinery process is about 200 °C. After it is transferred to storage tank, the temperature of asphalt drops to around 160 °C. It needs to be maintained at the temperature not lower than 160 °C so that it can be pumped into the special tank truck. To counter the heat loss, during the delivery process, the tank of asphalt is continuously heated to maintain the asphalt in liquid state. After delivery process, the asphalt is either mixed with the aggregates at a hot-mix plant or kept in the storage tank with heating unit. However, the asphalt cannot be kept more than three days at high temperature because of thermal aging [3, 6]. Moreover, the special truck as shown in Figure 1.1 is required to deliver the bulk liquid asphalt to a hot-mix plant shown in Figure 1.2.

Figure 1.1 Special truck for asphalt delivery process [7]

Figure 1.2 Hot mix plant [8]

To reduce the energy consumption during delivery and storage of asphalt, the asphalt should be delivered and kept in a solid form that can be delivered by using a normal truck at ambient temperature. However, due to the tackiness of solid asphalt, it should be covered with some plastic film which can be melted with asphalt without causing harm to the asphalt. This type of plastic film or package is called a zero-waste package. The proper asphalt package should consist of three functions: (i) endure heat during hot asphalt filling, (ii) good mechanical properties during delivery process, and (iii) able to melt with asphalt during mixing with hot asphalt without causing harm to the asphalt. The asphalt package that can be melted with asphalt was first invented in 1999. It has since been improved using many techniques to overcome its limitations [9-11]. More works are still needed.

Nowadays, a major environmental concern is plastic waste, especially single-use plastic packaging. Many countries provide policies to solve this problem such as the reduce-reuse-recycle or 3R waste management [12]. Thailand is ranked 6th in the world for mismanagement of plastic waste (equaled to 1.03 million tons per year being released to the ocean) [13]. According to the Thailand's roadmap on plastic waste management [14], plastic bags with thickness lower than 36 micrometers and single-use plastics (i.e., straws, tablewares, food boxes) must be reduced and banned within 2022. Moreover, the plastic waste must be 100% recycled within 2027. To support this roadmap, the plastic waste is recommended for producing the zero-waste asphalt package. Most of plastic packaging are produced from polyethylene (PE) and its copolymer which is an ethylene vinyl acetate copolymer (EVA). The advantages of EVA are high impact and puncture resistances and it is more transparent than PE. However, the melting temperature of EVA is around 86 °C while the temperature of liquid asphalt is more than 100 °C. From this reason, the thermal resistance of EVA should be improved to endure the hot asphalt during filling.

There are many methods to improve the thermal resistance of EVA such as blending with high melting temperature or high molecular weight polymer, incorporating with rigid particles to prepare polymer composite, and crosslinking the EVA to increase the molecular weight of polymer. In this work, blending with high melting temperature polymer as well as crosslinking were employed to increase the thermal resistance of EVA.

Natural rubber (NR) is an elastomeric polymer with high molecular weight (> 100,000 g/mol) [15]. Thailand is the world's biggest natural rubber production with the market share of 37% of global production [16]. The price of NR has fallen since 2014 due to the excess supply. To overcome this problem, the Association of Natural Rubber Producing Countries (ANRPC) have been continuously promoting more usage of natural rubber. In addition, the NR has been used as an additive for asphalt. The road constructed with asphalt and natural rubber has longer service life than the road constructed by normal asphalt [17]. Due to its high molecular weight, the NR has no melting point. Thus, it cannot flow like thermoplastic at high temperature. Therefore, it has a potential to be used to increase the thermal resistance of EVA. Moreover, dynamic vulcanization technique can be applied to EVA/NR blends to transform them into thermoplastic vulcanizate (TPV) [18-21]. TPV has better thermal resistance while can be reprocessed like thermoplastic.

This dissertation consisted of two parts which were the preparation of thermoplastic vulcanizates and the fabrication of asphalt package. For the first part, the effect of mixing method and peroxide content on the properties of EVA/NR TPVs were studied. In the second part, the asphalt package from TPV with different peroxide contents were prepared and tested by filling with hot asphalt. Moreover, the properties of asphalt blending with the TPV with different peroxide content were also investigated.

1.2 Objective and Scopes

The objective of this dissertation was to develop the zero-waste package for asphalt from natural rubber (NR) and ethylene vinyl acetate copolymer (EVA) thermoplastic vulcanizates (TPV).

Thermoplastic vulcanizates (TPV) was prepared by blending EVA with NR under the proper dynamic vulcanization (DV) technique. Afterwards, the TPV was prepared as a film package and tested with hot asphalt. To evaluate the performance of film package, the test on polymer modified asphalt was performed in this dissertation. The dissertation was separated into two parts which have two sub-objectives as followed:

1.2.1. To study effect of mixing method and peroxide on properties of ethylene vinyl acetate copolymer and natural rubber thermoplastic vulcanizates:

1.2.1.1. EVA type 18 wt% of vinyl acetate was used.

1.2.1.2. NR of air-dried sheet type was used.

1.2.1.3. The EVA and NR content at 50 wt% each were fixed.

1.2.1.4. Dicumyl peroxide (DCP) was used as a crosslinking agent

1.2.1.5. Three mixing methods which were designated as NR-DV, Split-DV, and All-DV (the details of these three methods were described in section 4.1.2 and illustrated in Figure 4.1) were compared.

1.2.1.6. The best method providing good processability and the best mechanical properties of TPV was used to study the effect of peroxide content. The DCP content was varied from 0 to 3 phr.

1.2.2. To evaluate the effect of gel content of TPV on properties of EVA/NR TPV modified asphalt:

  1.2.2.1. EVA and NR content at 50 wt% each were fixed.

  1.2.2.2. The Split-DV method was selected to prepare the TPV

  1.2.2.3. DCP content of 0, 0.5, 1, and 1.5 phr were compared.

  1.2.2.4. Asphalt graded AC 60/70 was used.

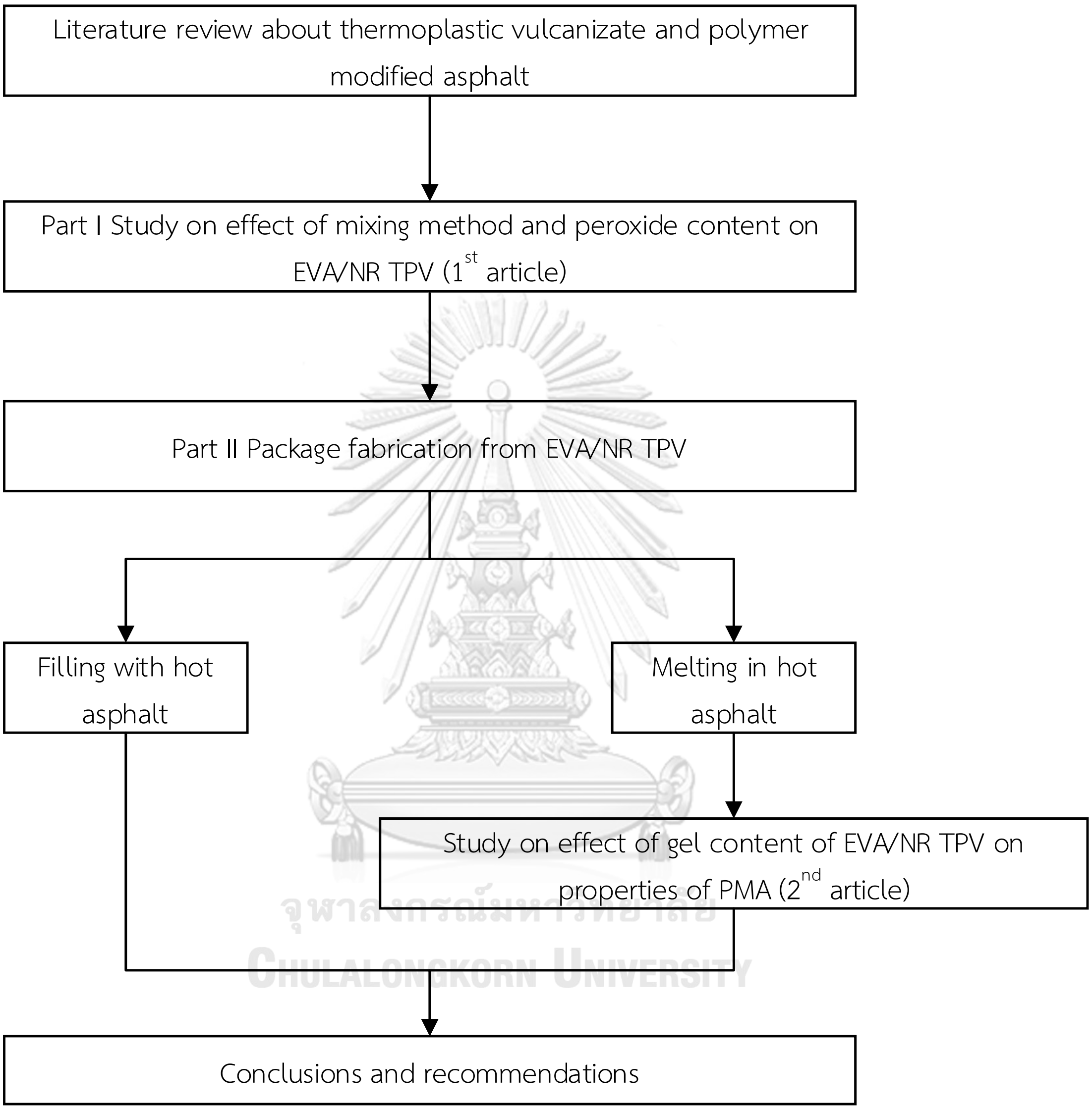
  1.2.2.5. TPV content of 5 wt% was fixed.

1.3 Organization of the Dissertation

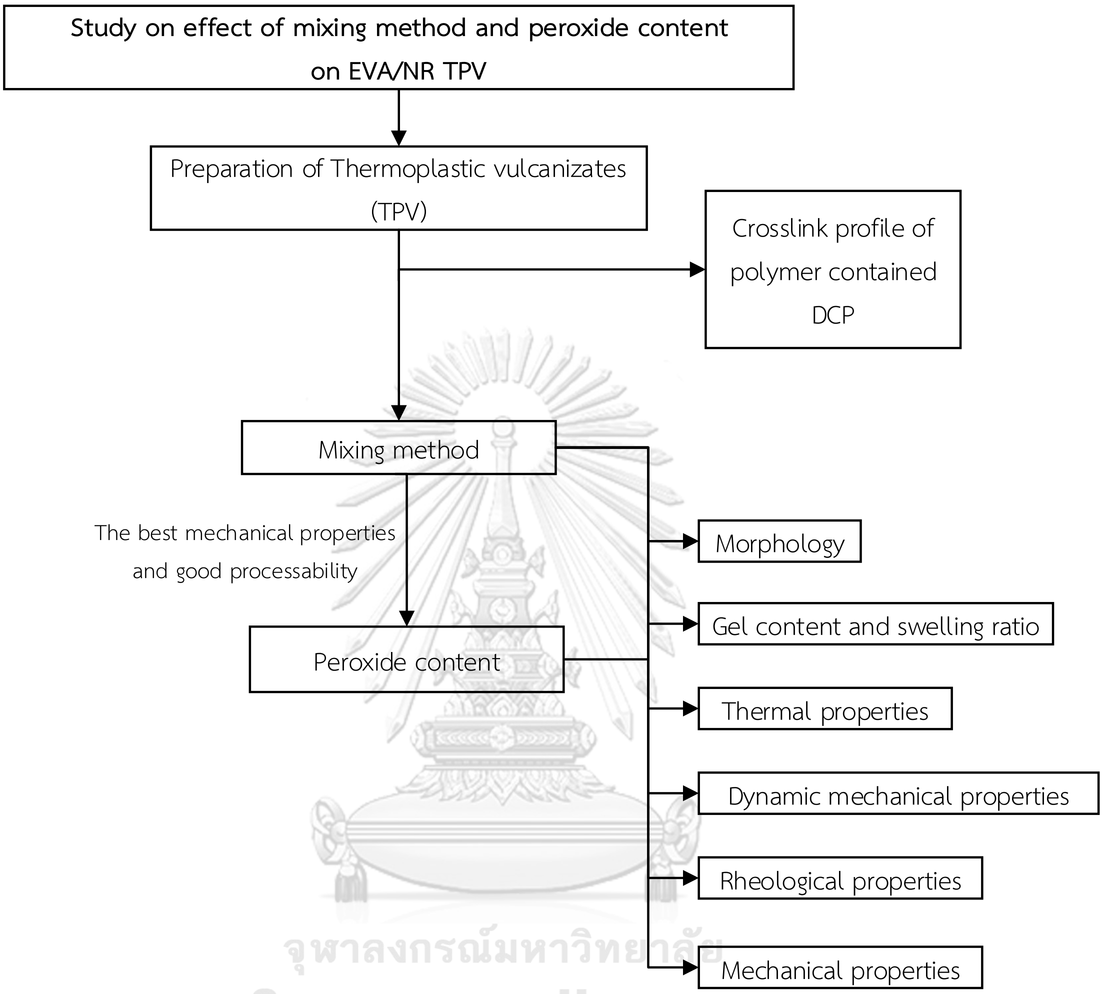
The dissertation was divided into six chapters. Chapter I introduced and gave some motivation about the development of zero-waste package for asphalt and stated the objective of this research. Chapter II was a theory and literature reviews related to asphalt, patent of asphalt package, thermoplastic vulcanizate, and polymer modified asphalt. Chapter III described the characterization techniques related to this research. Materials, sample preparation as well as results and discussion of ethylene vinyl acetate copolymer and natural rubber thermoplastic vulcanizates (TPV) were presented in Chapter IV. Consequently, the preparation and test of the package from TPV were shown in Chapter V. Finally, the Chapter VI gave the overall conclusions and recommendations for future works.

1.4 Research Methodology

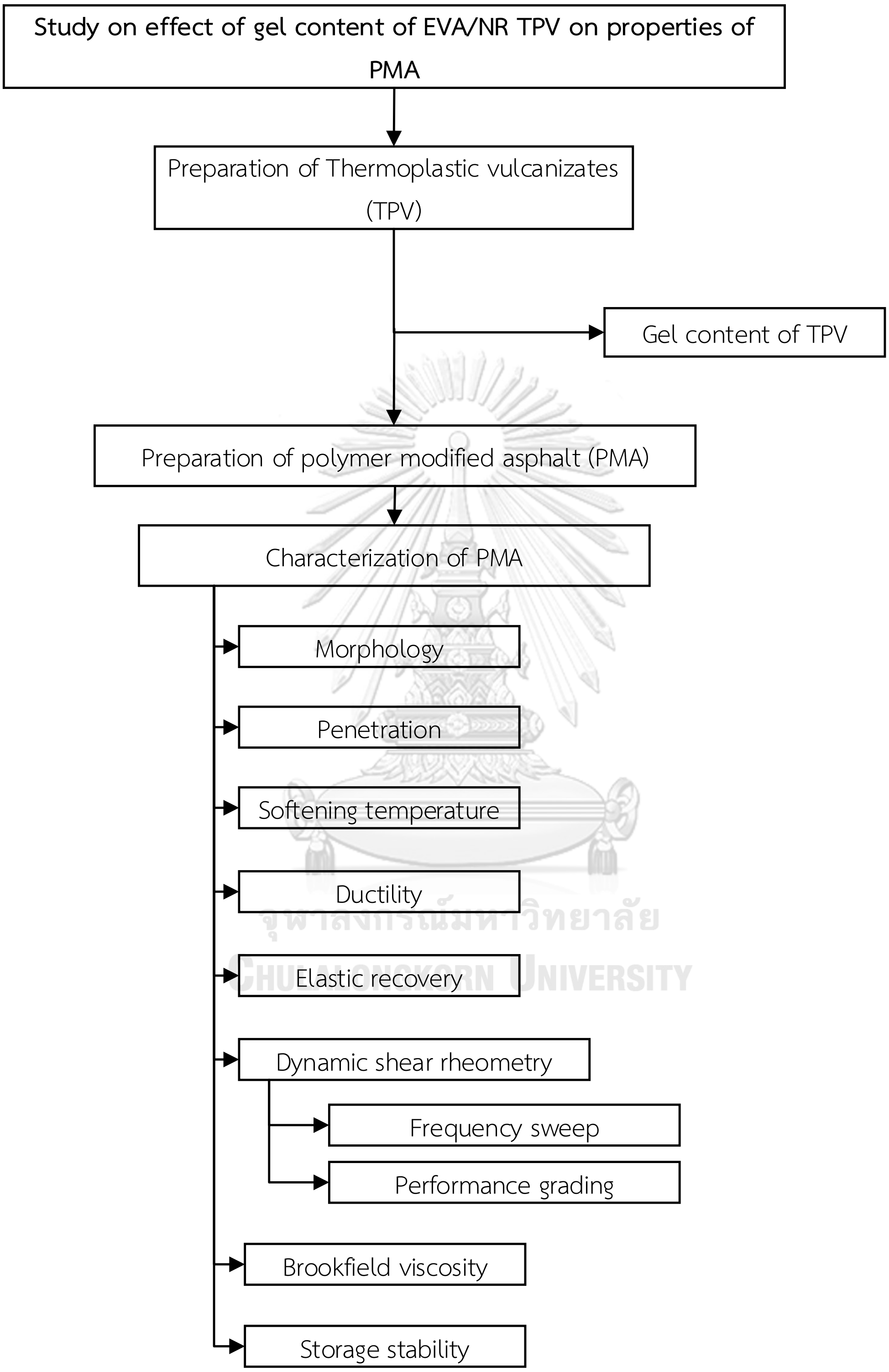
1.4.1 Overall Methodology



1.4.2 Study on Effect of Mixing Method and Peroxide Content on EVA/NR TPV



1.4.3 Study on Effect of Gel Content of EVA/NR TPV on Properties of PMA



CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter described about asphalt, patent of asphalt package, ethylene vinyl acetate copolymer, natural rubber blends, thermoplastic vulcanizates, peroxide vulcanization, and polymer modified asphalt.

2.1 Asphalt

2.1.1 General Information

Asphalt is a mixture of various hydrocarbons which the boiling temperature is more than 200 °C. It is commercially obtained from residue of petroleum refinery process. It consists of many aromatic hydrocarbons which make the asphalt color become black and it is a good binder. However, the asphalt material does not have exact molecular structure and amount of each hydrocarbon substance due to the variety of crude oil. Asphalt has been used in pavement, sealant, and roofing application due to its low-cost, thermoplastic behavior, and climate resistance [22].

Based on the processing temperature, the asphalt can be classified into three types which are hot mix asphalt (HMA), warm-mix asphalt (WMA), and cold-mix asphalt (CMA) [4]. The hot mix asphalt or HMA is a traditional asphalt which the processing temperature is higher than 160 °C while the processing temperature of warm mix asphalt or WMA is about 100 - 140 °C. The WMA was first developed in

1999 [23]. The viscosity of asphalt is reduced by blending with water or organic additive at temperature higher than their boiling temperatures. After the water or organic additive has evaporated, the micro voids inside the asphalt are created and the viscosity of asphalt decrease. Therefore, the processing temperature of WMA is lower than that of HMA. The benefits of low processing temperature of asphalt are low fumed emissions, reduced energy consumption, improved workability, compaction efficiency, and longer pavement life [3, 23, 24]. The CMA is an asphalt that is dispersed in media (i.e., water or organic solvent) which can be mixed with aggregate at ambient temperature. There are two types of CMA based on the media: asphalt emulsion which the media is water, and cutback asphalt which the media is organic solvent [25-27]. The CMA is normally used for road maintenance due to easy preparation. However, the evaporation of solvent in CMA should be concerned and it can affect the properties of asphalt mixture. Due to this reason, HMA has been used until now.

2.1.2 Grading Systems

At present, there are three popular systems for determining characteristics of asphalt which are penetration grade, viscosity grade, and performance grade. The grade is specified according to the usage condition.

Penetration grade is the oldest grade and still used at present because of the simple test method. Penetration of asphalt is measured according to ASTM D946

[28]. For example, the AC 40/50 means the asphalt with penetration value between 40 and 50. However, the penetration value refers only to hardness of asphalt at room temperature. That makes this system lack of some information such as viscosity. The viscosity of asphalt should be measured because it helps to decide the mixing temperature and compaction temperature.

The viscosity grade is according to ASTM D3381 [29]. The viscosity of asphalt is measured using a vacuum capillary viscometer. The number of viscosity grade relates to a viscosity value in the unit of poises at 60 °C. For example, AC-10 is the asphalt with its viscosity value of 1,000±200 poises or AC-20 is the asphalt with its viscosity value of 2,000±400 poises. However, these two grading systems do not provide overall important information such as the temperature range that the asphalt can be used. Therefore, the superpave performance grading system should be used, especially for polymer modified asphalt which is the special grade.

For the superpave performance grade according to ASTM D6373 [30], there are two specific number in the grade name as shown in Figure 2.1. The first is the expected maximum pavement design temperature (°C) and the second is the minimum pavement design temperature (°C). Both numbers are in unit of degree Celsius. Thus, a PG 64-22 is intended for use where the average seven-day maximum pavement temperature is 64 °C and the expected minimum pavement temperature is -22 °C. If this asphalt is used out of this range, the rutting can occur at high temperature and the thermal cracking at low temperature. To describe the grade, the dynamic shear rheometer is used to evaluate the former number and the bending beam rheometer is used to evaluate the latter number.

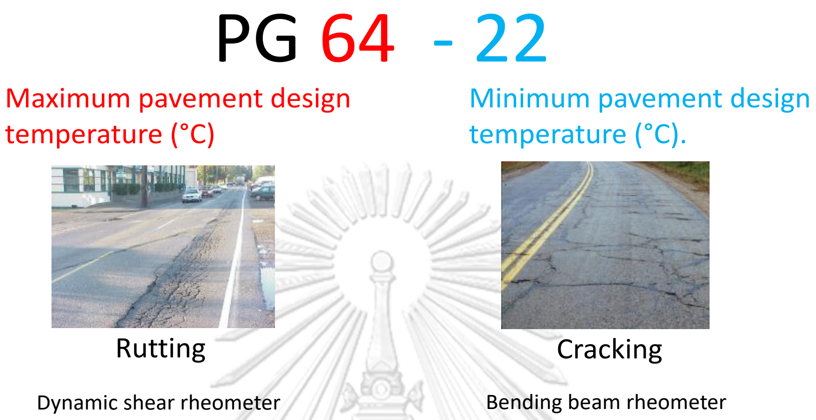


Figure 2.1 Illustration of superpave performance grade asphalt and the failure mechanism of road when the asphalt is used at inappropriate temperature [31].

2.2 Patents of Asphalt Package

The asphalt package, which can be molten in the asphalt during mixing, has been developed since 1999 by Vermilion et al. [9]. The asphalt package comprised of 60 - 90 wt% of asphalt and 10 – 40 wt% of plastic. The plastic used in this patent was blend of ethylene vinyl acetate copolymer (EVA) and polypropylene (PP). They claimed that the EVA had more impact resistance, while the PP provided high temperature stability to the package. Because the asphalt was a main component of this package, the recommended weight of this package should not be more than 6 wt% of total product weight. This recommended weight percent of package was the maximum weight percent that the properties of asphalt after blending with the package were not significantly changed. Marchal [10] developed the asphalt package in 2007. The asphalt was also a component of this package, but the content of asphalt was about 20 wt% which was less than the previous patent. It was combined with the plastic at 80 wt%. However, the density of package was less than that of asphalt which was about 0.9 g/cm^3. Therefore, the package floated over the surface of asphalt and was difficult to completely melt in the asphalt. To solve this problem, the metal oxide was added to increase the density of the package. The recommended weight of this package was 2.5 wt% due to the reduction of asphalt consisted in the package. Another package was invented in 2013 [11], the package was plastic film. First, LDPE film was laid on the wood box. Hot liquid asphalt was poured into the package and was left until it was cooled. The asphalt block was then covered with the spun bonded HDPE as a second layer to separate each asphalt block. The weight of asphalt block was about 25 lbs. The blocks were arranged on pallet and were wrapped with the spun bonded PP. However, the recommended weight percent of inner package should not be more than 0.5 wt% of whole product weight. However, this method also has the plastic waste from the outer package. The detail about material type and the recommended package weight percent were shown in Table 2.1.

Table 2.1 List of patents about asphalt consumable package

Year	**Title**	**Materials**	**Weight percent of package to total weight of package (wt% of total)**	**References**
1999	Asphalt packages with consumable containers	Asphalt (~60%) PP (~30 wt%) EVA (~10 wt%)	6	[9]
2007	Packaging for bitumen	EVA (~90%) Metallic oxide (~10%)	2.5	[10]
2013	Durable, Consumable Packaging System for Hot Melt Materials and Methods of Making and Using Same	Plastic Films Spun bonded PP Spun bonded HDPE LDPE film	0.3 – 0.5	[11]

From these patents, the package can be classified into two groups: thick package and thin package. This thick package was plastic sheet, normally EVA, blended with asphalt to increase compatibility with asphalt when in use. While the thin package used the commodity plastic such as polypropylene (PP) and polyethylene (PE) to cover the asphalt. These PP and PE could be used upon their melting temperatures which are higher than 160 °C. Since, EVA has lower melting point than PP and PE, it might be suitable to be used with a warm-mix asphalt where the viscosity of asphalt was reduced by adding some additives [3-5, 32]. This warm-mixed asphalt can be processed at lower temperature around 130 °C. Due to this reason, EVA should be considered as a main component for making the zero-waste package.

2.3 Ethylene Vinyl Acetate Copolymer (EVA)

Ethylene vinyl acetate copolymer (EVA) is a thermoplastic that consists of two monomer - ethylene and vinyl acetate - as its chemical structure was shown in Figure 2.2. The properties of EVA depend on the content of vinyl acetate in their molecular structure. The EVA with high content of vinyl acetate shows the elastomeric properties because the vinyl acetate disrupts the crystallization of polymer chains. Therefore, the melting temperature of EVA decreases as vinyl acetate content increases. The EVA has excellent resistance to heat, ozone, and weather as well as resistance to oil (hydrocarbon solvent) because of their saturated backbone chains and the vinyl acetate groups [33, 34]. The properties of EVA with various vinyl acetate contents were shown in Table 2.2.

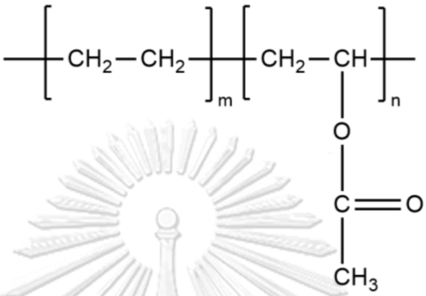


Figure 2.2 Chemical structure of ethylene vinyl acetate copolymer [33, 34]

Table 2.2 Properties of ethylene vinyl acetate copolymer with various contents of vinyl acetate [35]

Vinyl acetate content (wt%)	Melt flow index (g/10 min)	Softening temperature (°C) via Ring-and-Ball apparatus	Melting temperature (°C) via differential scanning calorimetry technique
0	-	-	110
9	2	-	100
12	2.5	193	96
18	2.5	199	88
25	2	188	78
28	3	171	75
32	43	110	63
40	57	104	43

2.4 Natural Rubber (NR)

Natural rubber (NR) is a natural elastomeric polymer which has high elasticity and high resilience. It is obtained from the rubber trees named *Hevea Brasiliensis*. The molecular structure of natural rubber is 1,4 cis-poly(isoprene) as shown in Figure 2.3. However, natural rubber has poor chemical, oil, ozone, and sunlight resistance [36]. Thus, the blend of EVA and NR could provide the blend with advantages of both polymers such as high elasticity and oil resistance.

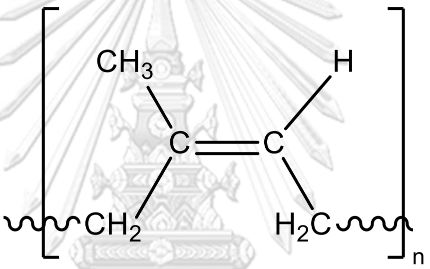


Figure 2.3 Chemical structure of natural rubber (1,4 cis polyisoprene)

2.5 EVA/NR Blends

From the literatures, EVA and NR polymer blends exhibit the immiscible blends [37-45]. Figure 2.4 showed the schematic diagram of NR and EVA blend of 30/70, 50/50, and 70/30 wt/wt. When the weight ratio of EVA was higher than NR, NR was the dispersed phase in EVA continuous phase. In contrast, when NR was more than EVA, the EVA was the dispersed phase in NR continuous phase. In case of equal content of EVA and NR, co-continuous phase was observed. The morphology of EVA/NR blend can be observed at cross-sectional fracture surface of EVA/NR using scanning electron microscope (SEM). NR phase was extracted using benzene. The remaining polymer in SEM micrographs was only EVA which were shown in Figure 2.5 [37].

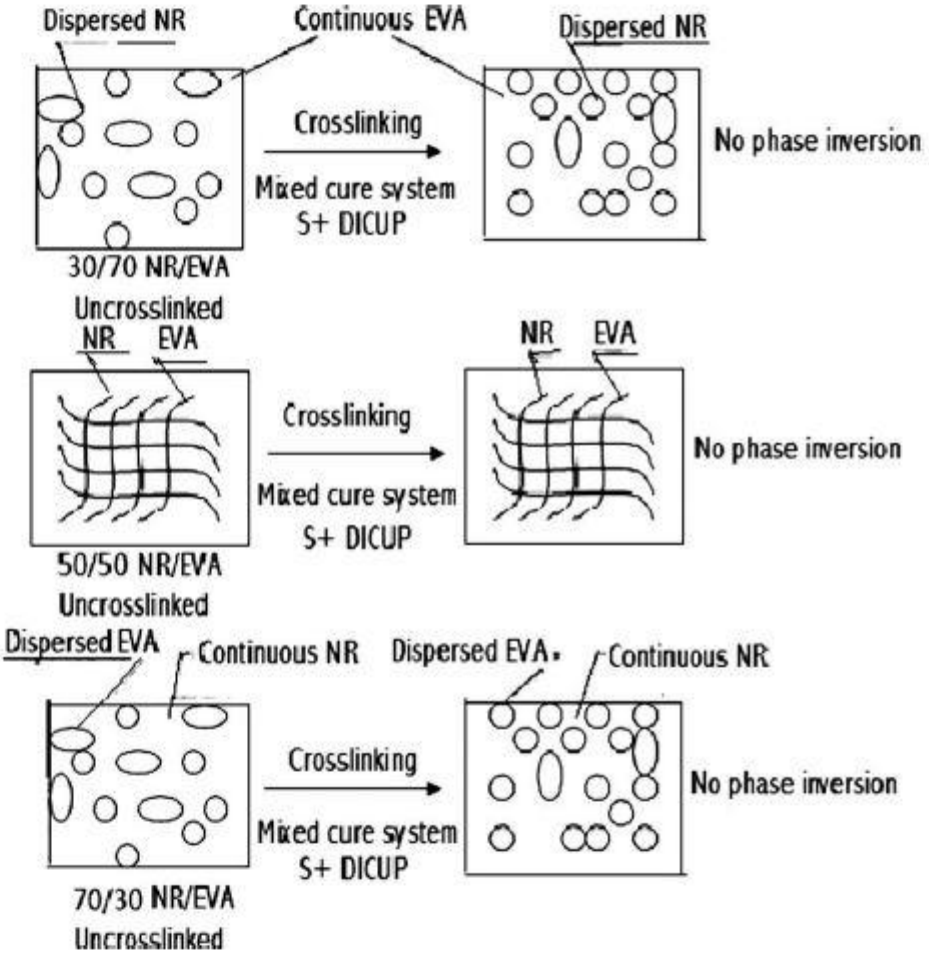


Figure 2.4 Schematic figure of NR and EVA blends

at 30/70, 50/50, and 70/30 weight ratio [44]

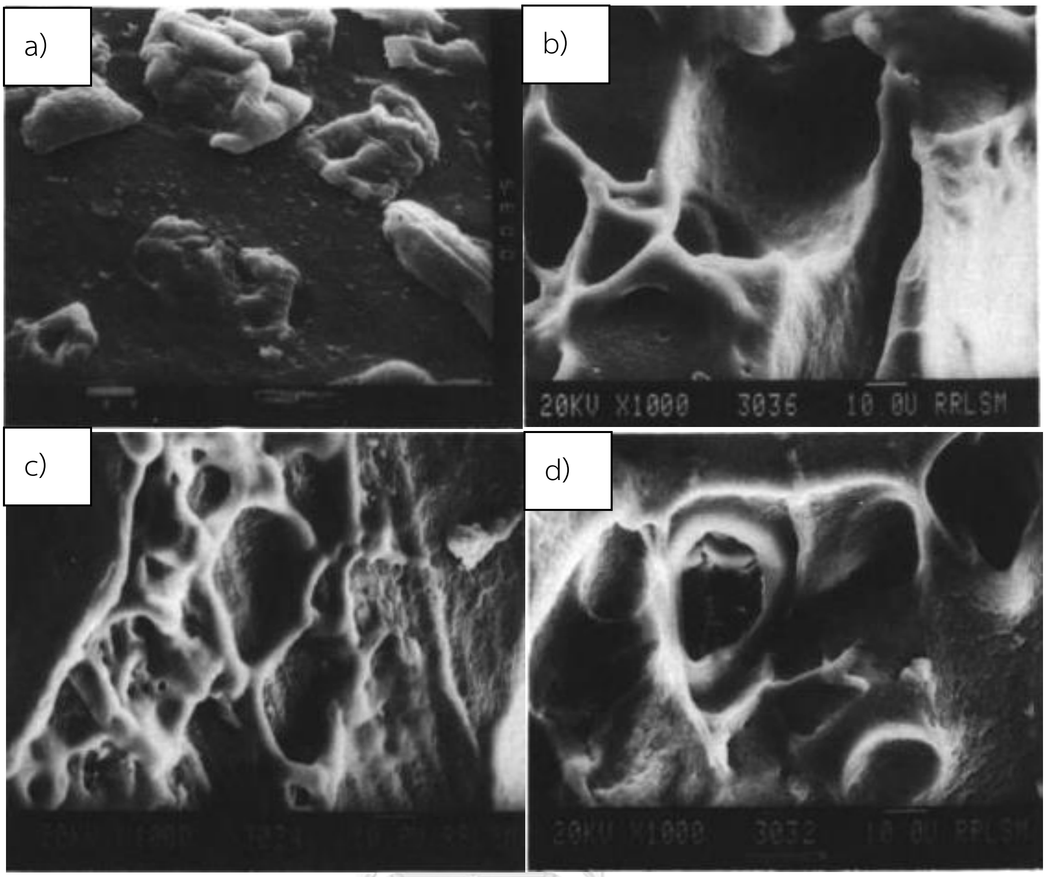


Figure 2.5 Morphology of EVA/NR blends (NR phase was extracted by benzene)

a) EVA30NR70, b) EVA40NR60, c) EVA50NR50 and, d) EVA60NR40 [39]

2.6 Thermoplastic Vulcanizates

Thermoplastic vulcanizate (TPV) is an interesting material which consists of both properties of thermoplastic and vulcanized rubber. The first commercial TPV was developed by Coran and coworkers [46, 47] which is a polypropylene (PP) / ethylene-propylene-diene rubber (EPDM) thermoplastic vulcanizate. The method used to prepare TPV is called dynamic vulcanization (DV) in which rubber dispersion and rubber crosslinking reaction occurs at the same time during mixing. This will make the rubber becomes the stable domain which will not agglomerate together [19]. The schematic figure of thermoplastic blend with rubber before and after dynamic vulcanization is shown in Figure 2.6. The target of making TPV is to achieve the material which has good mechanical properties similar to vulcanized rubber while the material can still be reprocessed [42, 48, 49].

Thermoplastic vulcanizates can be produced using either batch or continuous techniques. The most common batch mixers are internal mixers, such as the Banbury mixers, Brabender Plasti-Corder, and kneaders. For continuous techniques, twin screw extruder with co-rotating screw at high L/D is recommended [19]. Therefore, dynamic vulcanization of TPVs on extruders is more complex than that in batch mixer, because every step occurs simultaneously. For the batch mixer, the different steps of thermoplastic melting, rubber dispersion, and cross-linking are separated in time [48, 50].

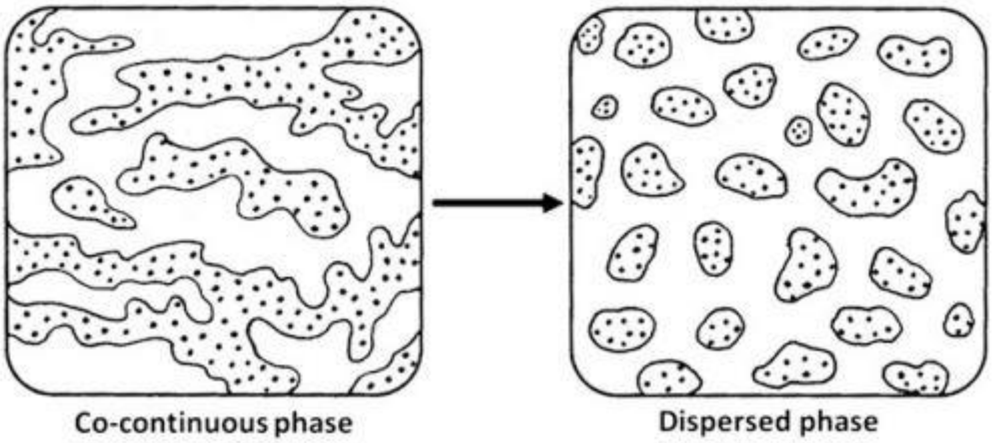


Figure 2.6 Morphology development of TPV by dynamic vulcanization [19]

(the dot area is rubber; the plain area is plastic)

The domain size of rubber in TPV is related to the mechanical properties of TPV. As reported in literature, EVA and NR was dynamic vulcanized using sulfur and incorporated with compatibilizer in order to reduce the rubber domain size as shown in Figure 2.7 [42]. From Table 2.3, the tensile strength and elongation at break of the EVA/NR 60/40 blend with 9 wt% of compatibilizer were both higher than those of blend without compatibilizer [42].

Table 2.3 Tensile properties of EVA/NR = 60/40 with and without compatibilizer [42]

EVA/NR = 60/40 weight ratio	Tensile strength (MPa)	Elongation at break (%)
Without compatibilizer	13.15	625
With 9 wt% compatibilizer	17.65	660

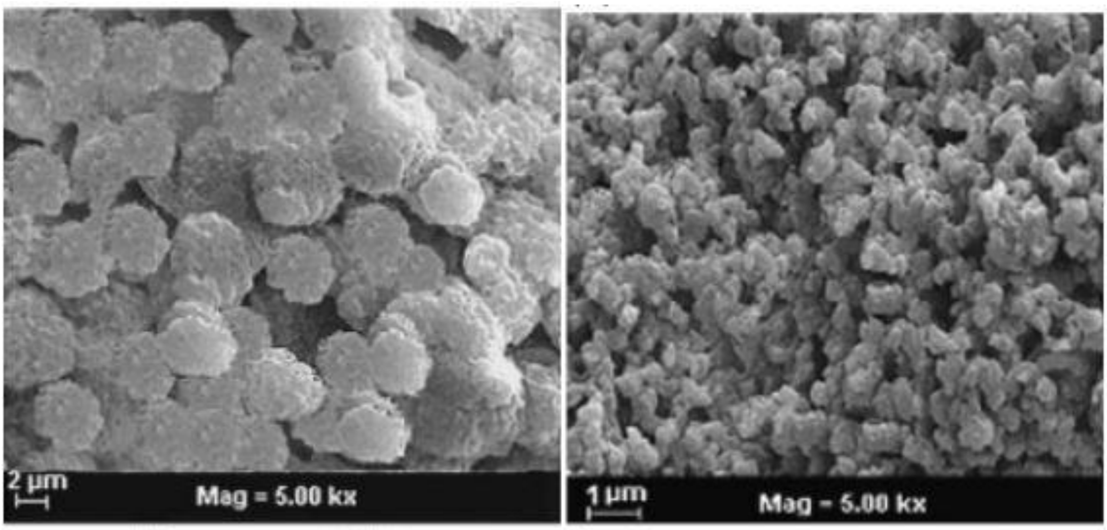


Figure 2.7 EVA/NR = 60/40 (left) without compatibilizer and (right) with 9 wt% compatibilizer [42]

2.7 Vulcanization Techniques

Vulcanization is a technical term refers to the crosslink process. This term normally uses for crosslinking process of elastomer or rubber. There are many vulcanization agents such as sulfur, phenolic resin, and peroxide [51-56]. For sulfur vulcanization, the advantages are good mechanical properties of vulcanized rubber and low cost of chemical ingredients. The limitation of sulfur technique is that the crosslinking reaction occurs only with rubber which has double bond in their molecules such as natural rubber (NR), ethylene-propylene-diene rubber (EPDM). Moreover, many chemical ingredients are necessary such as accelerators, activator, to achieve the good properties and reduce processing time of rubber via sulfur vulcanization. The peroxide has benefits over the sulfur vulcanization that it can be used to crosslink rubber both with and without double bonds to increase compatibility between plastic and rubber resulting in the small size of rubber particles. The detail of peroxide vulcanization was described in the section 2.8. Peroxide was selected to use as crosslinking agent in this research.

2.8 Peroxide Vulcanization

Peroxide is a compound which contains peroxy group (two oxygen atoms joined together) in its molecule. There are many types of peroxide such as hydrogen peroxide, hydro peroxides, and organic peroxides. Organic peroxide is commonly used in plastic and rubber processing. The popular organic peroxide is a dicumyl peroxide (DCP) because it is in a solid form and low price compared with other peroxides [19, 56, 57]. The chemical structure of DCP was shown in Figure 2.8. However, the DCP produces odor which is an acetophenone from the thermal decomposition reaction as shown in Figure 2.9 [55].

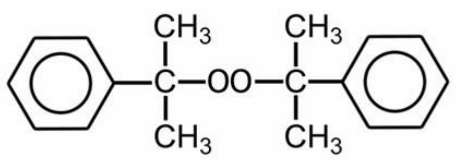


Figure 2.8 Chemical structure of dicumyl peroxide [55]

There are three steps in crosslinking reaction of polymer via peroxide. The first step is the thermal decomposition of peroxide. When the peroxide is heated, it decomposes to be the cumuloxy radicals. The second step is a radical transfer. The cumuloxy radical hits the polymer chain and then abstracts the hydrogen atom from the polymer chain. The polymer chain would be in excited state with some radical on its chain. Finally, the last step is crosslinking reaction where the polymer chains in excited state would hit together and form the carbon-carbon bond. In brief, the three steps are shown as followed:

Peroxide thermal decomposition: $R\text{-}O\text{-}O\text{-}R \rightarrow 2\ R - O*$

Radical transfer: $R - O* + P \rightarrow R - OH + P*$

Crosslinking reaction: $P* + P* \rightarrow P - P$

Where R-O-O-R is organic peroxide and P is polymer chain

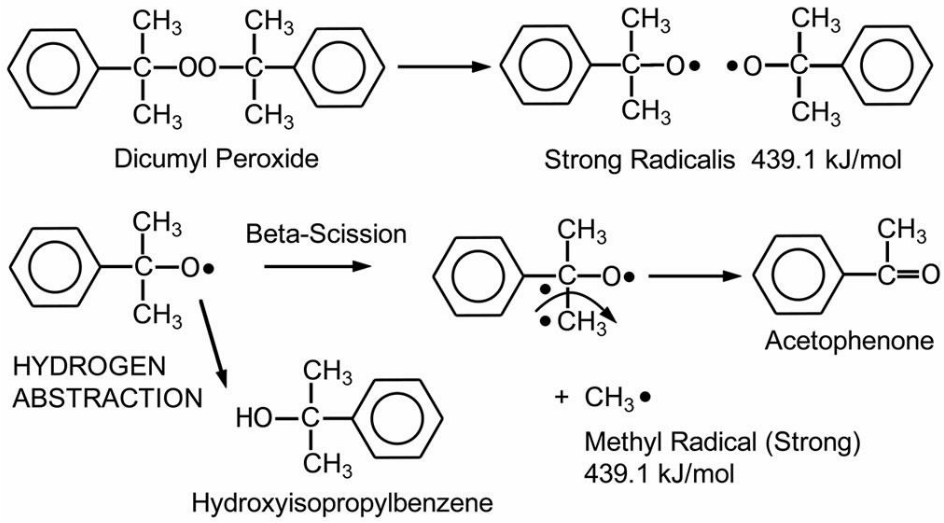


Figure 2.9 Thermal decomposition and radical formation of dicumyl peroxide [55]

From the literature, crosslink formation of natural rubber can occur in two forms via hydrogen abstraction and radical addition reaction as illustrated in Figure 2.10 [58]. The dominant crosslinking reaction of natural rubber is the hydrogen abstraction while the radical addition is dominant when the co-agent is introduced [58]. For ethylene vinyl acetate copolymer (EVA), there was a few literatures on the mechanisms of crosslinking reaction. Sato et al. [59] studied the effect of vinyl acetate content of EVA on crosslink formation of EVA using peroxide. They found that the torque of internal mixer during crosslinking EVA increased when vinyl acetate of EVA increased. The vinyl acetate group of EVA was also hydrolyzed to be the hydroxyl group. It was found that the crosslink density of EVA decreased with decrease of vinyl acetate group of EVA [59]. Therefore, the crosslinking reaction would occur more at vinyl acetate group of EVA than occur on ethylene part of EVA [59].

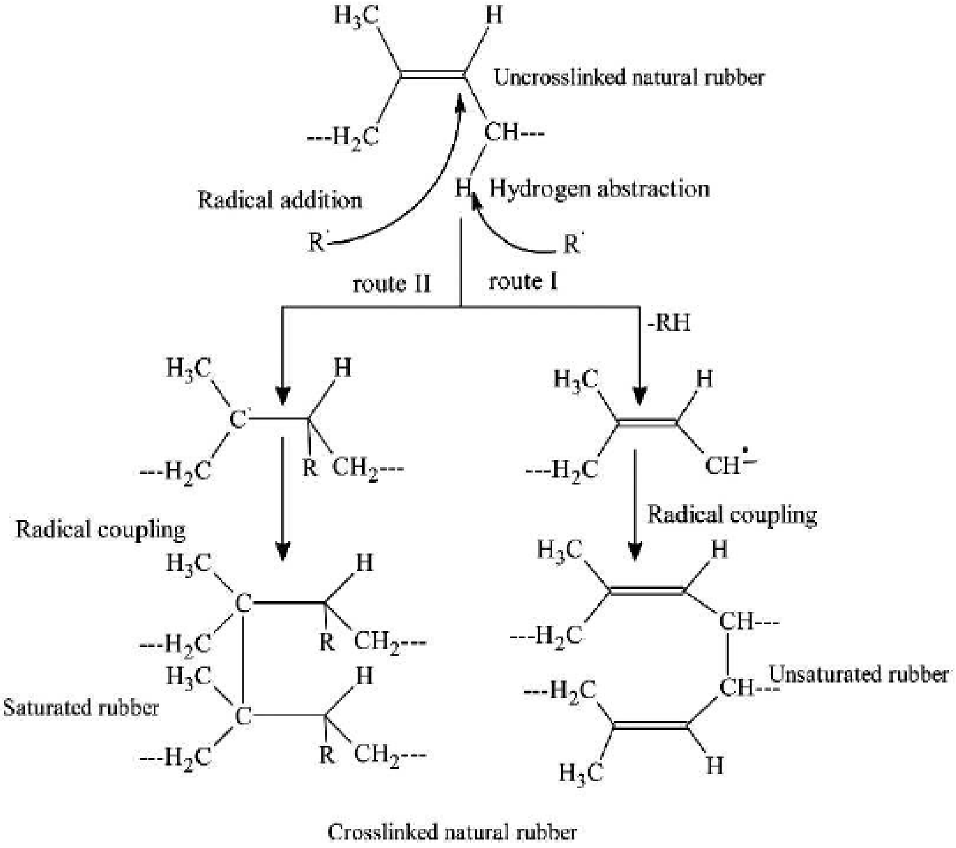


Figure 2.10 Possible mechanism of natural rubber vulcanization reaction using peroxide as crosslinking agent [58]

Peroxide is not only used to crosslink with elastomer, it can also increase the compatibility between polymer blends [20, 60]. Deetuam et al. [60] improved the properties of poly(lactic acid) (PLA) and natural rubber (NR) blown films by using a small amount of dicumyl peroxide (DCP). They found that adding a small amount of peroxide could increase the compatibility between PLA and NR, resulting in the improvement of the mechanical properties of the PLA/NR system. However, at high DCP content, the NR phase tended to self-crosslink rather than crosslink with PLA, which led to low compatibility between polymers. According to Samthong et al. [20], adding DCP could improve the thermal and mechanical properties of PLA/NBR composites by increasing the compatibility between PLA and acrylonitrile butadiene rubber (NBR), which led to the small domain size of rubber in the PLA matrix.

2.9 Mixing Method Affecting Properties of TPV

Normally, the thermoplastic phase should not be crosslinked, while the elastomer should be fully crosslinked. If the curing is introduced at the same time, it might crosslink both thermoplastic and elastomer phase. Therefore, the thermoplastic should be added after the elastomer is crosslinked. Babu et al. [48, 50] studied the effect of mixing method on the properties of polypropylene (PP)/ethylene octene copolymer (EOC) using peroxide vulcanization. Three mixing methods were compared. The first method was “Pre-Blending” where was the PP and EOC were melt-mixed before blending with peroxide to perform the dynamic vulcanization. The second method was “Phase-Mixing” where the peroxide was blended with the EOC to prepare the curative masterbatch. After that, the curative masterbatch was blended with the PP and then dynamically vulcanized. The last method was “Split Addition” where half of PP was added at first melt-mixing with EOC, then the other half was added after the dynamic vulcanization step. The sequences of mixing of Babu et al. work were shown in Figure 2.11 [48, 50]. The results showed that the mixing sequence affected morphological, thermal, mechanical, and dynamic mechanical properties. The “Phase-Mixing” showed the smallest rubber particles and best mechanical properties of TPV. The radicals from peroxide not only crosslinked the rubber, but the beta-scission reaction also occurred with PP leading to a shorter chain of PP. The mechanical properties of polymer with shorter chain was inferior to that of polymer with longer chain. They concluded that the optimal method to prepare the PP/EOC TPV was “Phase-Mixing” method because of the fully vulcanized rubber particles and small scission of thermoplastic.

In this research, the peroxide was used to crosslink the EVA as described in section 2.8. However, there was only few research concerning about the crosslinking reaction on thermoplastic in TPV, which might affect their properties, especially the flowability of materials. Therefore, study on mixing methods were carried out in this work.

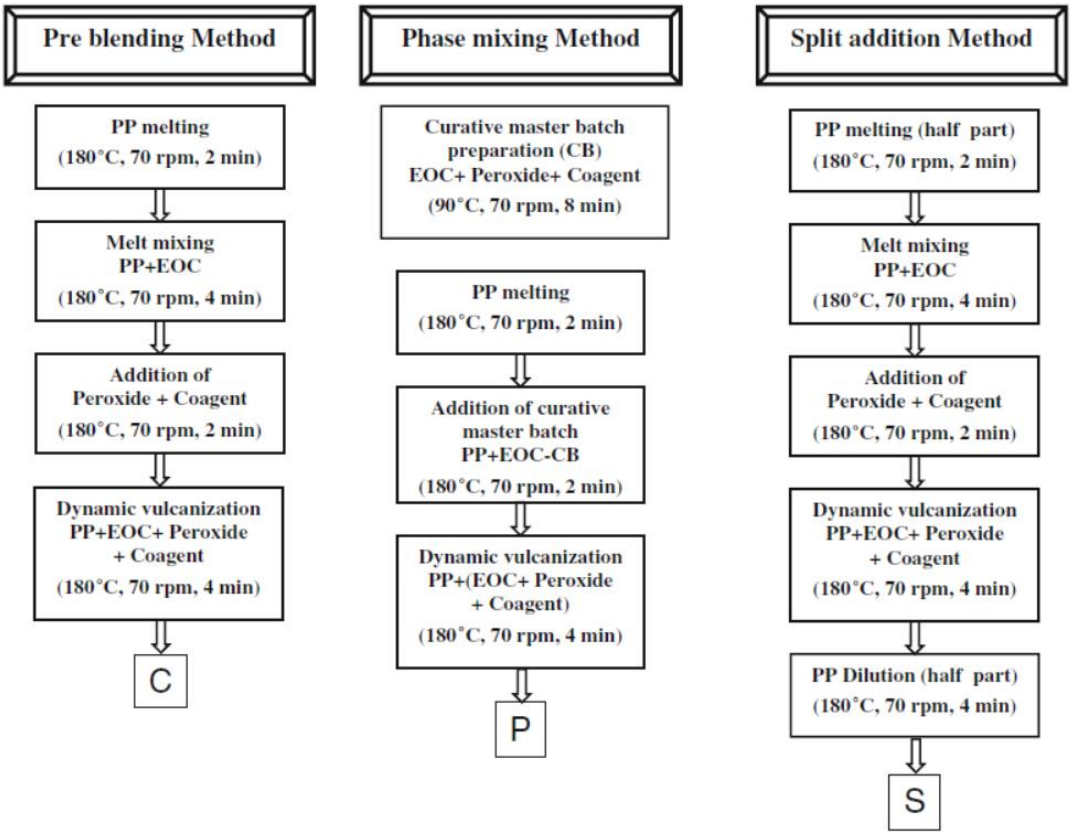


Figure 2.11 Mixing sequence of thermoplastic vulcanizate of polypropylene (PP) and ethylene octene copolymer (EOC) [48, 50]

CHAPTER III

CHARACTERIZATION TECHNIQUES

This chapter contained characterization techniques related to polymer and asphalt materials. The details of instruments, procedures, and sample preparation related to each characterization were described.

3.1 Morphology

Cross-sectional fractured surface of EVA/NR sheets were examined by means of a scanning electron microscope (SEM) (JEOL JSM 5410 LV, Tokyo, Japan) with and acceleration voltage of 15 kV. The sheet was fractured under liquid nitrogen and was fixed on stub. The samples were coated with osmium tetroxide (OsO_4) for 30 seconds to increase the contrast of NR in EVA phase because the OsO_4 selectively stained the double bonds of NR. The NR phase showed a light gray color while the EVA phase showed a dark gray color.

3.3 Degree of Crosslink by Solvent Extraction Technique

To evaluate the degree of crosslinking in terms of gel content and swelling ratio of the gel, the solvent extraction method was used. During the extraction, solvent (i.e., hot xylene) was diffused into the free volume between the crosslinking points, leading to the swelling behavior of the polymer. The non-crosslinked fraction was extracted from the blends, and the highly crosslinked fraction (gel) remained. This technique was performed according to ASTM D2765 [61].

The polymer sample was cut into small pieces which the size was less than 2 mm. It was weighed as W_0 before packed in the mesh bag and was weighed as W_1. It was then immersed in the boiled xylene (about 140 °C) for 8 hours in order to remove the soluble part of the polymer. The remained sample in mesh bag which was swollen was weighed as W_2. Eventually, it was vacuum dried at 80 °C for 6 hours to remove the xylene residue. Finally, the sample was weighed as W_3. The gel content and swelling ratio of gel were calculated using the following equations:

$$Gel\ content\ (\%) = \frac{W_3 - (W_1 - W_0)}{W_0} \times 100$$

$$Swelling\ ratio\ of\ gel\ (\%) = \frac{W_2 - (W_1 - W_0)}{W_3 - (W_1 - W_0)} \times 100$$

where W_0 = initial sample weight (g)

W_1 = initial sample weight + bag (g)

W_2 = swollen sample weight + bag (g)

W_3 = dried sample weight + bag (g)

3.4 Steady-state Shear Viscosity

The steady-state shear viscosity of polymer as a function of shear rate at 190 °C was measured using a capillary rheometer (Yasuda Seiki Seisakusho, 140 SAS-2002, Hyogo, Japan). The configuration of capillary rheometer was shown in Figure 3.1. A circular die of 20 mm in length and 2.0 mm in diameter (L/D ratio = 10) was used in this test. The shear rate was varied in the range of 2 – 120 s^{-1}. The polymer sample was added in the chamber that was preheated to the tested temperature. The machine was automatically set to push the polymer out from the die at each shear rate. Steady-state shear viscosities were recorded and were plotted against the shear rate. This graph is called “flow curve”. The photos of the extruded strand obtained at any shear rate were taken to observe their appearance.

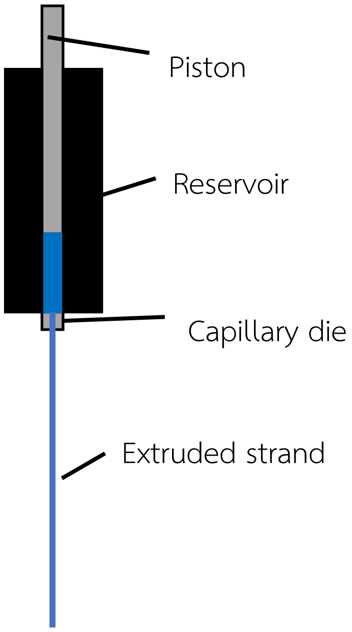


Figure 3.1 Configuration of capillary rheometer and obtained extruded strand

3.5 Thermal Properties

Thermal properties (i.e., glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), and enthalpy of melting (ΔH_m) were evaluated by means of differential scanning calorimetry (DSC) (DSC1 module, Mettler Toledo). The sample was firstly heated from −100 to 150 °C at a heating rate of 10 °C/min and maintained at 150 °C for 3 min. Then, it was cooled down to −100°C with a cooling rate of 10 °C/min. Finally, it was secondly heated from −100 to 150 °C again at a heating rate of 10 °C/min. The degree of crystallinity (X_c) was calculated using the following equation:

$$X_c\,(\%) = \frac{\Delta H_m}{\emptyset_{EVA} \times \Delta H_{m,100\%}} \times 100$$

Where ΔH_m = Enthalpy of melting (J/g)

$\emptyset_{EVA}$ = mass fraction of EVA in the blend (%)

$\Delta H_{m,100\%}$ = Enthalpy of melting of polyethylene with 100% crystallinity = 277.1 J/g [62]

3.6 Dynamic Mechanical Properties

Dynamic mechanical properties in the solid state including tensile storage modulus (E') and tensile loss modulus (E'') were characterized using a dynamic mechanical analyzer (DMA) (Rheogel E4l000, UBM, Kyoto, Japan). The sheet of polymer sample with thickness of 0.150 mm was cut into rectangular shape with length of 2.5 cm and width of 0.5 cm. The sample was gripped with the gap of 1 cm. The test was performed at temperature from -100 to 120 °C at a heating rate of 2 °C/min and a constant frequency of 10 Hz in a tension mode. The glass transition temperature (T_g) of the polymer sample was obtained from the peak of E''.

3.7 Mechanical Properties

The tensile test was performed according to ASTM D412 at room temperature using a tensile testing machine (Little Senstar, Tokyo, Japan) [63]. The dumbbell-shaped samples were punched from the sample sheets. The sample was gripped with the initial length of 1 cm then it was stretched until it was broken using the crosshead speed of 300 mm/min. The stress-strain curve of polymer sample was recorded. Ultimate strength and elongation at break of the polymer sample was obtained from the last point of stress and strain curve.

For the test of tension set as shown in Figure 3.2, the dumbbell-shaped samples were stretched to 100% elongation (two times of the initial length) without being broken and were held for 10 minutes at room temperature. After removing the force, the sample was left for 10 minutes. The gauge length was measured before and after the test. The tension set was calculated by using the following equation.

$$Tension\ set\ (\%) = \frac{\mathrm{L} - \mathrm{L}_0}{\mathrm{L}_0} \times 100$$

where L = length after stretched (mm)

L_0 = initial length (mm)

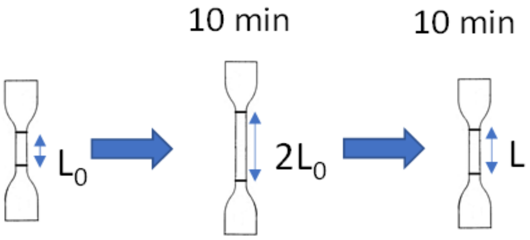


Figure 3.2 Test of tension set.

3.8 Penetration Test

Penetration value of asphalt indicates the hardness of asphalt. The test was performed according to ASTM D534 [64]. The asphalt sample was melted and poured into a test cup. It was left at room temperature until it was solid. The place where the sample cup was placed on should be calibrated to be horizontal with ground. The sample was immersed in the water at 25 °C for 1 hour before tested. A needle with 100 g weight was placed over asphalt surface and dropped onto asphalt for 5 seconds then it was removed. The penetration value unit was recorded automatically and reported with unit of 0.1 mm. For example, if the needle penetrated for 0.6 mm, the penetration value was reported as 60 (0.1 mm). The penetration apparatus was shown in Figure 3.3.

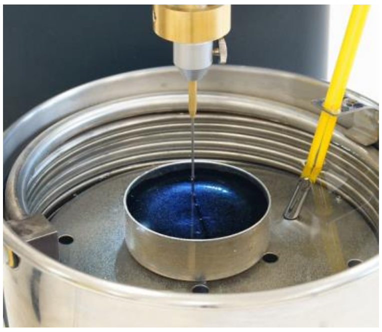


Figure 3.3 Penetration apparatus

3.9 Softening Temperature Test

Ring-and-ball softening temperature was measured according to ASTM D3635 [65]. The asphalt was heated until it melted, then poured into the ring. The ring with asphalt was placed in the apparatus and was immersed in a water bath as shown in Figure 3.4 (left). The bath was heated with a heating rate of 5 °C/min. The softening temperature was recorded when the ball dropped to the base of apparatus as shown in Figure 3.4 (right).

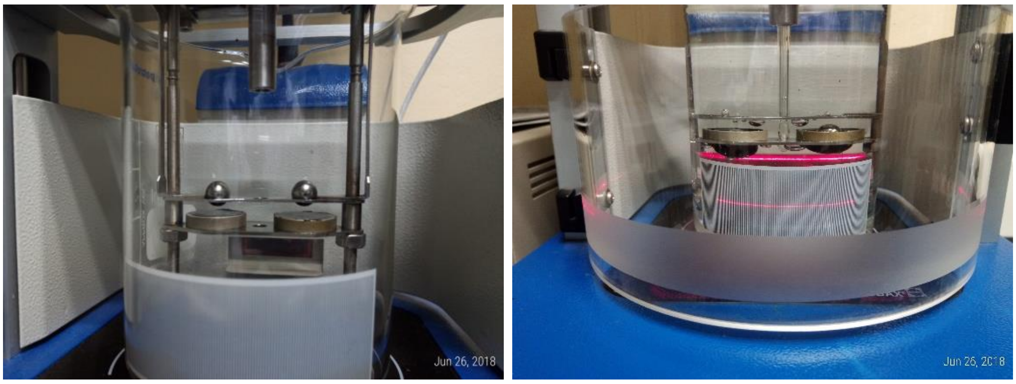


Figure 3.4 Softening temperature apparatus at start test (left) and end test (right)

3.10 Ductility Test

Ductility relates to an ability of asphalt to stretch as a thin film to cover the aggregate. The test was performed according to ASTM D113 [66]. The asphalt was heated and poured into the specific mold as shown in Figure 3.5. The plate under the mold should be applied with the silicone grease to prevent the asphalt stuck on the mold. Then, the mold with asphalt was immersed in the ductility tester with controlled the temperature of 25 °C for 1 hour before test. The pull speed was 5 cm/min. The value of ductility was recorded in term of length at break in unit of centimeters. However, the ductility test has the limited bath length of 150 cm. Therefore, for the sample that was not broken even it was stretched to 150 cm, the value of ductility was reported as “>150 cm”.

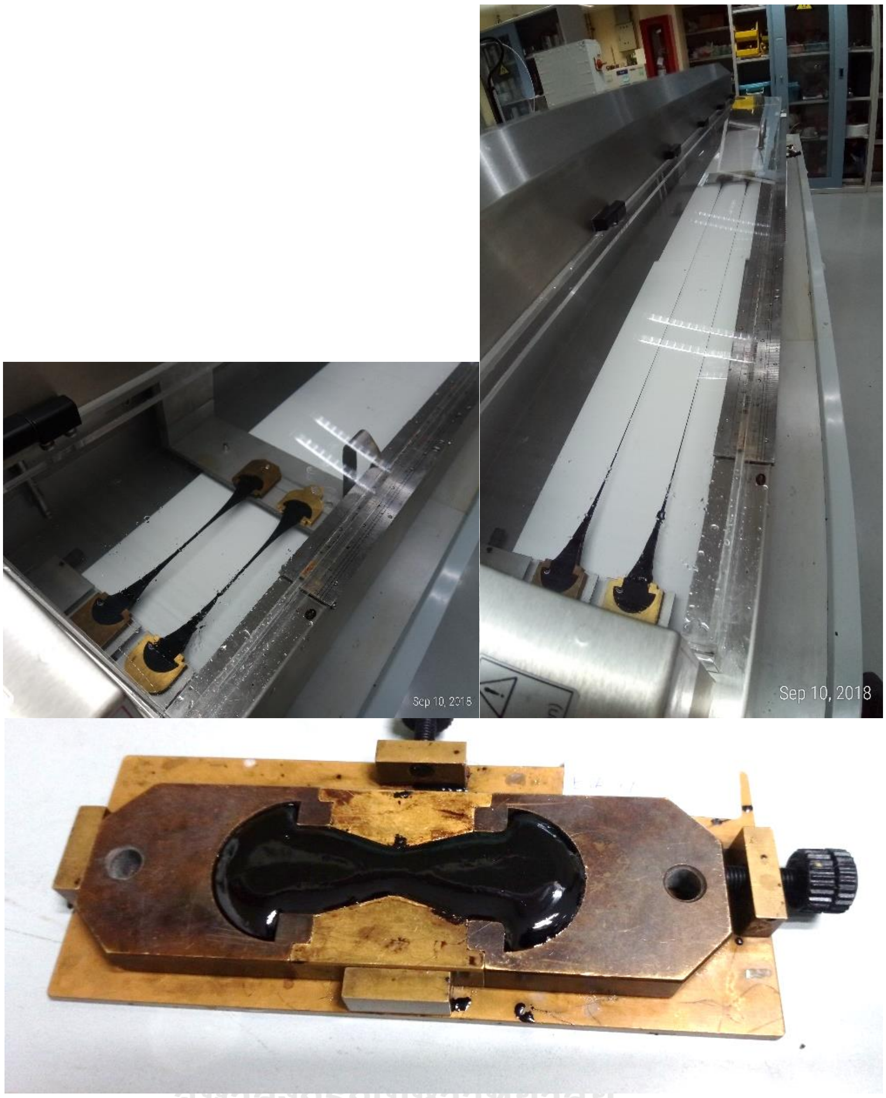


Figure 3.5 Ductility test of asphalt

3.11 Elastic Recovery Test

Elastic recovery is an ability of asphalt material to return to its original shape. The test was performed according to ASTM D6084 [67]. The sample was heated and poured into the specific mold as shown in the Figure 3.6. The plate under the mold should be applied with the silicone grease to prevent the asphalt stuck on the mold. After the asphalt sample became solid, it was immersed in the water bath of ductility apparatus with controlled temperature of 25 °C for 2 hours before test. The test was started with the sample being stretched at rate of 5 cm/min until the length equal to 10 cm. The sample was cut at the middle and left for 1 hour. Eventually, the distance between each cut-end was measured and the elastic recovery was calculated from the ratio of the distance between cut-end to the stretch length which was 10 cm.

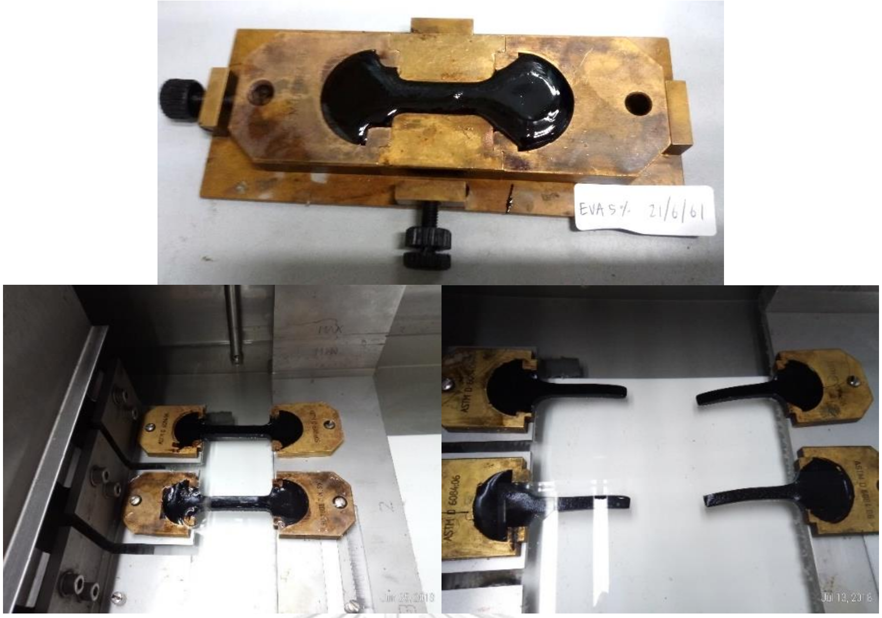


Figure 3.6 Elastic recovery of asphalt

3.12 Dynamic Shear Rheometry

For the test performed using dynamic shear rheometer, the asphalt was heated and poured into the rubber mold with diameter of 1 cm and thickness of 2 mm. The test was performed using dynamic shear rheometer (Physica MCR 501, Anton Paar, Austria). First, the gap was automatically set to zero value. Second, the chamber was heated to the test temperature and maintained for 2 minutes. The asphalt sample was placed between the parallel plate and left in the chamber for 5 minutes. The gap was set to 1 mm. Excess asphalt released from the plate was wiped out using the hot spatula which was prior exposed to fire. Then, the test was performed. In this work, there were two tests performed which were performance grading (temperature sweep mode) and frequency sweep test at 60 °C. The detail of each test was provided in the following topics.

3.12.1 Performance Grading

Performance grade of PMA was evaluated according to ASTM D7175 [68] by dynamic shear rheometer (Physica MCR 501, Anton Paar, Austria) using a constant strain of 12% and frequency of 10 rad/s. The initial temperature was 58 °C for neat asphalt and 64 °C for the PMA. The temperature was increased at an increment of 6 °C for each test until the value of rutting parameter ($G^*/\sin\delta$) was lower than 1. The temperature with value of $G^*/\sin\delta$ equaled to 1 is called the fail temperature.

3.12.2 Rheological Properties at 60 °C in a Frequency Mode

Rheological properties such as storage modulus (G'), loss modulus (G''), phase angle (δ), complex viscosity (η^*) were measured using dynamic shear rheometer (Physica MCR 501, Anton Paar, Austria), a strain-controlled parallel-plate type rheometer in frequency-sweep mode with a plate diameter of 25 mm. The test was performed with a gap of 1 mm at constant temperature of 60 °C with angular frequency of 100 – 0.1 rad/s and a constant strain of 12% which is within the linear viscoelastic region of the asphalt.

3.13 Fluorescence Microscopy

Microstructure of polymer modified asphalt was observed by fluorescence microscope (DM 2500P, Leica) with a magnification of 20x. The sample was collected from mixer and placed on microscopic glass slide then covered with cover glass. The glass slide was placed at hot stage apparatus (T95-HS, Linkam, UK) and heated from room temperature to 150 ˚C and then held at constant temperature of 150 ˚C until the molten asphalt become thin film under the cover glass. The sample preparation was shown in Figure 3.7. The photographs were recorded using digital camera attached to the microscope.

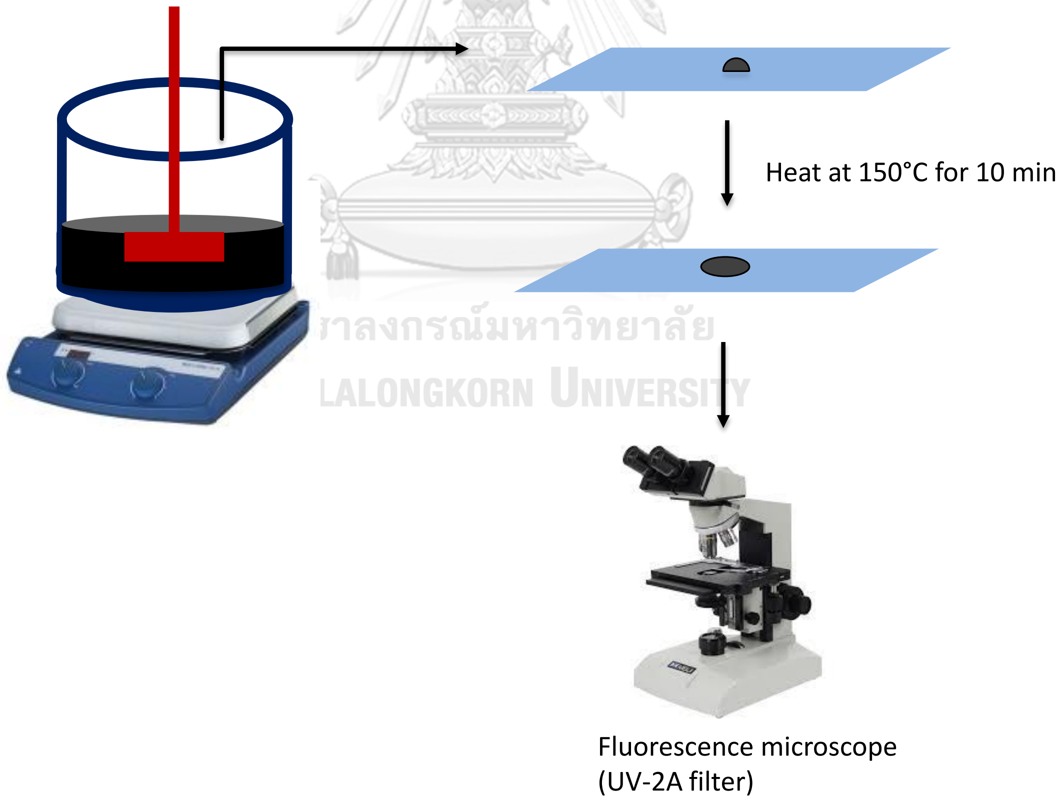


Figure 3.7 Sample preparation for fluorescence microscopy

3.14 Brookfield Viscosity Test

Brookfield viscosities of neat asphalt and polymer modified asphalt were measured by Brookfield viscometer (DV-III, Brookfield) at constant shear rate of 18.6 s^{-1} (rotor speed of 20 rpm) using spindle 21 geometry as shown in Figure 3.8. The asphalt was melted at test temperature and poured into the test tube for about 8 g. The test tube was placed in the chamber and the rotor equipped with test spindle was dipped into the asphalt with the marked level on the apparatus. The viscosities were recorded every 1 minute from 0 to 10 minutes and every 5 minutes until 60 minutes. It was found that the viscosity was constant after 10 minutes. The viscosities of asphalt at test temperature of 135, 150, and 165 °C recorded after 1 hour. For the 135 °C, the equipment was setup according to ASTM D4402 [69].

Figure 3.8 Brookfield viscometer and the spindle number 21

3.15 Storage Stability of Polymer Modified Asphalt

Storage stability or separation tendency of polymer from polymer modified asphalt was evaluated according to ASTM D7173 [28]. This test was performed only on the asphalt blended with polymer. The asphalt sample was poured into an aluminum tube with a diameter of 25.4 mm and height of 136.7 mm as shown in Figure 3.9. The tube was closed and stored in the oven at 163 °C for 5 days. The tube was cooled to -10 °C for 2 hours and cut into three section as shown in Figure 3.9. The difference of softening temperature of PMA collected from top and bottom sections of the tube were used to evaluate the storage stability of PMA.

Figure 3.9 Appearance of aluminum tube (left) and its three sections: Top, Middle, and Bottom (right)

CHAPTER IV

STUDY ON NATURAL RUBBER / ETHYLENE VINYL ACETATE COPOLYMER THERMOPLASTIC VULCANIZATES

This chapter focused on the preparation of thermoplastic vulcanizates (TPV) based on ethylene vinyl acetate copolymer (EVA) and natural rubber (NR). The effects of mixing method and peroxide content on properties of TPV were investigated to find the suitable method to produce EVA/NR TPV. In this work, three mixing methods were compared (i.e., NR-DV, Split-DV, and All-DV). Appearance, morphology, gel content, swelling ratio as well as thermal, dynamic mechanical, rheological, and mechanical properties were investigated. The DCP content of sample from the method resulting in the best mechanical properties was varied to investigate effect of peroxide content on properties of TPV.

4.1 Materials

Ethylene vinyl acetate copolymer (EVA) grade N8038 with vinyl acetate content of 18 wt% was used as a thermoplastic and purchased from TPI Polene Public Co., Ltd. (Thailand). Natural rubber sheet (NR) was used as an elastomer and purchased from Bothong Rubber Fund Cooperative Ltd. (Thailand). Dicumyl peroxide (DCP) with 95 % purity was used as a crosslinking agent and obtained from Nacalai

Tesque, Inc. (Japan). Octadecyl-3-(3,5-di-tertbutyl-4-hydroxyphenyl)-propionate (Irganox 1076) and tris(2,4-di-tert-butylphenyl)phosphate (Irgafos 168) were used as thermal stabilizers where Irganox 1076 was a primary TS and Irgafos 168 was a secondary TS and supplied from Ciba (Japan). Solvent-grade mixed xylene was used as received without further purification as the solvent to evaluate the gel content of thermoplastic vulcanizate.

4.2 Preparation of EVA/NR TPVs

EVA pellets and NR sheets were dried in a vacuum oven at 60 °C for 4 hours to remove moisture. The EVA and NR were melt-mixed using an internal mixer with a chamber size of 30 cm^3 (Labo-Plastomill, Toyoseiki, Nagano, Japan). The mixing method was separated into two steps. The first step was the dynamic vulcanization at 190 °C by pre-melting the polymer for 1 minute and then mixing with DCP for 5 minutes in order to crosslink the polymer at this step. The dynamic vulcanization time of 5 minutes was enough to decompose all DCP as the crosslinking profiles shown in Figure A.1 (the DCP decomposed within 1 minute at temperature of 190 °C). The second step was the further blending of the product from the first step with the remaining polymers and thermal stabilizers (TS) at 130 °C for 6 minutes to obtain the EVA/NR blends with the final EVA/NR weight ratio of 50/50. Each TS was added at 0.5 phr in order to inhibit the thermal degradation and stop the vulcanization reaction by consuming the free radicals in the systems. Hence, the first mixing step was the vulcanizing step, while the second mixing step was the un-vulcanizing step. The rotor speed was fixed at 60 rpm throughout the mixing process. After finishing all mixing steps, the thermoplastic vulcanizates (TPVs) were obtained. Herein, three different mixing methods were carried out, as shown in the Figure 4.1.

Method 1 NR-DV: Only the NR was specifically dynamically vulcanized, while the EVA was un-vulcanized and was added in the un-vulcanizing mixing step.

Method 2 Spilt-DV: The NR and half of the EVA were dynamically vulcanized. Subsequently, the remaining EVA was added in the un-vulcanizing mixing step.

Method 3 All-DV: All the NR and EVA were dynamically vulcanized. Only thermal stabilizers were added in the un-vulcanizing mixing step.

The abbreviations of the TPVs prepared by the NR-DV, Split-DV, and All-DV were denoted as nTPVDx, sTPVDx, and aTPVDx, respectively, the letter “x” denoted DCP content in the TPV blends. To compare each method, the DCP content was fixed at 2 phr. The final formulation of EVA/NR TPVs were given in Table 4.1. Moreover, the detailed calculation of the actual sample compositions were shown in Appendix B. Finally, the obtained blends were compressed into rectangular films using a compression-molding machine at a temperature of 130 °C under 20 bars for 10 minutes for further characterization.

Moreover, to compare the properties between uncured and cured samples, the cured EVA and NR samples were prepared by conventional crosslinking process. The DCP content at 2 phr was mixed with the polymer (EVA or NR) using an internal mixer at 100 °C (the decomposition of DCP at this temperature is negligible [70, 71]) with a screw speed of 60 rpm for 6 minutes. Then, the obtained sample was compressed into a thin film and crosslinked using a compression molding machine at 190 °C under 20 bars for 10 minutes. The nomenclatures of uncured EVA, uncured NR, cured EVA, and cured NR are uEVA, uNR, cEVA, and cNR, respectively.

Table 4.1 Formulations of the EVA/NR thermoplastic vulcanizates

Formula	Mixing method	EVA (wt%)	NR (wt%)	DCP (phr)	TS1* (phr)	TS2* (phr)
nTPVD2	NR-DV	50	50	2	0.5	0.5
sTPVD0	Split-DV	50	50	0	0.5	0.5
sTPVD1	Split-DV	50	50	1	0.5	0.5
sTPVD2	Split-DV	50	50	2	0.5	0.5
sTPVD3	Split-DV	50	50	3	0.5	0.5
aTPVD2	All-DV	50	50	2	0.5	0.5

*TS1: Irganox 1076, TS2: Irgafos 168

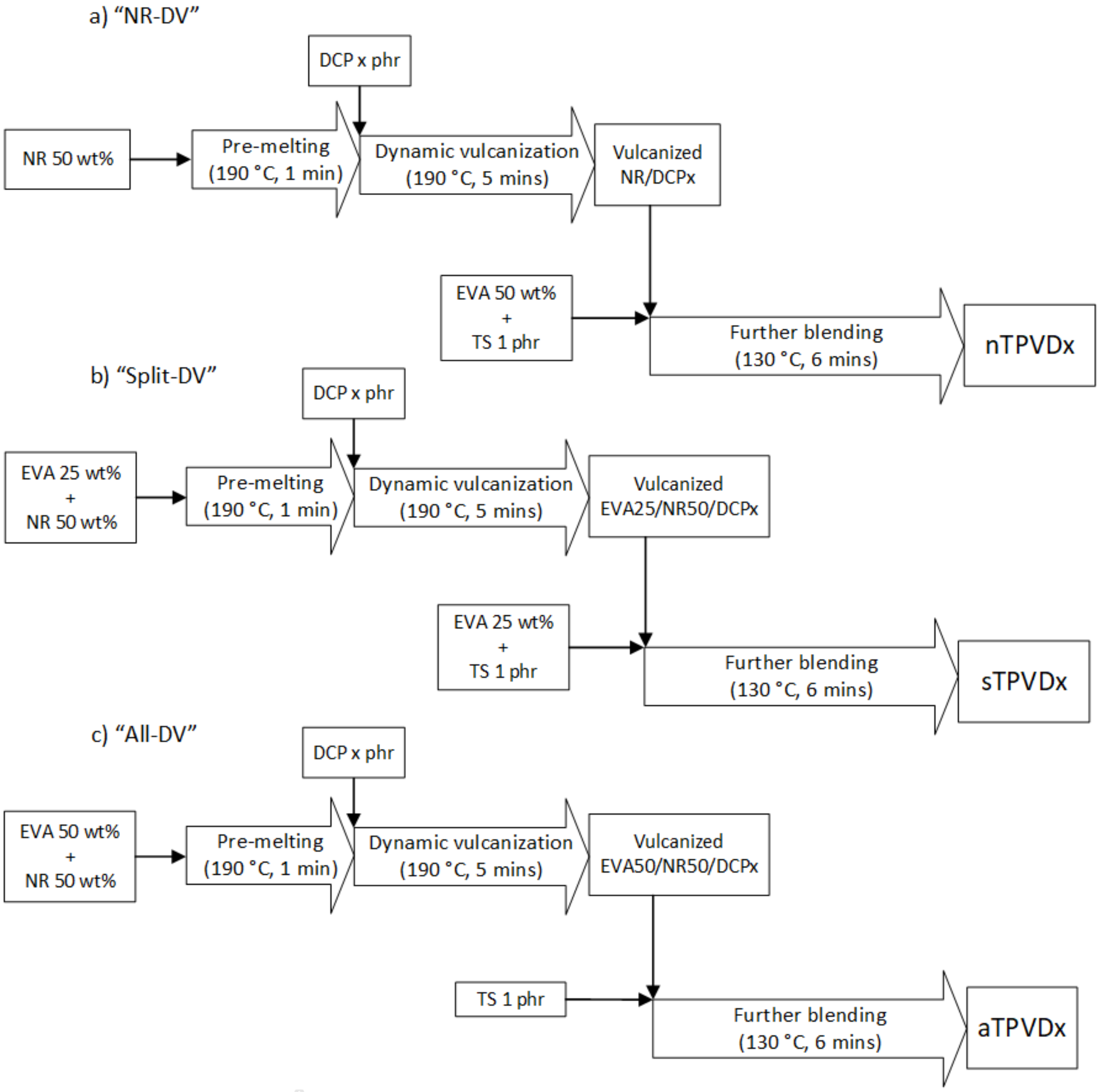


Figure 4.1 Schematic diagram of mixing methods: a) NR-DV b) Split-DV c) All-DV

"x" is DCP content (phr)

4.3 Result and Discussions

4.3.1 Effect of Mixing Method

4.3.1.1 Morphology

The optical photographs of the compressed film containing 2 phr of DCP prepared by three different methods were shown in Figure 4.2. The sample from NR-DV method (nTPVD2) had a rough surface with numerous clearly large rubber particles than those from Split-DV method (sTPVD2) and All-DV method (aTPVD2) because the rubber phase in nTPVD2 sample was preferentially vulcanized in the vulcanizing mixing step, leading to a formation of the highly crosslinked NR domains, which were hardly dispersed in the blend. In contrast, the surface of samples prepared by Split-DV and All-DV methods were relatively smooth, implying good appearance owing to well dispersion of NR phase in the matrix. Note that there were small white particles dispersed on the surface of aTPVD2 sample, which might be the self-crosslinked EVA domain because the EVA phase was also introduced in the dynamic vulcanization step at the same time as NR phase. The different appearance of sample prepared via different methods could imply the different properties of TPV. Because the nTPVD2 sample contained large rubber particles in the matrix, making it not suitable to use in any application, it was not further examined.

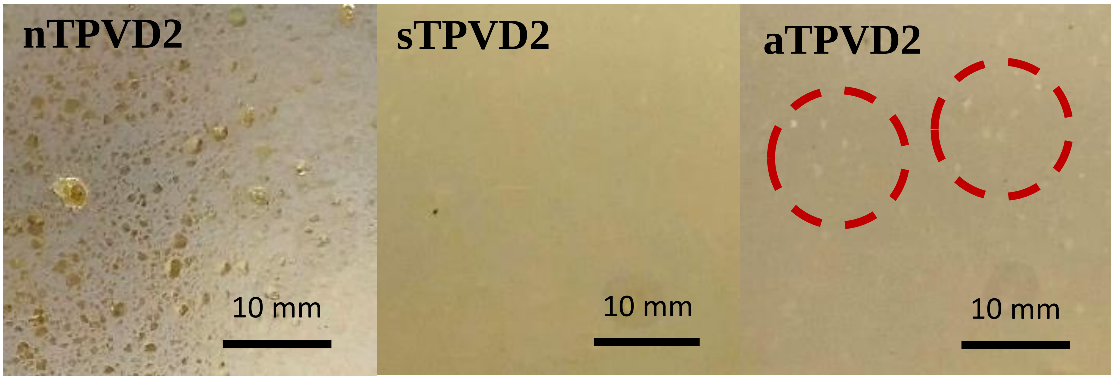


Figure 4.2 Optical appearance of compression molded TPV samples

The SEM images of the fractured surfaces of sTPVD2 and aTPVD2 with the magnification of 2,000 and 5,000 times were shown in Figure 4.3. The samples were stained with osmium tetroxide to increase the contrast between NR and EVA. According to Rajan et al. [58], peroxide-initiated crosslink reaction for NR only occurred at the secondary carbon atom; thus, the double bonds still remained in the NR chains. The osmium can attach to the double bond of hydrocarbon molecule improving the contrast between NR and EVA phases. From the SEM images, the grey area was NR phase while the black area was EVA phase. It was observed that the fractured surface of sTPVD2 was smoother than that of aTPVD2 as shown in Figure 4.3a and Figure 4.3c. However, the size of rubber domain of both samples were similar which could be observed at higher magnification as shown in Figure 4.3b and Figure 4.3d.

During dynamic vulcanization at the first step of the Split-DV and All-DV methods, the NR phase was broken by the high shear force of highly viscous EVA into the dispersed domains and distributed throughout the EVA matrix while simultaneously crosslinked by peroxide radical. However, aTPVD2 in which all EVA were dynamically crosslinked with NR at the first step might contain more self-crosslinked EVA than that of sTPVD2. Therefore, degree of crosslink in the sample should be evaluated to understand the crosslink mechanism of these systems.

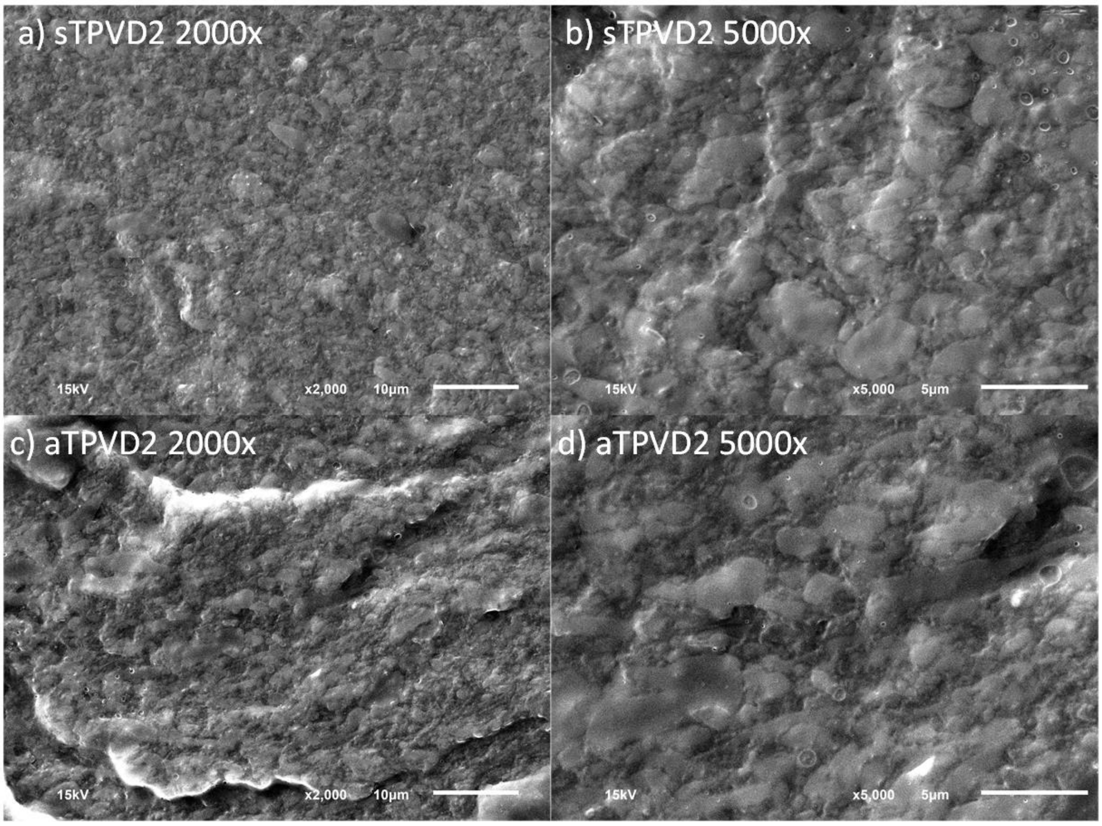


Figure 4.3 Fractured surfaces of EVA/NR TPVs with magnification of 2,000 and 5,000 a) sTPVD2 2000x, b) sTPVD2, 5000x, c) aTPVD2 2000x, and d) aTPVD2 5000x

4.3.1.2 Gel Content and Swelling Ratio

The gel content and swelling ratio of cured EVA, cured NR, and EVA/NR TPVs were shown in Table 4.2. Gel content (%gel) refers to the amount of highly crosslinked fraction in the TPVs, while the swelling ratio of gel (%swell) refers to the crosslink density.

As expected, the uncured samples (uEVA, uNR) were totally soluble in hot xylene and no gel was detected. Whereas the cured samples showed high value of gel content. The cured sample was prepared by the conventional vulcanization, the polymer sample was blended with DCP at low temperature and was compressed in the mold and the peroxide radicals made the polymer chains connected together to form the crosslinking points. For the dynamic vulcanization, the sample was sheared and was crosslinked simultaneously. Some of crosslinking points can be formed only in the crosslinked polymer domain. Therefore, the TPVs showed lower gel content and higher swelling ratio of gel than those of cured samples. The gel contents of sTPVD2 and aTPVD2 were similar and more than that of nTPVD2. As can be observed from the sample prepared from NR-DV method, nTPVD2 had lower swelling ratio than sTPVD2 and aTPVD2. The crosslink reaction occurred only in NR phase for nTPVD2, while DCP randomly crosslinked both EVA and NR for sTPVD2 and aTPVD2. However, the gel content of polymer refers only to the overall crosslinking points occurred in the polymer sample. More techniques should be used to evaluate the crosslinking points of EVA and NR, separately.

Table 4.2 Gel content (%gel) and swelling ratio of gel (%swell) of uncured samples, cured samples, and EVA/NR TPVs

Formula	%gel	%swell
uEVA	Totally soluble	
uNR	Totally soluble	
cEVA*	92.86 ± 0.05	764.92 ± 30.36
cNR*	94.39 ± 1.01	500.65 ± 30.79
nTPVD2	36.73 ± 8.36	900.85 ± 171.00
sTPVD2	47.53 ± 0.46	1,051.75 ± 19.15
aTPVD2	46.45 ± 13.51	1,135.71 ± 133.68

*cEVA and cNR were cured sample contained DCP 2 phr.

4.3.1.3 Thermal Properties

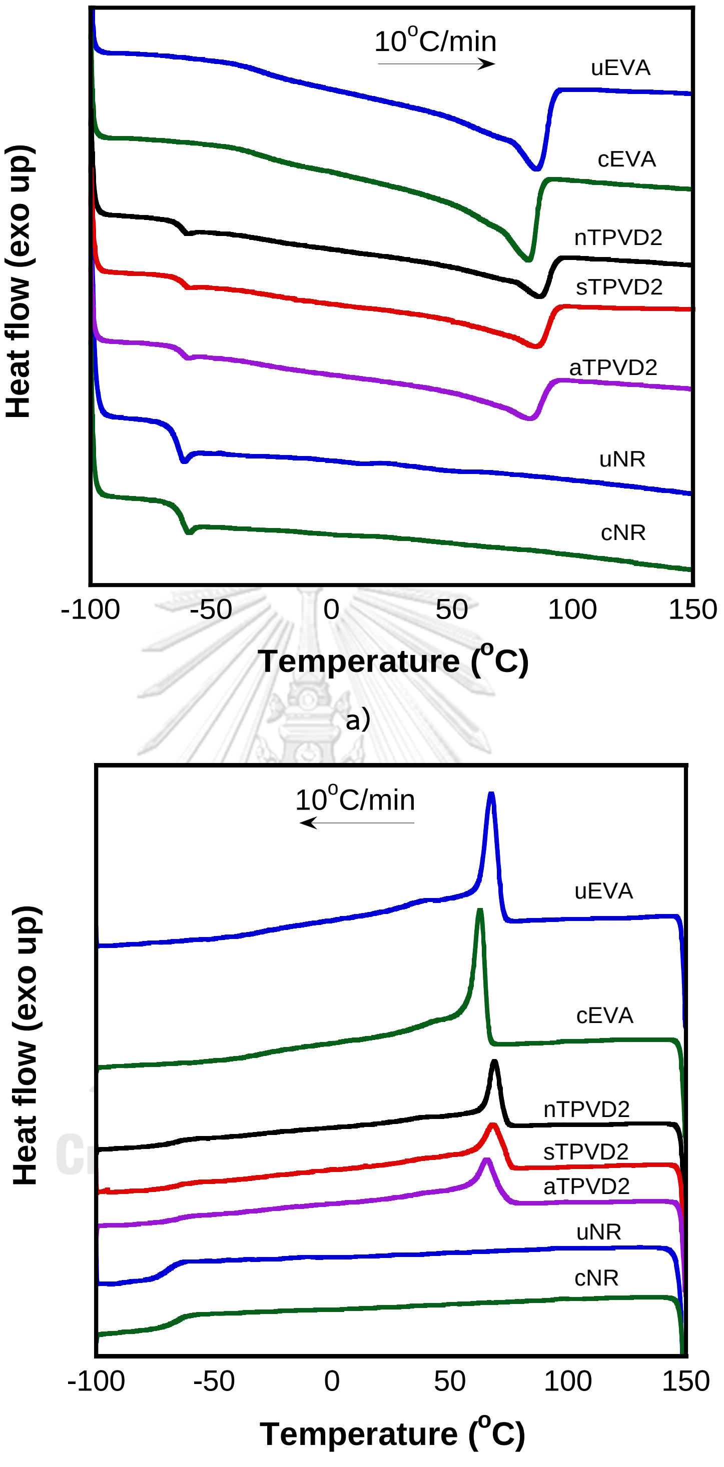
The thermal properties were used to indirectly evaluate the type of crosslinking points in the TPVs. The DSC thermogram of uncured EVA, uncured NR, cured EVA, cured NR and EVA/NR TPVs at the 2nd heating and cooling scans were shown in Figure 4.4 and their thermal properties were summarized in Table 4.3. It was found that cured EVA had lower crystallization temperature (T_c) and melting temperature (T_m) than uncured EVA because the crosslinked part in EVA restricted the crystallization behavior of EVA in cooling state, resulting in the formation of imperfect crystals which required less thermal energy to melt. The decrease of melting temperature was also found in peroxide-crosslinked HDPE [72] and crosslinked EVA [73-75]. For NR, the crosslinking reaction could be observed from the shift of glass transition temperature (T_g). It was found that T_g of uncured NR was -65.09 °C, while that of cured NR was -62.53 °C. When the motion of polymer chains is restricted by the crosslink structure, it can be observed by the shift of T_g to higher temperature [76]. However, the T_g of both uncured and cured EVA were observed around -30 °C. These results were consistent with Wang and Deng [75] work that the crosslink reaction did not affect on T_g of EVA with its content of vinyl acetate lower than 31 wt%.

The EVA/NR TPV obtained from the All-DV method had lower T_c and T_m than that from the Split-DV and NR-DV methods, respectively. This was understandable because in the All-DV method, all EVA was added in the vulcanizing step (first step) in which the peroxide-initiated dynamic vulcanization occurred, leading to larger amount of self-crosslinked EVA and, in turn, significantly change T_c and T_m of EVA in aTPVD2 sample. This result also confirmed that the peroxide radicals randomly crosslinked both EVA and NR. Conversely, for NR-DV method only NR was dynamically vulcanized in the vulcanizing mixing step without EVA, resulting in less significant change in T_c and T_m of EVA in the nTPVD2 sample. Therefore, sTPVD2, where some EVA was added and crosslinked with NR at first mixing step, showed the T_m and T_c values between those of nTPVD2 and aTPVD2. Moreover, the T_g of NR in sTPVD2 and aTPVD2 were closed to T_g of cured NR which meant that the NR in sTPVD2 and aTPVD2 were completely crosslinked.

Table 4.3 Thermal properties of uncured and cured EVA, NR, as well as EVA/NR TPVs samples prepared with different methods

Formula	**2nd Heating**				**Cooling**	
	T_g (NR) (°C)	**T_m (EVA) (°C)**	**ΔH_m (J/g)**	**X_c (EVA) (%)**	**T_c (EVA) (°C)**	**ΔH_c (J/g)**
uEVA	-	85.20	53.65	19.36	67.56	70.90
uNR	-65.09	-	-	-	-	-
cEVA*	-	81.69	49.61	17.90	62.47	63.09
cNR*	-62.53	-	-	-	-	-
nTPVD2	-63.70	86.56	25.93	18.71	68.81	31.03
sTPVD2	-62.82	84.75	24.77	17.88	68.27	34.89
aTPVD2	-63.32	82.40	26.75	19.31	65.62	31.39

*cEVA and cNR were cured samples contained DCP 2 phr.



a)

b)

Figure 4.4 DSC thermograms of uncured and cured EVA, NR, as well as EVA/NR TPVs: the second heating scan (a) and cooling scan (b) at heating/cooling rate of 10 °C / min

4.3.1.4 Dynamic Mechanical Properties

Storage moduli (E') and loss moduli (E'') of uncured and cured EVA and NR as well as EVA/NR TPVs were shown in Figure 4.5. The E' and E'' of uncured NR at glassy state were higher than those of uncured EVA. In the rubbery region, the E' of uncured NR was significantly dropped at temperature around 110 °C because sample was broken due to low thermal stability of uncured NR. The E' of uncured EVA greatly decreased at the temperature higher than its melting temperature (86 °C), while E' of the cured sample was constant at rubbery plateau. Peak of E'' implied the glass transition temperature (T_g) of polymer. The T_g values of uncured NR and EVA were obviously observed at -58 and -20 °C, respectively. For the cured samples, T_g of cured NR shifted to -54 °C because the crosslink network restricted the mobility of the polymer chains. However, T_g of cured EVA did not shift to high temperature which was consistent with DSC results. Moreover, the crosslink of NR and EVA could be observed at rubbery plateau of both E' and E'' which remained constant.

For EVA/NR TPVs systems, the obvious peaks of E'' at -50.25 and -51.25 °C were observed for sTPVD2 and aTPVD2, respectively, which corresponded to T_g of NR. However, it was difficult to observe the E'' peak of EVA around -20 °C because the peak height was small compared with the peak of NR. It was worth mentioning that the DMA graph of sample prepared by All-DV method (aTPVD2) had the greatest decreases of both E' and E'' at temperature around 110 °C because the sample was broken during DMA test, which might be due to high self-crosslinking of EVA inducing the phase separation in the blends. Therefore, this reduced the strength of the sample and the sample broke when receiving the applied force at elevated temperature. Samples prepared by Split-DV method at various DCP contents showed the similar behaviors. The E' and $E"$ at rubbery plateau did not decrease as much as that of uncured EVA at elevated temperature. This result showed that the dynamic vulcanization process could improve the mechanical properties of sample at high temperature. When the crosslinking reaction takes place, it restricts the movement of polymer chains.

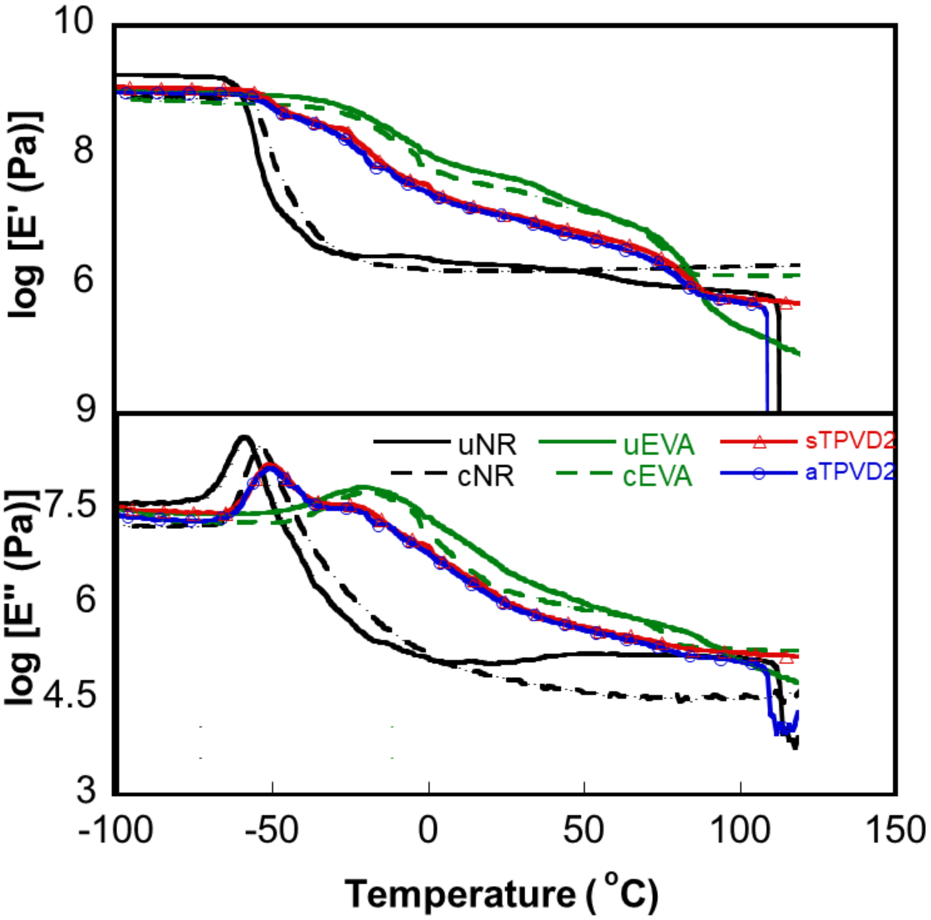


Figure 4.5 Tensile storage and loss moduli of uncured EVA (uEVA), uncured NR (uNR), cured EVA (cEVA), cured NR (cNR), EVA/NR TPVs samples prepared with Split-DV (sTPVD2) and All-DV (aTPVD2) methods

4.3.1.5 Rheological Properties and Extruded Strands from Capillary Rheometer

The rheological properties of EVA/NR TPVs were characterized using a capillary rheometer. Steady state shear viscosity of uncured EVA and TPVs at 190 °C at each shear rate were shown in Figure 4.6 in log scale, and the values were given in Table 4.4. The graph showed the non-Newtonian behavior, which was a typical rheological phenomenon of the thermoplastic vulcanizates. It was found that the steady-state shear viscosity of aTPVD2 was higher than that of sTPVD2 and uncured EVA.

Optical photographs of the extruded strands from the capillary rheometer equipped with circular die (D = 2 mm) at shear rate of 120 s^{-1} were shown in Figure 4.6. The extruded strands of uncured EVA exhibited the smooth surface. The highest die swell of 3.0 mm was observed in uncured EVA. The extruded strands of sTPVD2 did not exhibit die swell owing to the suitable amount of crosslinking part which was shown in gel content value. For the extruded strand of the aTPVD2, both melt fracture and sharkskin behavior were observed. The melt fracture is one type of the flow instability that occurs due to the high elasticity of molten polymer. The gel content of both aTPVD2 and sTPVD2 were similar as shown in Table 4.2. The excess self-crosslinking of EVA might cause the TPV sample to not have enough thermoplastic fraction to hold the sample, resulting in the rough surface of extruded strand. However, the aTPVD2 had more self-crosslinked EVA than that of sTPVD2 as confirmed by the DSC and DMA analysis which reduced the flowability of the TPVs. Therefore, the TPV should have enough non-crosslinked thermoplastic part and suitable crosslinked elastomer to provide the good processability of TPV.

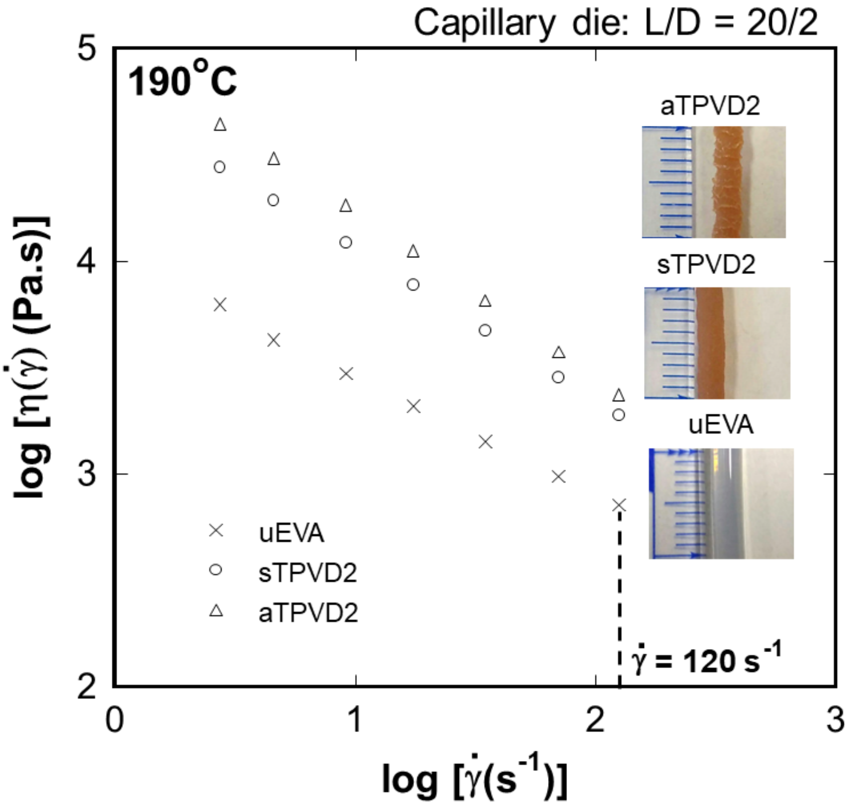


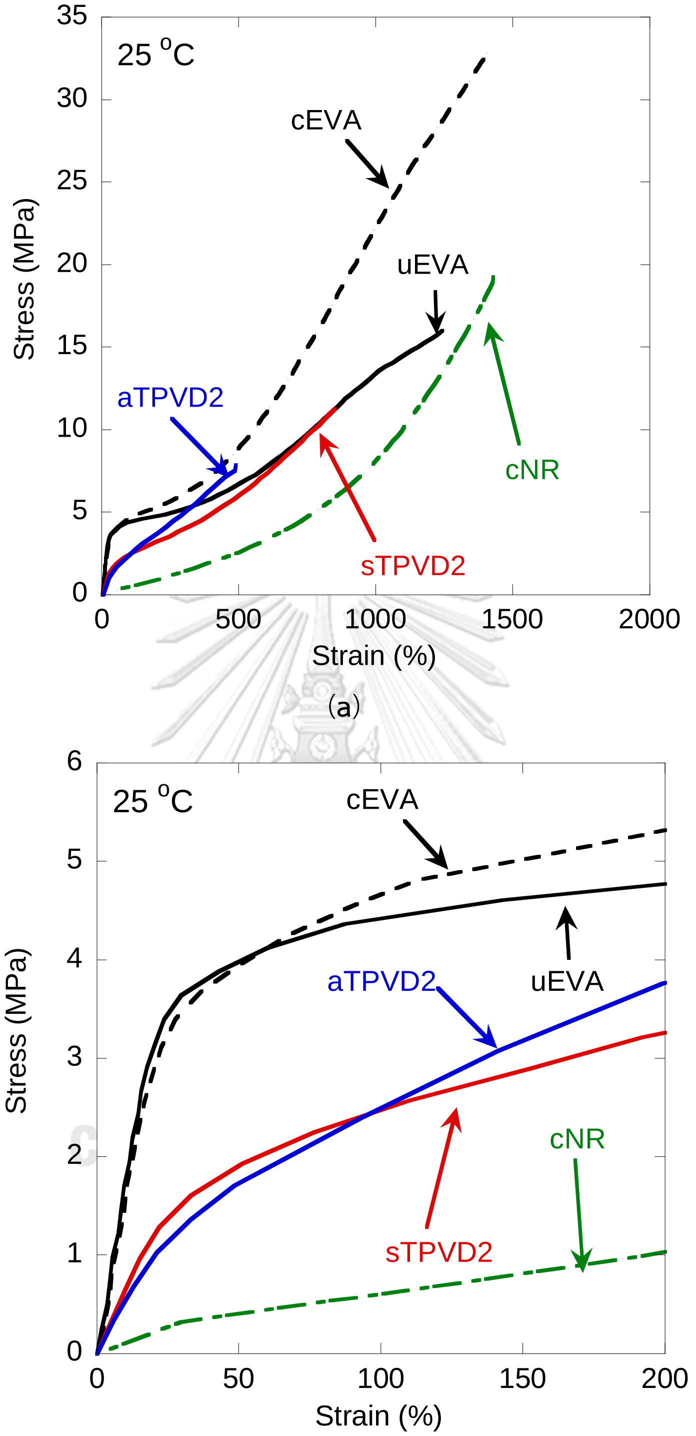
Figure 4.6 Steady-state shear viscosity of uncured EVA, and EVA/NR TPVs as a function of shear rate at 190 °C from capillary rheometer and their extruded strands

Table 4.4 Values of steady-state shear viscosity of uncured EVA and EVA/NR TPVs as a function of shear rate at 190 °C from capillary rheometer

Shear Rate (s^{-1})	**Steady-state shear viscosity (Pa·s)**		
	Uncured EVA	**sTPVD2**	**aTPVD2**
2.7×10^0	6,293	27,912	44,417
4.6×10^0	4,312	19,350	30,530
9.1×10^0	2,985	12,274	18,383
1.7×10^1	2,096	7,804	11,222
3.5×10^1	1,436	4,737	6,548
7.0×10^1	976	2,873	3,761
1.2×10^2	719	1,900	2,361

4.3.1.6 Mechanical Properties

The stress-strain curves of uncured EVA, cured EVA, cured NR, and EVA/NR TPVs at room temperature were shown in Figure 4.7 and their mechanical properties (i.e. ultimate strength, elongation at break) were summarized in Table 4.5. Ultimate strength and elongation at break of samples were obtained from the tensile stress and tensile strain at break, respectively. The uncured and cured EVA showed similar behavior at strain below 50 % as shown in Figure 4.7b. For the strain value over 50%, the cured EVA showed the higher strength than the uncured one due to its crosslink structure. Unfortunately, uncured NR could not be tested because it could not be prepared as sheet due to its tackiness. The cured NR showed elastomeric behavior as its nature. It was found that the behavior of TPV sample prepared with Split-DV method (sTPVD2) and All-DV method (aTPVD2) located in between that of EVA and NR. Both sTPVD2 and aTPVD2 also had same behavior at strain below 100%. However, the behavior of aTPVD2 at the strain higher than 100% was similar to that of cured EVA; while, the sTPVD2 showed the behavior like the uncured EVA because aTPVD2 contained more self-crosslink structure of EVA than that of sTPVD2 leading to the phase separation (Figure 4.2), and poor elongation at break. This result corresponded to the DMA results in which aTPVD2 broke easier than sTPVD2.



(a)

(b)

Figure 4.7 Stress-strain curves of uncured EVA, cured EVA, cured NR, and EVA/NR TPVs samples prepared with different methods at a) overall b) 0 – 200% strain

The value of tension set describes the ability of material to recover to its original shape after receiving the tension force under the specific temperature and condition. Thus, tension set directly relates to the elastic properties of the crosslinked polymer. The tension set of uncured EVA, cured EVA, cured NR, and EVA/NR TPVs at room temperature were summarized in Table 4.5. It was found that the tension set of cured EVA was higher than that of the uncured EVA which could be due to the testing method in which the sample was stretched over its elastic region as could be seen in Figure 4.7b. Therefore, the cured EVA could not return to its original shape as the cured NR. The TPVs showed lower tension set than uncured EVA and cured EVA. It was confirmed that the elastic recovery of TPVs depended only on the crosslinked NR part [53]. Moreover, the tension sets of sTPVD2 and aTPVD2 were in the same range, implying that the mixing method did not affect the tension set value. This result was in agreement with gel content and swelling ratio.

Table 4.5 Tensile properties and tension set of uncured EVA, cured EVA, cured NR, and EVA/NR TPVs samples prepared with different methods

Formula	Ultimate strength (MPa)	Elongation at break (%)	Tension set (%)
uEVA	16.0 ± 0.6	1,185.4 ± 55.3	23.00 ± 0.69
cEVA	32.8 ± 1.3	1,402.5 ± 40.6	26.10 ± 1.23
cNR	18.8 ± 1.9	1,408.9 ± 23.1	1.22 ± 0.75
sTPVD2	9.2 ± 1.4	732.0 ± 84.1	8.92 ± 1.00
aTPVD2	6.4 ± 1.1	410.6 ± 71.9	9.60 ± 1.40

4.3.2 Effect of Peroxide Content

4.3.2.1 Morphology

The SEM micrographs of samples prepared by the Split-DV method with various DCP content were shown in Figure 4.8. The sTPVD0 (Figure 4.8a) which was the EVA/NR blend without addition of DCP showed the co-continuous morphology. It was because the amount of EVA and NR in blend were equal and densities of EVA and NR were similar (EVA 0.93 g/cm^3, NR 0.92 g/cm^3) [77]. During the mixing process, the high shearing force of highly viscous EVA broke the NR phase into the dispersed domains distributed in the EVA matrix. However, the uncrosslinked polymer could agglomerate again and formed co-continuous phase due to the similar volume fraction. For sTPVD1 (Figure 4.8b), both co-continuous rubber phase and dispersed rubber particles were observed. It might be because the DCP content of 1 phr was not enough to completely crosslink all NR phase. Therefore, some of uncrosslinked NR domain could agglomerate to form the co-continuous phase due to the same causes of the morphology of sTPVD0. The rubber particles in spherical shape were clearly observed at higher DCP contents, i.e., sTPVD2 and sTPVD3. The number of free radicals in the system might be adequate to complete the crosslinking reaction between EVA and NR. The sufficient content of DCP was confirmed by the insignificant changes of gel content and swelling ratio of gel at DCP content above 2 phr (Table 4.2).

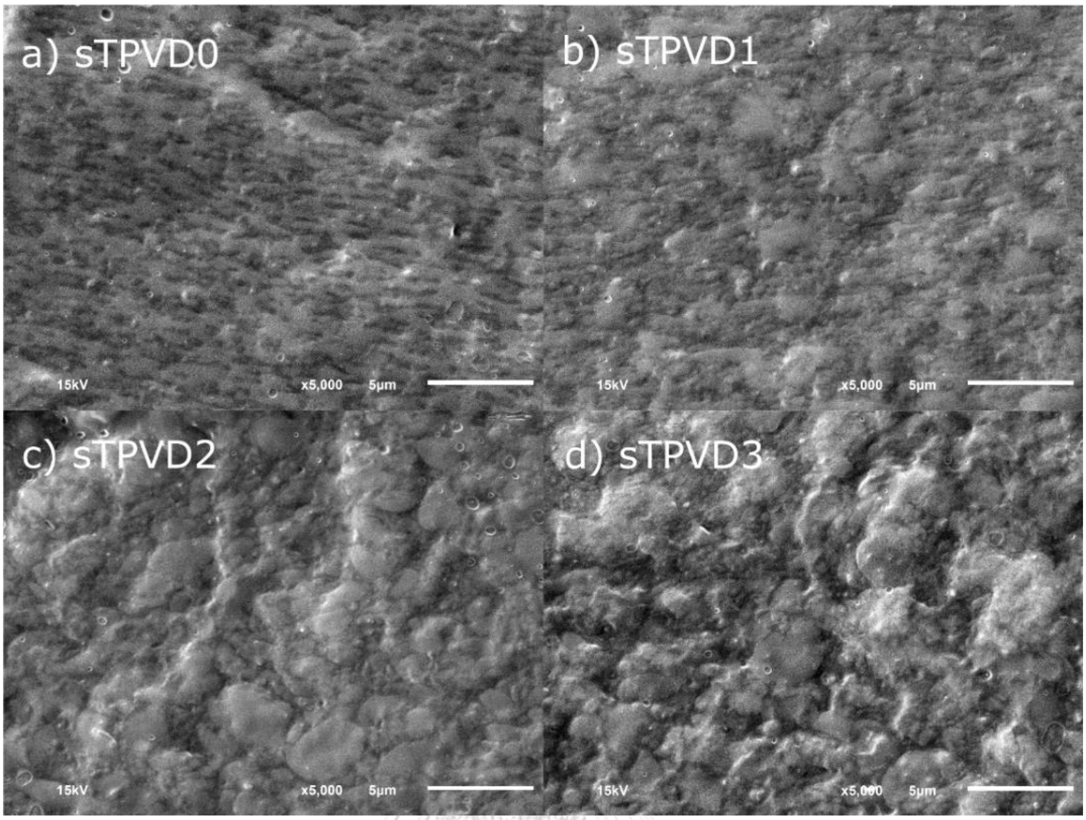


Figure 4.8 Fractured surfaces of EVA/NR TPVs prepared with Split-DV method at various DCP content a) 0 phr b) 1 phr c) 2 phr, and d) 3 phr

4.3.2.2 Gel Content and Swelling Ratio

The gel content and swelling ratio of EVA/NR TPVs prepared with the Split-DV method at different DCP content were shown in Table 4.6. The blend without an addition of DCP during mixing (sTPVD0) was totally soluble in hot xylene. For the samples prepared via Split-DV method at various DCP content, the sTPVD1 showed the highest swelling ratio of gel and the lowest gel content meaning that the crosslinking part was a loose gel. When DCP content increased, the swelling ratio of gel gradually decreased and the gel content increased, reflecting that the crosslinking part became denser because the higher DCP content led to larger number of free radicals formed in the system for the crosslinking reaction. The free radicals were generated and the more crosslinking points between polymer chains occurred resulting the denser gel and more crosslinking parts.

Table 4.6 Gel content (%gel) and swelling ratio of gel (%swell) of uncured samples, cured samples, and EVA/NR TPVs

Formula	**%gel**	**%swell**
sTPVD0	Totally soluble	
sTPVD1	29.17 ± 8.23	1,551.42 ± 175.59
sTPVD2	47.53 ± 0.46	1,051.75 ± 19.15
sTPVD3	50.82 ± 5.15	953.96 ± 56.52

*cEVA and cNR were cured sample contained DCP 2 phr.

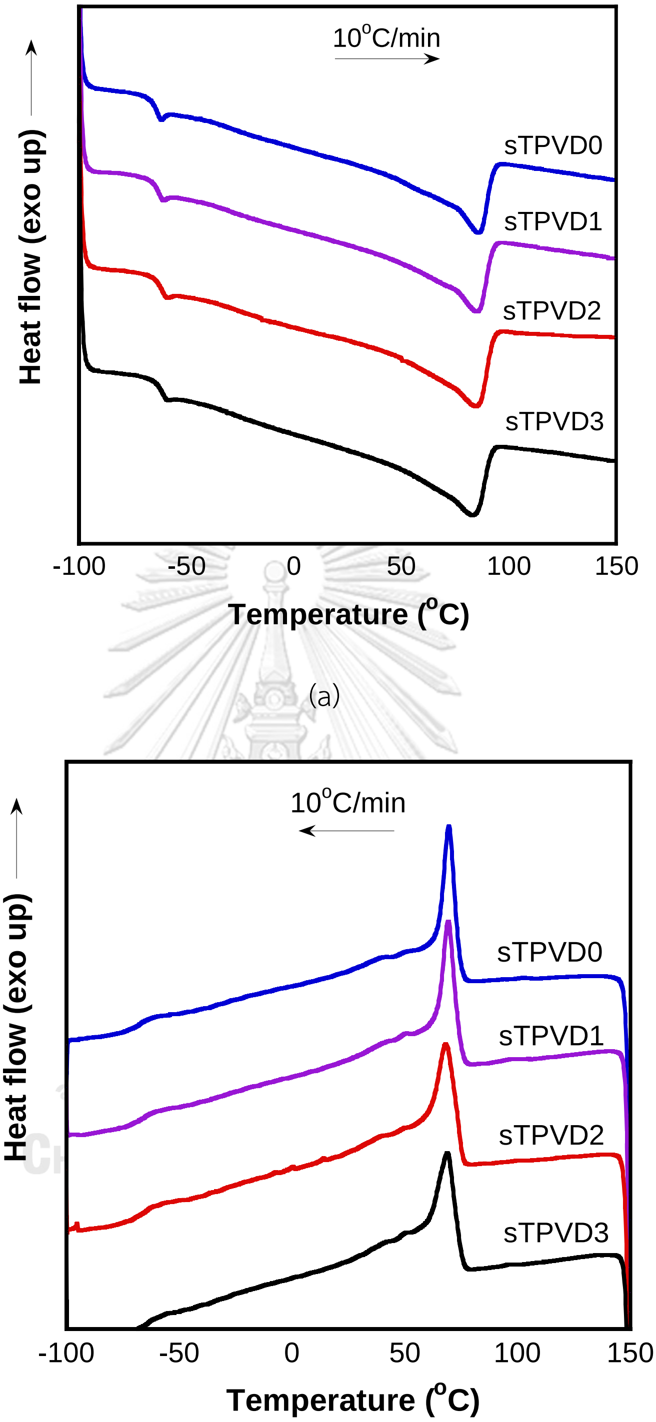
4.3.2.3 Thermal Properties

The DSC thermograms of EVA/NR TPVs at the 2nd heating and cooling scans were shown in Figure 4.9 and their thermal properties were summarized in Table 4.7. The result from this work had shown that the DCP content also affected the crosslink reaction of both EVA and NR. However, the T_g of NR in sTPVD2 and sTPVD3 were not different. This might be because NR at 2 phr of DCP was the fully crosslinked.

Moreover, decrease of T_m of EVA was found when DCP content was increased from 2 to 3 phr, while the T_g of NR did not change. This implied that excess DCP remaining from the crosslink reaction of NR fraction might crosslink EVA fraction instead. However, it was difficult to observe the T_g of EVA which was around -30 °C in the TPV system due to the small transition of heat flow compared with the single component system.

Table 4.7 Thermal properties of EVA/NR TPVs samples prepared with different DCP contents

Formula	2nd Heating				Cooling	
	T_g (NR) (°C)	T_m (EVA) (°C)	ΔH_m (J/g)	X_c (EVA) (%)	T_c (EVA) (°C)	ΔH_c (J/g)
sTPVD0	-65.55	86.06	28.91	20.87	69.47	31.19
sTPVD1	-64.46	85.25	27.16	19.60	69.29	30.42
sTPVD2	-62.82	84.75	24.77	17.88	68.27	34.89
sTPVD3	-62.32	83.41	24.36	17.58	68.95	34.97



(a)

b)

Figure 4.9 DSC thermograms of EVA/NR TPVs with different DCP content: the second heating scan (a) and cooling scan (b) at heating/cooling rate of 10 °C / min

4.3.2.4 Dynamic Mechanical Properties

Storage moduli (E') and loss moduli (E") of EVA/NR TPVs were shown in Figure 4.10. Samples prepared by Split-DV method at various DCP contents showed the similar behaviors. The E' and E" at rubbery plateau did not decrease as much as that of uncured EVA at elevated temperature. This result showed that the dynamic vulcanization process could improve the mechanical properties of sample at high temperature. When the crosslinking reaction takes place, it restricts the movement of polymer chains.

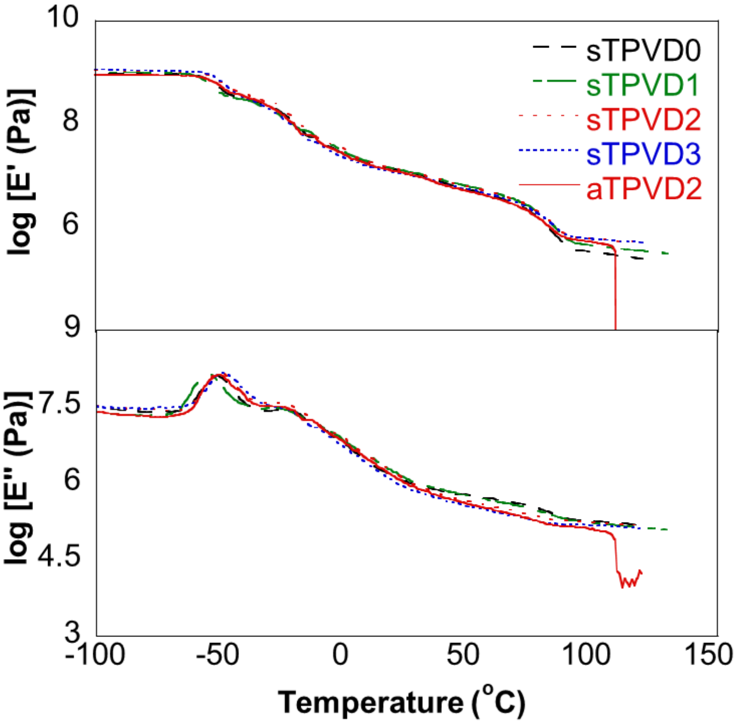


Figure 4.10 Tensile storage and loss moduli of (a) uncured EVA, uncured NR, cured EVA, cured NR, (b) and EVA/NR TPVs samples prepared with Split-DV and All-DV methods

4.3.2.5 Rheological Properties and Extruded Strands from Capillary Rheometer

The rheological properties of EVA/NR TPVs were characterized using a capillary rheometer. Steady state shear viscosity of uncured EVA and TPVs at 190 °C at each shear rate were shown in Figure 4.11 in log scale, and the values were given in Table 4.8. The graph showed the non-Newtonian behavior. Without DCP addition, the steady-state shear viscosity of sTPVD0 was more than that of uncured EVA. Furthermore, the steady-state shear viscosity of TPV sample increased when increasing DCP content because of higher degree of highly crosslinked gel in the blends, as seen in Table 4.2 (gel content).

The optical photographs of the extruded strands from the capillary rheometer equipped with circular die (D = 2 mm) at shear rate of 120 s^{-1} were shown in Figure 4.12. The extruded strands of uncured EVA and sTPVD0 exhibited the smooth surface. The highest die swell of 3.5 mm was observed in sTPVD0. After introducing the DCP, the extruded strand of sTPVD1 showed the melt fracture with an uneven die swell behavior because of a partially crosslinking of NR phase in the blend. The extruded strands of sTPVD2 and sTPVD3 did not exhibit die swell owing to the suitable amount of crosslinking parts which were shown in gel content value; however, the extruded strand of sTPVD3 showed the sharkskin behavior (rough surface) which occurred when the strength of molten polymer was higher than the stress at capillary-rheometer's wall [78-80]. For the extruded strand of the aTPVD2, both melt fracture and sharkskin behavior were observed. The melt fracture is one type of the flow instability that occurs due to the high elasticity of molten polymer. The gel content of both aTPVD2 and sTPVD2 were similar as shown in Table 4.2. The excess self-crosslinking of EVA might cause the TPV sample to not have enough thermoplastic fraction to hold the sample, resulting in the rough surface of extruded strand. However, the aTPVD2 had more self-crosslinked EVA than that of sTPVD2, as confirmed by the DSC and DMA analysis, leading to reduction of the flowability of the TPVs. Therefore, the TPV should have enough non-crosslinked thermoplastic part and suitable crosslinked elastomer to provide the good processability of TPV.

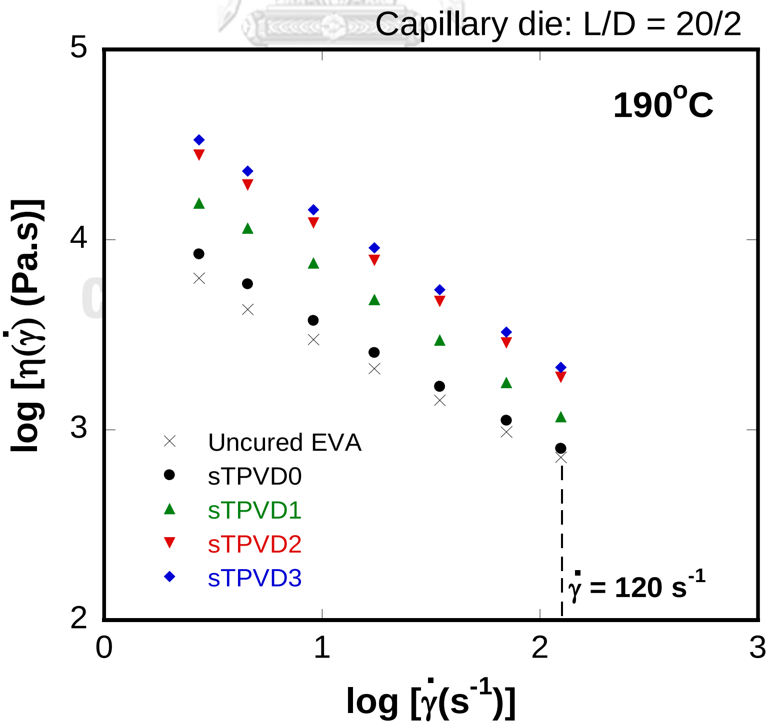


Figure 4.11 Steady-state shear viscosity of uncured EVA, and EVA/NR TPVs prepared with Split-DV method as a function of shear rate at 190 ˚C from capillary rheometer

Table 4.8 Values of steady-state shear viscosity of uncured EVA and EVA/NR TPVs as a function of shear rate at 190 °C from capillary rheometer

Shear Rate (s^{-1})	Steady-state shear viscosity (Pa·s)				
	Uncured EVA	sTPVD0	sTPVD1	sTPVD2	sTPVD3
2.7×10^0	6,293	8,391	15,564	27,912	33,444
4.6×10^0	4,312	5,853	11,492	19,350	22,964
9.1×10^0	2,985	3,762	7,531	12,274	14,370
1.7×10^1	2,096	2,556	4,857	7,804	9,038
3.5×10^1	1,436	1,693	2,974	4,737	5,460
7.0×10^1	976	1,121	1,782	2,873	3,266
1.2×10^2	719	802	1,173	1,900	2,135

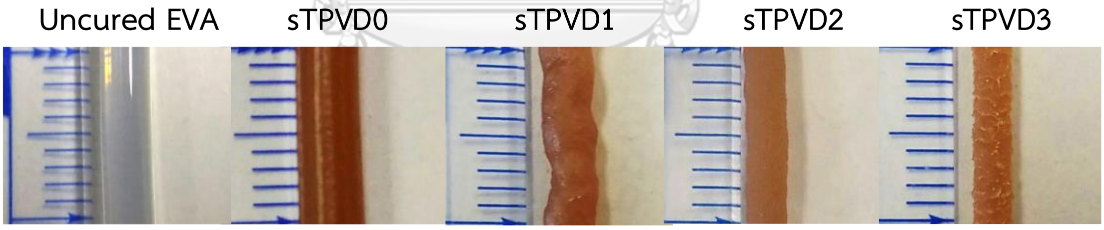
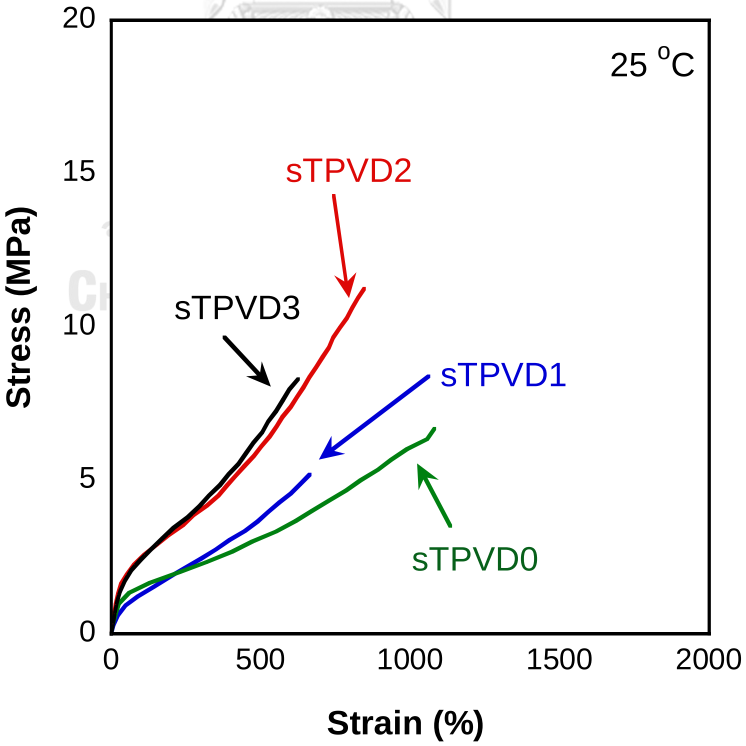


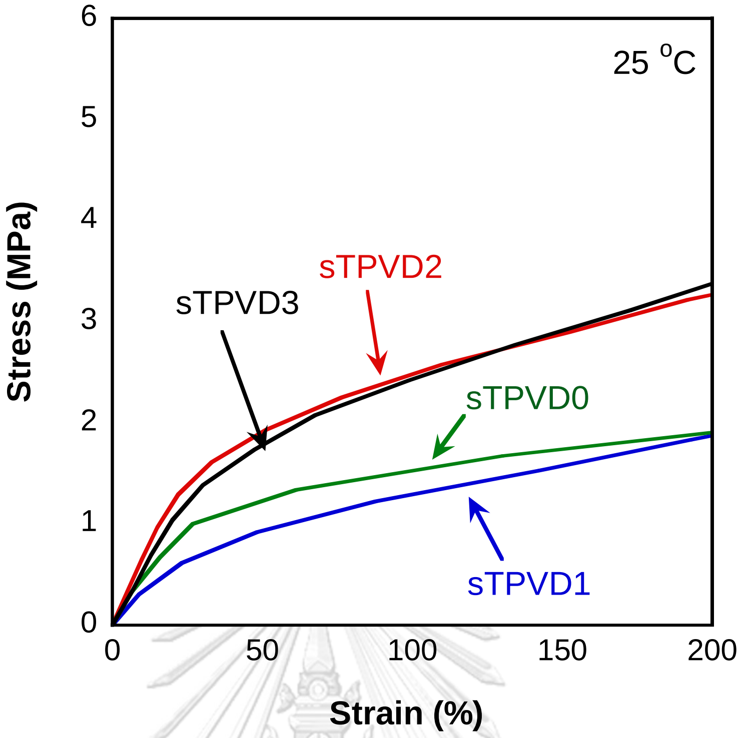
Figure 4.12 Extruded strands of uncured EVA and EVA/NR TPVs at 190 °C and shear rate of 120 s^{-1}

4.3.2.6 Mechanical Properties

The stress-strain curve of TPV samples prepared by Split-DV method at various DCP contents were shown in Figure 4.13. The mechanical properties (i.e. ultimate strength, elongation at break) were summarized in Table 4.9. The stress of sample with higher crosslink showed no correlation with DCP content. However, the sTPVD2 showed the highest ultimate strength among of TPV samples. Tension set value of samples prepared by Split-DV method at various DCP contents were shown in Table 4.9. The tension set decreased with an increase of DCP content. It could be implied that the elastic recovery of TPVs depended only on the crosslinked NR part [53].



(a)



(b)

Figure 4.13 Stress-strain curves of EVA/NR TPVs prepared with Split-DV method at various DCP content at a) overall b) 0 – 200% strain

Table 4.9 Tensile properties and tension set of EVA/NR TPVs samples prepared with Split-DV method at various DCP content

Formula	Ultimate strength (MPa)			Elongation at break (%)			Tension set (%)		
sTPVD0	6.4	±	1.2	1,019.2	±	143.5	25.13	±	1.31
sTPVD1	4.3	±	1.3	553.8	±	155.9	12.39	±	1.96
sTPVD2	9.2	±	1.4	732.0	±	84.1	8.92	±	1.00
sTPVD3	7.5	±	0.8	582.5	±	41.2	7.22	±	0.24

4.4 Summary

The properties of TPV samples were given in Table 4.10. From these results, the suitable method to prepare EVA/NR TPV was the Split-DV method because the sample provided better mechanical properties and processability than others. These TPV prepared via the Split-DV method were made into the package and tested with asphalt as described in the Chapter V.

Table 4.10 Properties of EVA/NR TPVs

Properties	**nTPVD2**	**sTPVD0**	**sTPVD1**	**sTPVD2**	**sTPVD3**	**aTPVD2**
Texture	Rough	Smooth	Smooth	Smooth	Smooth	Smooth
Gel content (%)	36.73	N/A	29.17	47.53	50.82	46.45
Swelling ratio of gel (%)	900.85	N/A	1,551.42	1,051.75	953.96	1,135.71
Viscosity (Pa·s) at 120 s^{-1}	N/A	802	1,173	1,900	2,135	2,361
Ultimate strength (MPa)	N/A	6.4	4.3	9.2	7.5	6.4
Elongation at break (%)	N/A	1,019.2	553.8	732.0	582.5	410.6
Tension set (%)	N/A	25.13	12.39	8.92	7.22	9.60

CHAPTER V

PREPARATION OF ASPHALT PACKAGE AND ASPHALT MODIFICATION WITH THERMOPLASTIC VULCANIZATE

This chapter described the fabrication of asphalt package and test of asphalt after blending with the thermoplastic vulcanizate (TPV) sample with various gel content from the previous chapter. The asphalt package was tested by filling with hot asphalt. Afterwards, the TPV with various gel content was blended with the asphalt at fixed content of 5 wt%. The properties of asphalt such as penetration, softening temperature, ductility, elastic recovery, rheological properties, Brookfield viscosity, and storage stability were evaluated. Moreover, the possible microstructure of TPV in asphalt with different gel content was also illustrated in this chapter to understand the effect of gel content of TPV on the properties of polymer modified asphalt.

5.1 Materials

Ethylene-vinyl acetate copolymer (EVA) (VA content of 18 wt% and MFI = 2.3 g/10min @190°C, 2.16kg) was used as the thermoplastic and purchased from TPI Polene Co., Ltd. (Thailand). Natural rubber sheet (NR) (air-dried sheet type, 59 ML(1+4)100 °C) was used as the rubber and purchased from Bothong Cooperation

(Chonburi, Thailand). Dicumyl peroxide (DCP) (Luperox DCP with 95 wt% purity) was used as a crosslinking agent and supplied by Arkema (USA). Octadecyl-3-(3,5-di-tert butyl-4-hydroxyphenyl)-propionate (Irganox1076) and tris(2,4-di-tert-butylphenyl)phosphate (Irgafos168) were used as thermal stabilizers and purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Asphalt binder (penetration grade, AC60/70) was obtained from Thai Lube Base Co., Ltd (Thailand). Properties of the asphalt binder were shown in Table 5.1. Solvent-grade mixed xylene was used as received without further purification as the solvent to evaluate the gel content of thermoplastic vulcanizate.

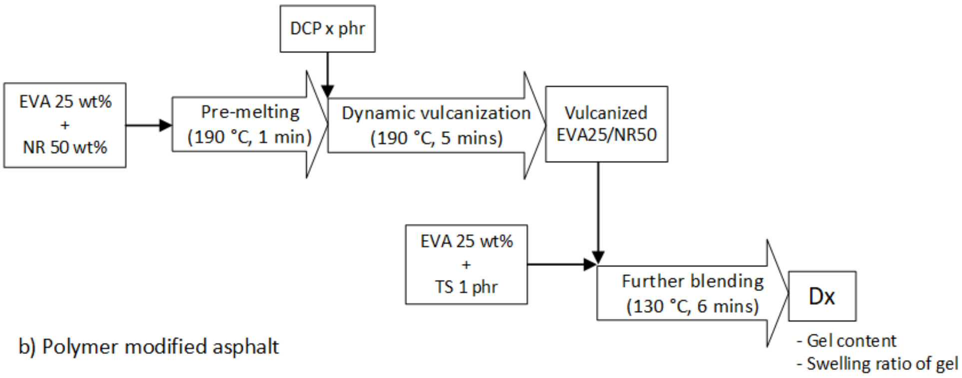
Table 5.1 Properties of neat asphalt (penetration grade AC60/70)

Properties	**unit**	**value**	**Standard**
Penetration at 25 °C (100 g, 5 seconds)	0.1 mm	64	ASTM D5
Ring-and-ball softening temperature	°C	47	ASTM D113
Brookfield viscosity at 135 °C Shear rate 18.6 s^{-1}, spindle 21	cP	297.5	ASTM D4402
	Pa s	0.2975	
G*/sin δ (10 rad/s, 12%strain) at	kPa		ASTM D7175
58 °C		3.06	
64 °C		1.29	
70 °C		0.592	
G*/sin δ = 1 at 65.9 °C			

5.2 Sample Preparation

The sample preparation contained two steps: preparation of EVA/NR thermoplastic vulcanizates, and preparation of polymer modified asphalt (PMA). The overall experimental procedure was shown in Figure 5.1.

a) Thermoplastic vulcanizate



b) Polymer modified asphalt

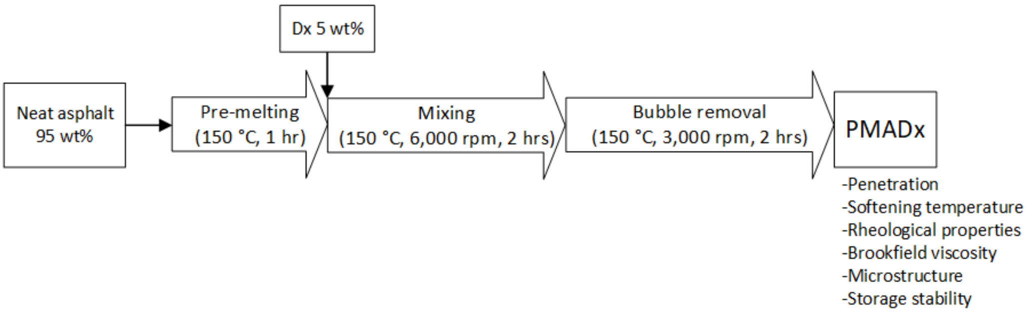


Figure 5.1 Experimental procedure of this research a) preparation of thermoplastic vulcanizate b) preparation of polymer modified asphalt

5.2.1 Preparation of EVA/NR TPVs at Various DCP Content

For the preparation of EVA/NR thermoplastic vulcanizates (EVA/NR TPVs), the EVA pellets and NR sheets were dried in a vacuum oven at 60 °C for 4 hours to remove moisture. The EVA/NR TPVs were prepared by melt-mixing in an internal mixer (Charoen Tut, Thailand) with chamber size of 60 cm^3. According to the previous section, the suitable method used to prepare EVA/NR thermoplastic vulcanizate was Split-DV method which was shown in Figure 5.1a. Firstly, 25 wt% of EVA and 50 wt% of NR were pre-melted for 1 minute and then dynamically vulcanized with the DCP for 5 minutes at 190 °C with rotor speed of 60 rpm. After that, the product obtained from the previous step were melt-mixed with 25 wt% of EVA and each thermal stabilizer (TS) at 0.5 phr was added at 130°C with rotor speed of 60 rpm for 6 minutes.

According to Chapter IV, the suitable DCP content for producing TPV using the Split-DV method was 2 phr. The sample was prepared using the internal mixer with chamber size of 30 cm^3. In this part, the internal mixer with chamber size of 60 cm^3 was used to prepare the TPV sample. The TPV sample with DCP content of 2 phr showed excess crosslink as described in Appendix B. It was not suitable to prepare the film package because the excess crosslink of rubber attributed to poor mechanical properties and processability of the blends. It might be due to the different mixing phenomena. Although the mixing condition was the same as the previous chapter, the different size of mixer and different design of screw might result in the different shear rate and different heat accumulation in the sample during the mixing process. Then, the DCP content of TPV should be defined again.

Therefore, in this part, the DCP content was varied from 0 – 1.5 phr to obtain the sample with different crosslinked degree. The samples were denoted as D0, D0.5, D1, and D1.5 and their appearances were shown in Figure 5.2. Degree of crosslink of TPV was described in terms of gel content which were evaluated by xylene extraction method as described in the section 3.3. The formulation and gel content were shown in Table 5.2.

Table 5.2 Formulations of EVA/NR thermoplastic vulcanizates as well as their gel content and swelling ratio

Sample name	Composition				Gel content (%)	Swelling ratio (%)
	EVA (wt%)	NR (wt%)	DCP (phr)	TS (phr)		
D0	50	50	0	1	Totally soluble	
D0.5	50	50	0.5	1	23.9 ± 2.9	1,491.0 ± 45.8
D1	50	50	1	1	41.7 ± 1.3	1,133.5 ± 48.9
D1.5	50	50	1.5	1	42.6 ± 0.6	1,064.5 ± 16.2

Figure 5.2 Appearances of EVA/NR thermoplastic vulcanizates at various DCP contents

5.2.2 Preparation of Asphalt Package from TPV and Filling with Hot Asphalt

Asphalt package was prepared by compressing the 5 g of TPV into a thin film using a compression molding machine (Labtech, Thailand) at 130 °C under 20 bars for 5 minutes. The thickness of film was about 150 micrometers. The film was placed in the paper box and fastened using staples. Asphalt cement graded AC 60/70 was heated at temperature of 150 °C until it melted. Then, 150 g of liquid asphalt was poured in the package as shown in Figure 5.3. It was left until the asphalt become solid. The package was removed from the paper box and the appearance of package was observed.

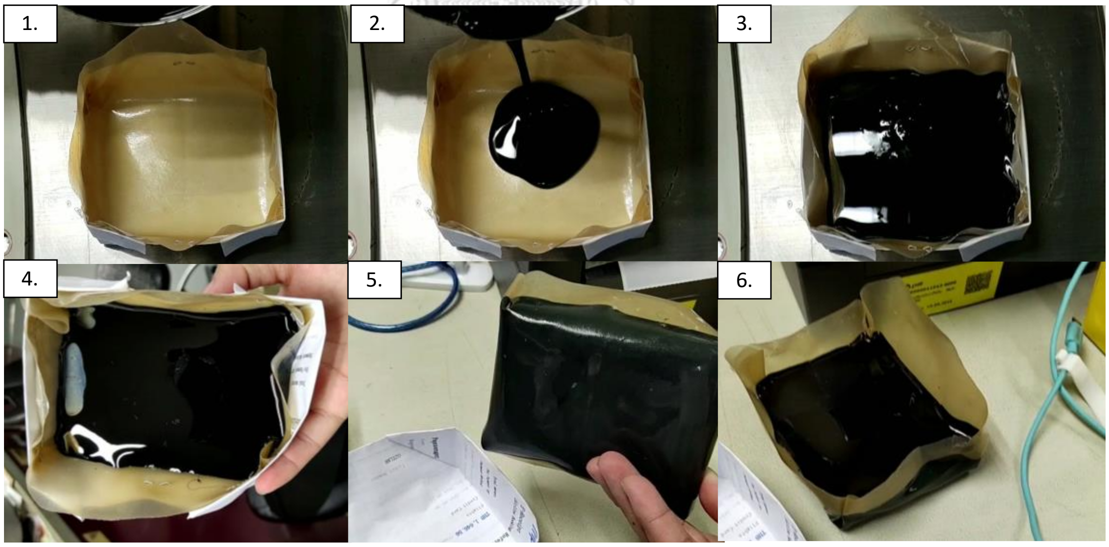


Figure 5.3 Test of filling hot asphalt into the TPV package

5.2.3 Preparation of Polymer Modified Asphalt

For the preparation of polymer modified asphalt (PMA), the asphalt was melted at 150 °C in metal container. Each TPV sample obtained from previous section was cut into small pieces (≤ 2 mm) and gradually mixed with asphalt using a high-speed shear mixer (Figure 5.4) (L5M model, Silverson, US) at 150 °C with a rotor speed of 6,000 rpm for 2 hour and 3,000 rpm for 2 hours in order to remove air bubbles from asphalt. The mixing diagram was shown in Figure 5.1b. After that, the appearance of neat asphalt and PMA was observed by pouring the neat asphalt or obtained samples into water at room temperature. After the sample solidified, the solid asphalt was then stretched by hand and the texture was observed as shown in Figure 5.6. The formulation of PMA used were shown in Table 5.3 with their nomenclatures. For example, PMAD0 was the asphalt modified with 5 wt% of TPV D0 sample.

Figure 5.4 Preparation of PMA and the head of high-speed mixer

Table 5.3 Formulations of polymer modified asphalt

Sample name	Asphalt (wt%)	TPV sample	TPV content (wt%)
Neat asphalt	100	-	-
PMAD0	95	D0	5
PMAD0.5	95	D0.5	5
PMAD1	95	D1	5
PMAD1.5	95	D1.5	5

5.3 Results and Discussions

5.3.1 Appearance of TPV sheet After Filling with Hot Asphalt

The appearance of asphalt package prepared with different TPV samples after filled with hot asphalt, were shown in Figure 5.5. The D0 was EVA/NR blend without DCP, while the D0.5, D1, and D1.5 were TPV with DCP of 0.5, 1, and 1.5 phr, respectively. It was found that the crosslink reaction of TPV resulting in less tackiness of EVA/NR TPVs. The D0 sample showed tackiness after the hot asphalt was poured as the paper could be observed to stuck to the D0 package. Whereas the paper did not stuck to the package made from D0.5, D1, and D1.5 samples. The D0.5 package showed some shrinkage when contacted with hot asphalt showing that the thermal stability was not as high as D1 and D1.5 packages. The texture of D1 and D1.5 packages were smooth. Therefore, all asphalt packages were not broken after contacted with the hot asphalt. Next, the TPV sample was intentionally blended with asphalt at 5 wt% which is the maximum package weight compared with whole sample to study the effect of TPV with different gel content on polymer modified asphalt.

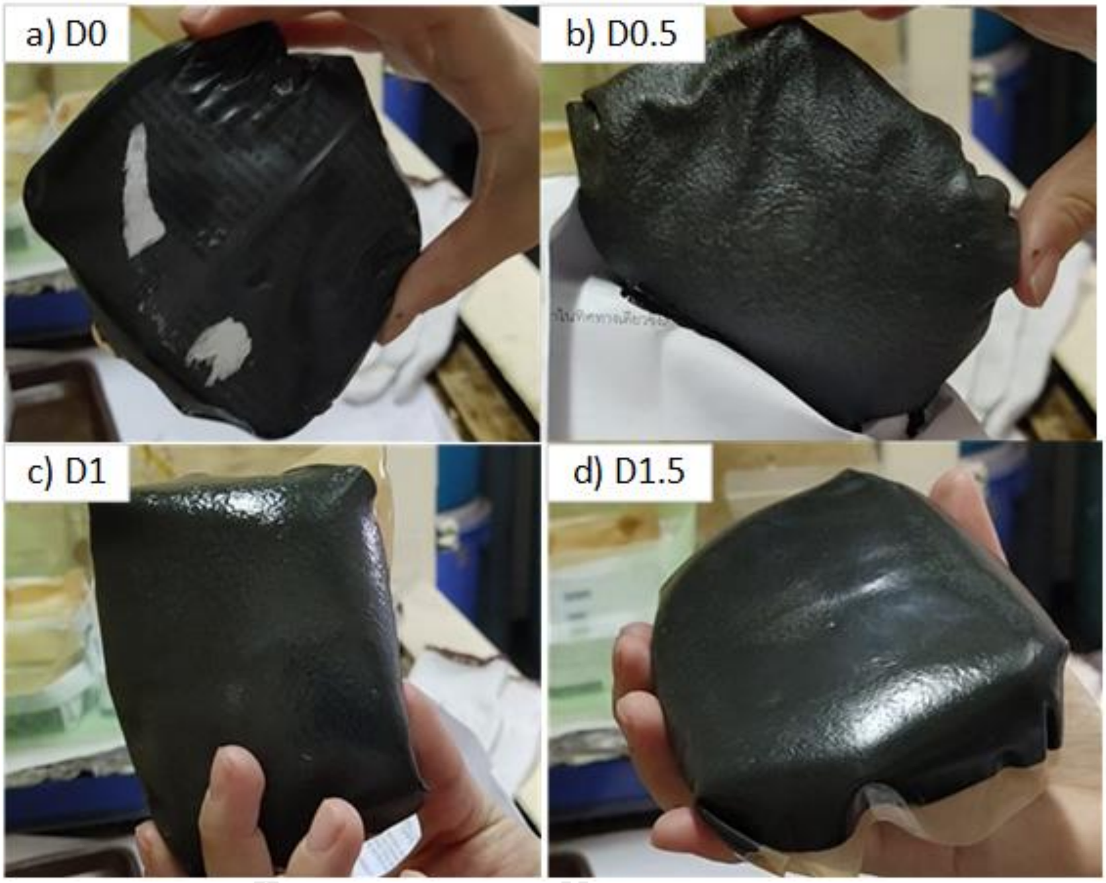


Figure 5.5 Appearance of asphalt package after filling of hot asphalt

(a) D0, (b) D0.5, (c) D1, and (d) D1.5

5.3.2 Appearance, Microstructure, and Physical Properties

The appearance of neat asphalt and polymer modified asphalt (PMA) at room temperature as well as their microstructures at 150 °C observed by fluorescence microscope were shown in Figure 5.6. It was found that the neat asphalt (Figure 5.6a) exhibited a glossy texture, while the PMAD0 exhibited a matte texture (Figure 5.6c). The smooth texture were observed only in neat asphalt and PMAD0 while the PMAD0.5, PMAD1, and PMAD1.5 showed the rough texture as seen in Figure 5.6e, Figure 5.6g, and Figure 5.6i, respectively. The TPV consisted of thermoplastic and crosslinked rubber particle which could be observed by SEM as shown in Figure 4.4 and Figure 4.5 (section 4.2.2). Therefore, the dispersion of TPV in PMA was observed in the PMA micrographs at higher magnification.

The optical micrograph of polymer modified asphalt (PMA) with magnification of 20 times after heated to 150 °C for 10 minutes exhibited heterogeneous phase of PMA with different shape of dispersed phase (Figure 5.6d, 5.6f, 5.6h, and 5.6j). The dispersed phase of PMAD0 was in spherical shape while those in PMAD0.5, PMAD1, and PMAD1.5 were in irregular shape. The microstructure of asphalt blended with TPV was similar to that blended with the crumb rubber because the crumb rubber also consisted of the crosslinked rubber.

Physical properties such as penetration and softening temperature were shown in Table 5.4. It was found that polymer modified asphalt (PMA) exhibited less penetration of needle and higher softening temperature of PMA than those of neat asphalt. With the increase of gel content of thermoplastic vulcanizate (TPV), the penetration of needle increased and the softening temperature slightly increased. Moreover, higher gel content led to higher degree of crosslinking in TPV causing the samples to be more rigid and difficult to deform, improving the asphalt properties.

From Table 5.4, the ductility of asphalt incorporated with TPV showed lesser value than that of neat asphalt due to the heterogeneous phase. However, the increase of gel content of TPV caused the increase in ductility of PMA. Addition of TPV could improve elastic recovery of asphalt due to the crosslinked points between polymer chains showed the elastic properties. However, more crosslink made the rubber in TPV to be hard particles and the elastic recovery of TPV could not be improved due to lack of elasticity of rubber. The improvement in penetration and softening temperature of modified asphalt indicated that the samples here were suitable for use in hot climate region. However, these values represented only the properties in static situation which did not reflect real world usage. During traffic, the road experienced continuous loading and unloading of forces which might have a significant impact on the rheological properties of asphalt, as such the characteristics of the materials under such situation were further investigated.

Table 5.4 Physical properties: penetration, softening temperature, ductility, and elastic recovery of polymer modified asphalt with different gel content of TPV

Sample name	**Penetration (0.1 mm) at 25 °C**	**Ring and ball softening temperature $T_{R\&B}$ (°C)**	**Ductility (cm)**	**Elastic recovery (%)**
Neat asphalt	64	47.0 ± 0.2	> 150	0
PMAD0	47	53.9 ± 0.3	64.0 ± 8.8	44.0 ± 8.1
PMAD0.5	46	54.5 ± 0.1	74.8 ± 9.5	53.5 ± 5.4
PMAD1	45	55.8 ± 0.8	76.8 ± 11.8	49.5 ± 4.3
PMAD1.5	41	54.8 ± 0.4	77.4 ± 24.0	43.2 ± 5.1

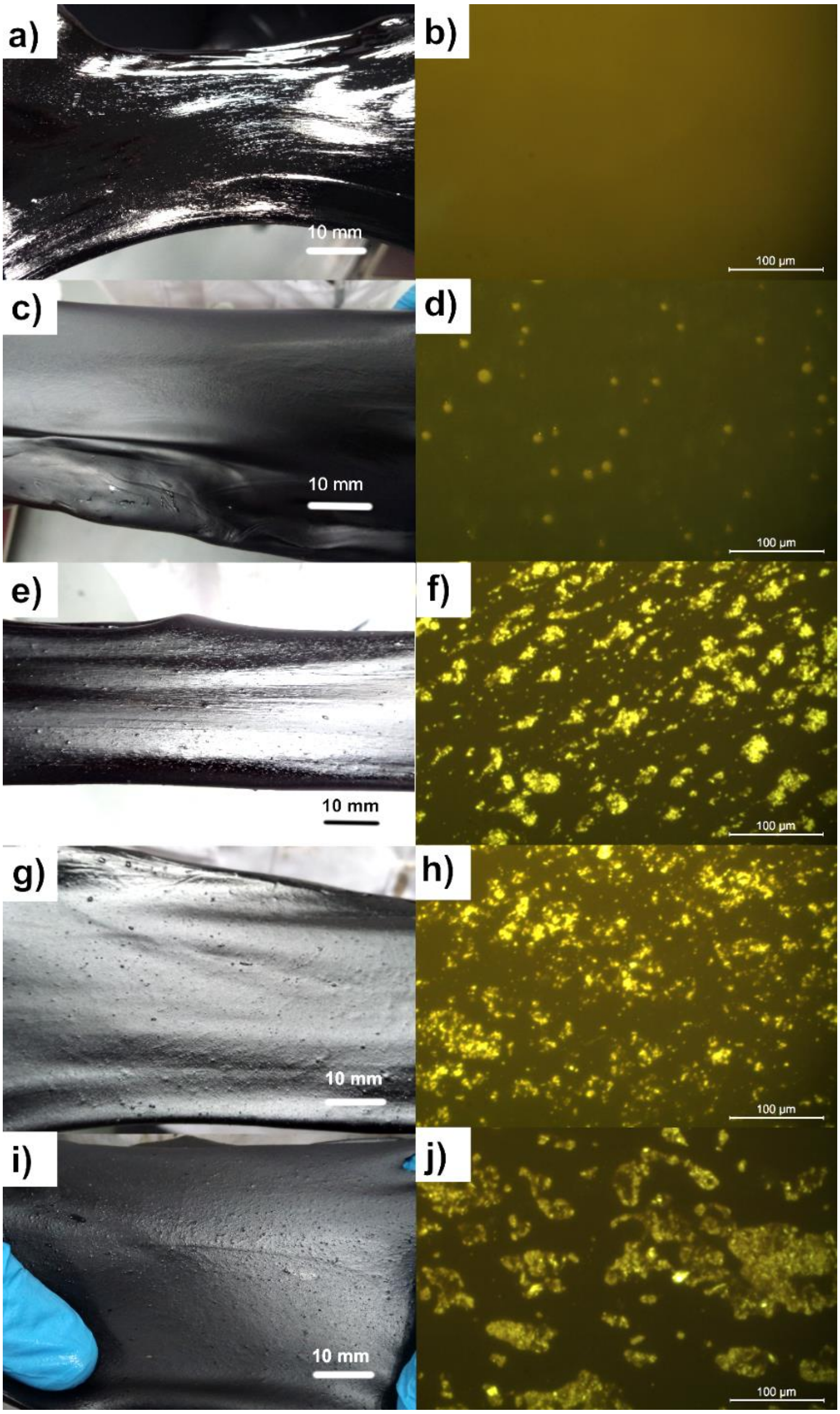
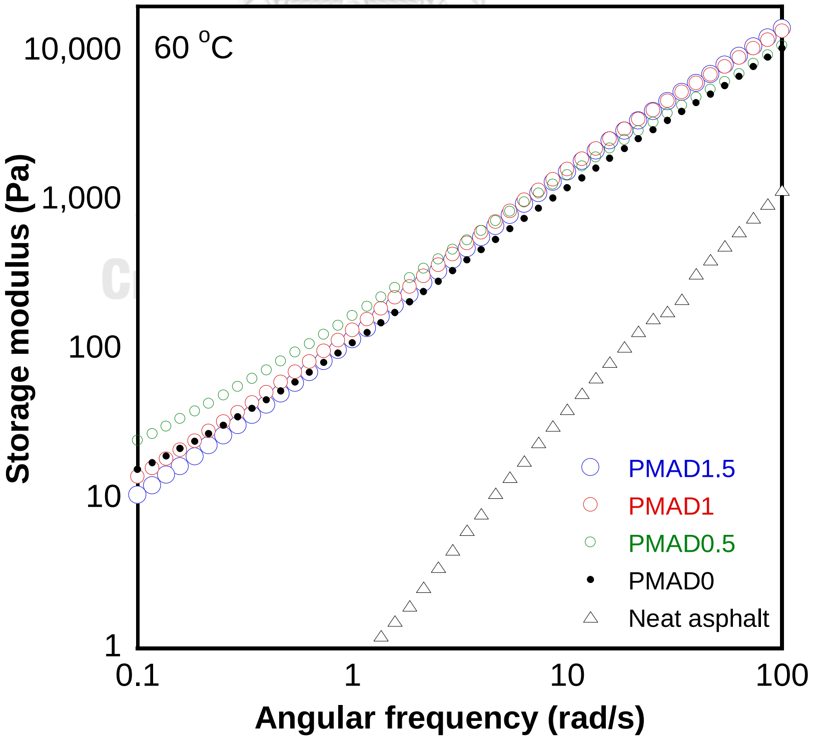


Figure 5.6 Optical appearance at room temperature and microstructure at 150 °C of neat asphalt (a, b), PMAD0 (c, d) PMAD0.5 (e, f) PMAD1 (g, h), and PMAD1.5 (i, j)

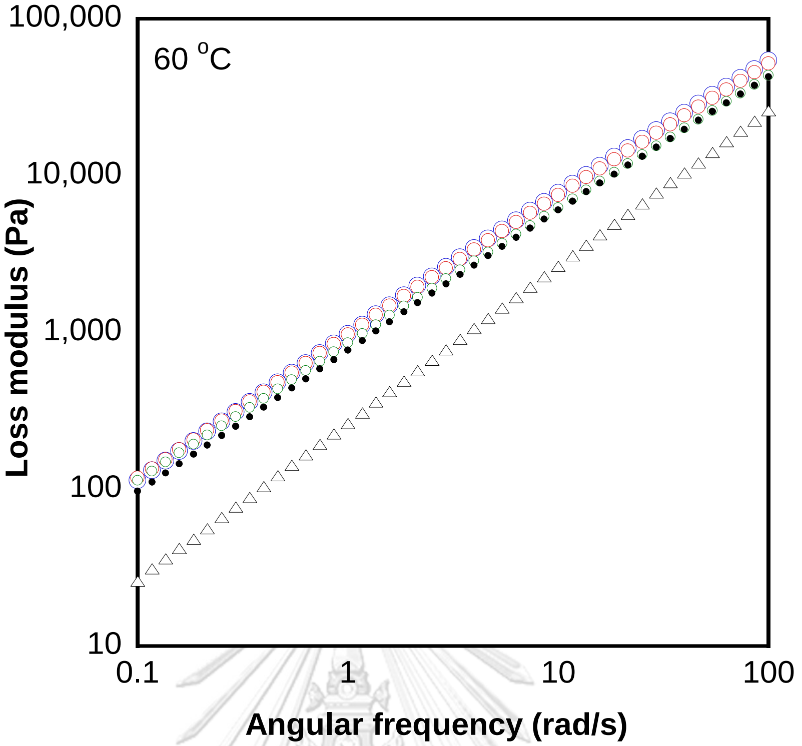
5.3.3 Rheological Properties

The rheological properties of neat asphalt and polymer modified asphalt (PMA) were investigated using dynamic shear rheometer (DSR). Two tests were performed: frequency sweep at 60 °C which was the road average surface temperature in hot climate region [81-84]. The performance grading refers to final temperature that the rutting parameter (G*/sin δ) is more than 1. For example, if the last tested temperature of PMA was 64 °C, the grade was PG64.

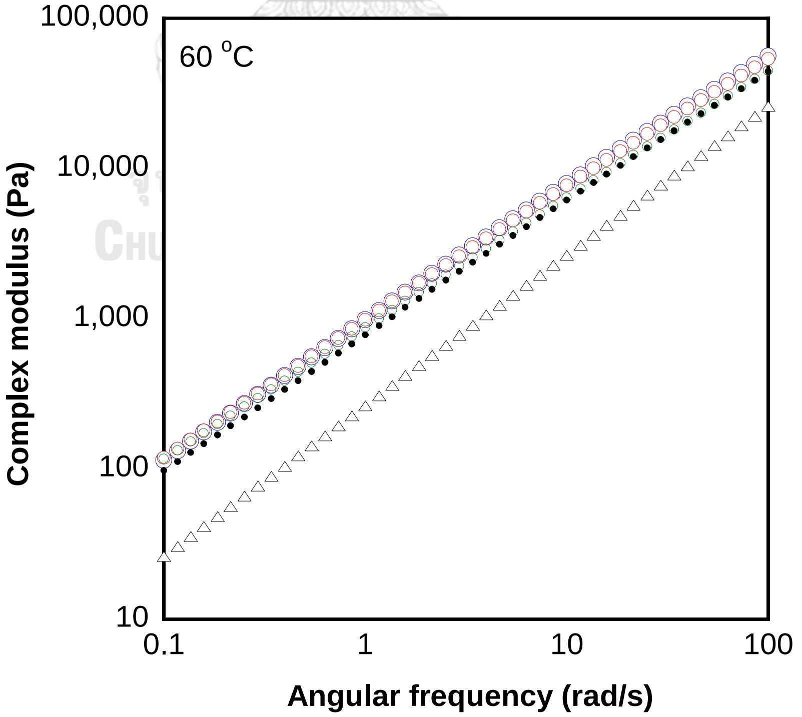
From Figure 5.7, it was found that storage modulus (G'), loss modulus (G"), complex modulus (G*) and complex viscosity (η*) of asphalt incorporating thermoplastic vulcanizate (TPV) increased from that of neat asphalt. The increase of gel content of TPV blended with asphalt caused the increase of rheological properties of PMA indicating that the material was more difficult to deform and flow. The viscoelastic behavior of both moduli of neat asphalt and PMA increased with increasing angular frequency. It could be observed that the loss modulus (Figure 5.7b) and complex modulus (Figure 5.7c) showed similar values which suggested that the behavior of PMA was viscous dominant at tested condition. For complex viscosity shown in Figure 5.7d, the complex viscosity of neat asphalt was independent of angular frequency which meant that the neat asphalt was a Newtonian fluid in the testing range. Whereas the complex viscosity of PMA which contained TPV showed a frequency dependent behavior; the complex viscosity decreased with an increase in angular frequency. This behavior was non-Newtonian in nature with the type being pseudoplastic or shear thinning. The value of complex viscosity increased with increasing gel content of TPV at both low and high angular frequencies. As mentioned in the previous section, more gel content of TPV attributed to the more degree of crosslink of rubber particles made TPV to be difficult to deform. In this condition, the TPV acted as particles to restrict the deformation of PMA. As observed from the Figure 5.7 that rheological property parameters had a positive correlation with gel content of TPV. This result corresponded with the results from Yu et al. [85] that the rheological properties of gel type bitumen was more than that of the sol type bitumen.



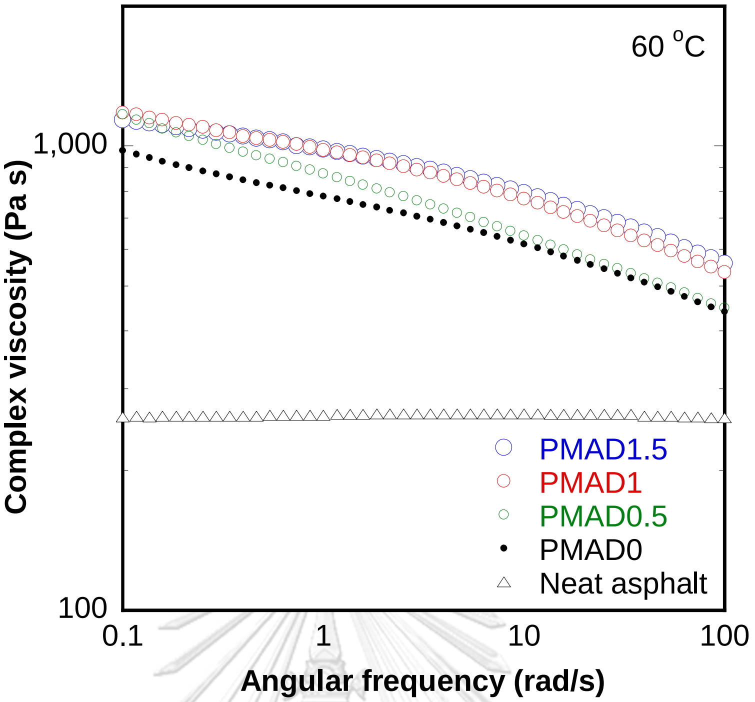
a)


60 °C
Loss modulus (Pa)
100,000
10,000
1,000
100
10
0.1
1
10
100
Angular frequency (rad/s)

b)


60 °C
Complex modulus (Pa)
100,000
10,000
1,000
100
10
0.1
1
10
100
Angular frequency (rad/s)

c)



d)

Figure 5.7 Rheological properties of neat asphalt and PMA at 60 °C in frequency sweep mode: storage modulus (a), loss modulus (b), complex modulus (c), and complex viscosity (d)

The neat asphalt and PMA were classified as superpave performance grade classification. The performance grade was classified by using the DSR to measure the complex modulus (G^*) and phase angle (δ) at specific strain and angular frequency. Afterwards, the rutting parameter ($G^*/\sin\delta$) was calculated. This parameter was introduced by the American Strategic Highway Research Program (SHRP). It is related to the stiffness of asphalt at specific temperature. The rutting parameter represents the property of asphalt in real traffic under cycled loading. Figure 5.8 showed the rutting parameter at each temperature test. It was found that incorporation of TPV made the temperature value for $G^{*}/\sin\delta$ to be more than 1 shifted from 64 °C to 70 °C for all PMA formulation. As seen from Figure 5.8, the fail temperature of neat asphalt, PMAD0, PMAD0.5, PMAD1, and PMAD1.5 were 65.9 °C, 73.2 °C, 73.3 °C, 73.5 °C, and 73.7 °C, respectively. It can be said that the grade of modified asphalt was improved from the neat asphalt.

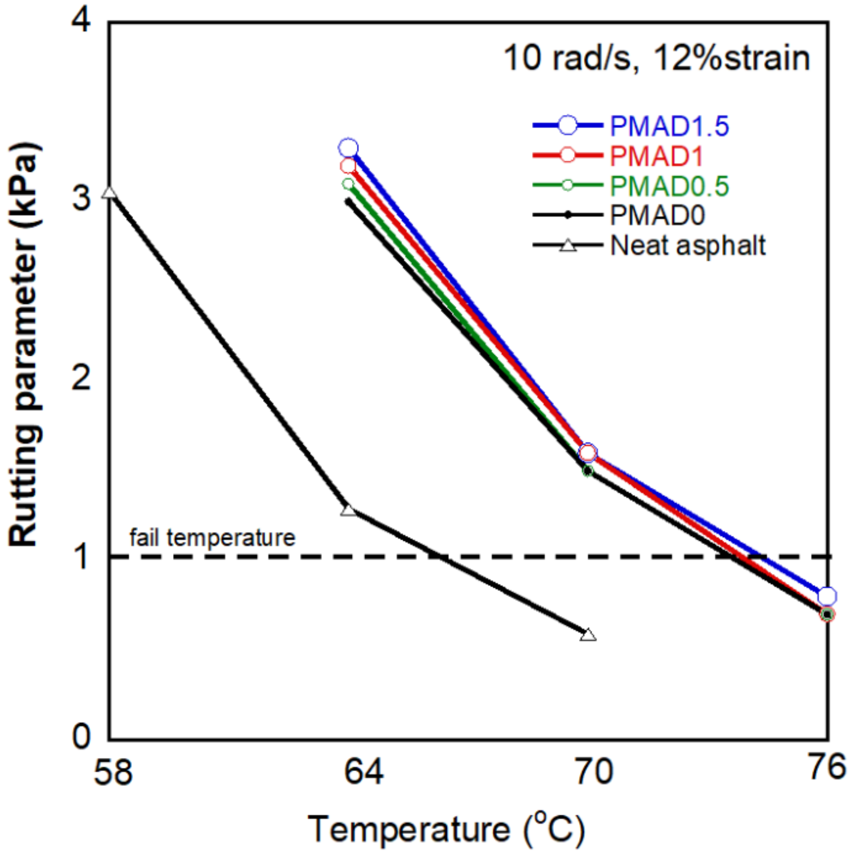
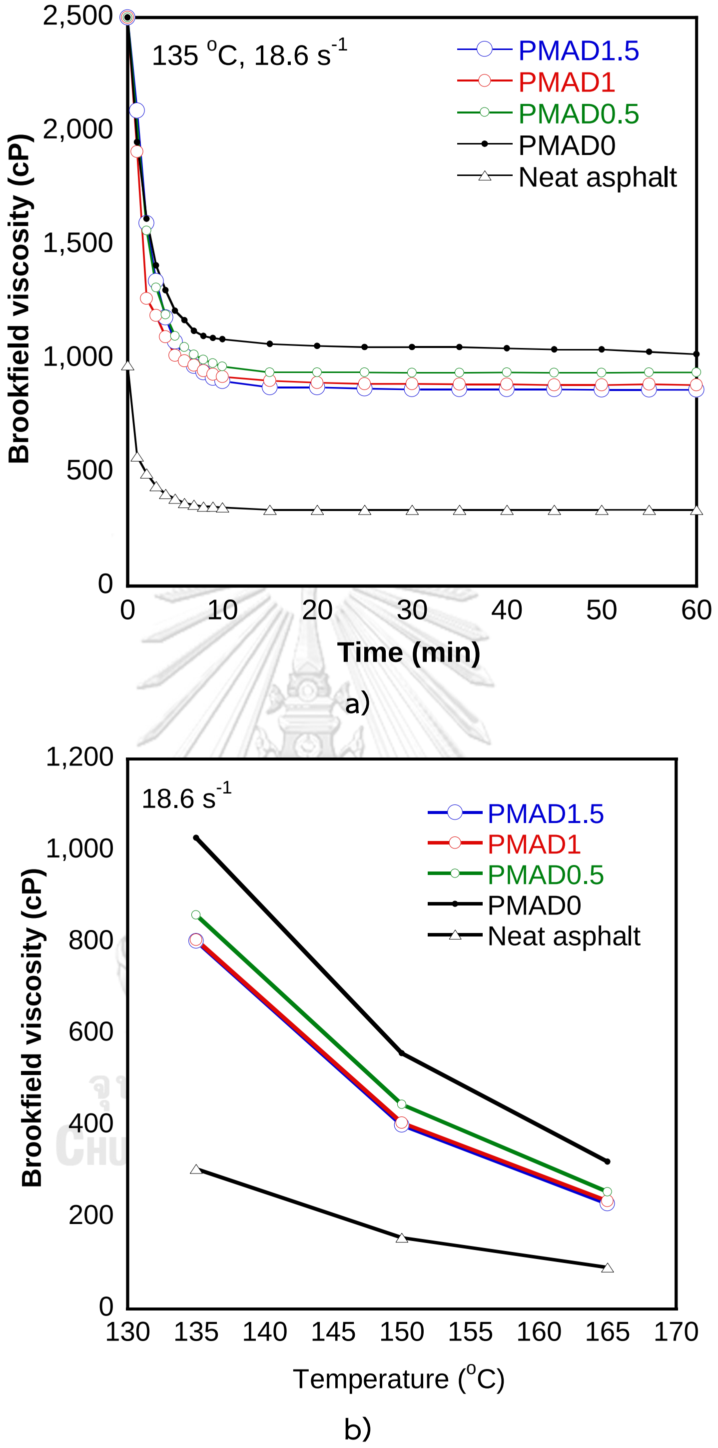


Figure 5.8 Temperature dependence of rutting parameter (G*/sin δ) of neat asphalt and PMA

5.3.4 Brookfield Viscosity

Brookfield viscosity was measured using the Brookfield rotational viscometer. For measurement at 135 °C, the time dependence of viscosity of neat asphalt and PMA was recorded for 60 minutes as shown in Figure 5.9a. The initial Brookfield viscosity value from the instrument was recorded at 2,500 cP (2.5 Pa·s) which was the maximum value that could be measured by the instrument. The viscosities of neat asphalt and PMA decreased with time and remained stable after 10 minutes as shown in Figure 5.9a. It was found that the Brookfield viscosity of all PMA were higher than that of the neat asphalt due to the TPV restricting the mobility of asphalt. The PMAD1.5 which had the highest gel content showed the lowest viscosity, while the PMAD0 which had no gel content exhibited the highest viscosity among all the PMA samples. The Brookfield viscosity of neat asphalt and PMA at 150 and 165°C also showed the same correlation as shown in Figure 5.9b.



a)

b)

Figure 5.9 Brookfield viscosity of neat asphalt and PMA (a) time dependence at 135 °C, and (b) temperature dependence which the value was recorded at 60 minutes (1 cP = 0.001 Pa•s)

The trend of viscosities of each sample measured by the Brookfield viscometer were different from those from the DSR. It might be due to the different state of polymer contained in the asphalt. The Brookfield viscosity was measured at temperature higher than 135 °C while the complex viscosity from DSR was measured at 60 °C. According to the melting temperature of EVA which is 86 °C, the state of EVA in asphalt during DSR test is solid, while that of EVA during Brookfield test is in the molten state. In the molten state, the polymer chains were dispersed in asphalt as random coil. The TPV which had no crosslinked part (D0) were in the form of long-chain polymer which could entangle together. Whereas the TPV with dynamically vulcanized fine rubber (D0.5, D1, D1.5) might have lower content of long-chain polymer compared with the D0 sample.

Figure 5.10a showed the schematic drawing of TPV dispersed in asphalt in molten state which had different gel content. The difference between long-chain and short-chain polymers was the degree of entanglement which affected the mobility of the asphalt, with short chain polymer resulting in low viscosity due to the low to non-existent degree of entanglement. The dispersion of TPV during Brookfield viscosity measurement was illustrated in Figure 5.10b with the change in microstructure of PMA when the shear force was applied (Figure 5.10c). The longer polymer chain could be stretched, and the entangled points restricted the movement which needed shear stress to disentangle the polymer chains. According to previous studies [86, 87], the fiber with high aspect ratio showed the higher viscosity than the fiber with low aspect ratio and also spherical particles.

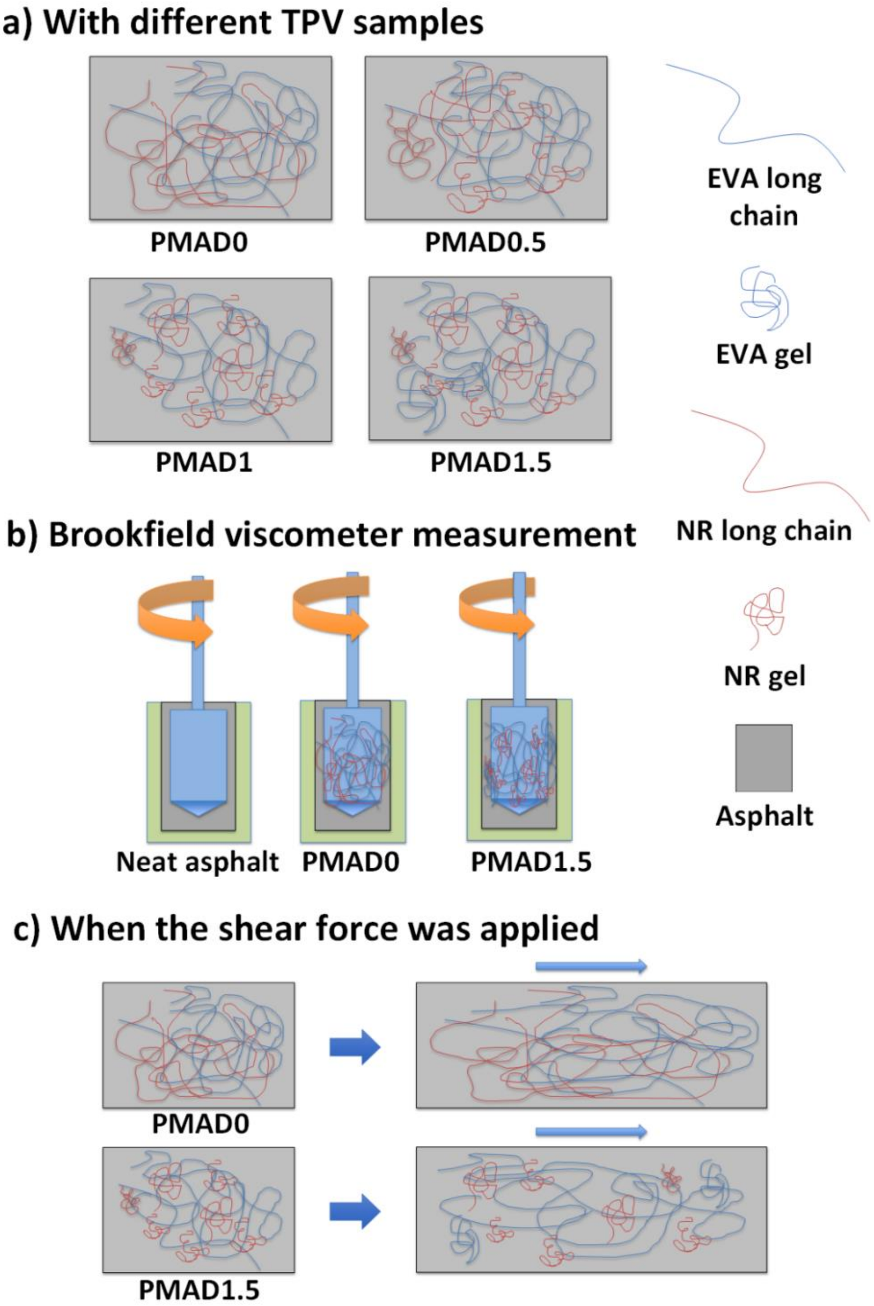


Figure 5.10 Schematic drawing of neat asphalt and PMA (a) with different TPV samples (b) during Brookfield viscosity measurement, and (c) when the shear force was applied to PMA samples.

5.3.5 Storage Stability

The storage stability of polymer modified asphalt was evaluated by the difference of softening temperature of asphalt collected from the top and bottom section of tested aluminum tube. The higher difference in temperature refers to more polymer separation from the asphalt. The density of polymer is lower than that of asphalt. Therefore, the polymer tends to float over the asphalt surface during separation. The value of softening temperature of before and after storage at 163 °C for 5 days were shown in Table 5.5. It was found that PMAD0 showed the lowest difference in softening temperature while the PMAD1.5 showed the highest value. As described in Table 5.2, the gel content of D1 and D1.5 is similar while the swelling ratio of D1.5 was lower than that of D1, showing that the D1.5 has denser 3D network. The dense 3D network could absorb less solvent. Therefore, the interaction between asphalt and D1.5 might be lower than the other TPV that had the looser gel. It was consistent with Rasool et al. [88] work that the more crosslinked rubber had lower compatibility with asphalt.

Table 5.5 Storage stability of PMA contained different TPV after storage at 163 °C for 5 days

Formula	Softening temperature (°C)			
	Original	After storage at 163 °C for 5 days		
		Top	Bottom	Difference
Neat asphalt	47.0	-	-	-
PMAD0	53.9	55.4	53.6	1.8
PMAD0.5	54.5	57.2	55.0	2.2
PMAD1	55.8	58.5	56.1	2.4
PMAD1.5	54.8	60.8	52.1	8.7

5.4 Summary

Properties of asphalt modified with EVA/NR TPVs were summarized in Table 5.6. It was found that the properties of asphalt were improved such as lower penetration value, higher softening temperature, higher elastic recovery, and higher performance grade. The Brookfield viscosity of asphalt increased when blending with TPV. Increase in gel content of TPV resulted in decrease of Brookfield viscosity. This result could imply that that TPV could be used as modifier for asphalt.

Table 5.6 Properties of neat asphalt and polymer modified asphalt

Properties	**AC60/70**	**PMAD0**	**PMAD0.5**	**PMAD1**	**PMAD1.5**
TPV sample	-	D0	D0.5	D1	D1.5
Gel content of TPV (%)	-	0	23.9	41.7	42.6
Penetration (0.1 mm)	64	47	46	45	41
Softening temperature (°C)	47.0	53.9	54.5	55.8	54.8
Ductility (cm)	>150	64.0	74.8	76.8	77.4
Elastic recovery (%)	0	44.0	53.5	49.5	43.2
Complex viscosity (Pa•s)					
at 60 °C, 100 rad/s	260	440	448	535	559
Brookfield viscosity (cP)					
at 135 °C	298	1,030.0	860	805	803
at 150 °C	155	560	445	405	401
at 165 °C	90	320	255	235	230
Performance grading	PG64	PG70	PG70	PG70	PG70
Storage stability (°C)	-	1.8	2.2	2.4	8.7

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this dissertation, the formulation of natural rubber (NR) and ethylene vinyl acetate copolymer (EVA) thermoplastic vulcanizates using dicumyl peroxide (DCP) as crosslinking agent, was successfully developed to prepare the zero-waste asphalt package. The zero-waste asphalt package can endure hot asphalt at 150 °C and it can be melted with asphalt at 150 °C with the improvement of asphalt properties. This research consists of two parts which are study on effect of mixing method and peroxide content on properties of EVA/NR TPVs, and improvement of asphalt properties by blending the TPVs with different gel content. The conclusions of each part were as followed.

In the first part, the effect of mixing method and peroxide content on properties of EVA/NR TPVs was investigated. Three mixing methods (i.e., NR-DV, Split-DV, and All-DV) were compared at peroxide content of 2 phr. The result in this work had shown that the samples obtained from the NR-DV method exhibited a non-homogeneous texture. Therefore, NR-DV is not a preferred method for TPV production. The gel content and swelling ratio of NR-DV samples were lower than those of the other two methods, reflecting the lower degree of crosslinking within the samples. The samples of NR-DV had a similar glass transition temperature (T_g) but higher melting temperature (T_m) than those of the other two methods. This indicates the ineffectiveness of crosslinked NRs on the crystallization of EVA in the TPV samples. Samples of Split-DV and All-DV had similar appearance and morphology. The gel content and swelling ratio were similar. The T_m values of the Split-DV samples were higher than those of the All-DV samples, indicating the lower degree of self-crosslinking of EVA. The samples of All-DV were easily broken during the dynamic mechanical tests (at 110 °C), which is attributed to an excess self-crosslinking of EVA. There was some effect on the rheological and mechanical properties of samples obtained from the All-DV method, which resulted in the rough surface of extruded strands and were easily broken when stretched over 400% strain. The Split-DV samples showed overall better quality regarding the dynamic mechanical, rheological, and mechanical properties. Their extruded strands showed smooth surfaces and remained unbroken during the dynamic mechanical test and can be stretched over than 700% strain. It can be concluded that Split-DV is the most efficient method to produce EVA/NR TPVs.

Moreover, the peroxide content also affected the properties of TPV prepared via the Split-DV method. The uncrosslinked sample showed co-continuous phase of NR and EVA. Whereas the NR became particles and dispersed in the EVA phase. The morphology of TPV contained 2 and 3 phr of DCP were not different, indicating the fully crosslinked NR in this blend system. It was also confirmed by unchanged of T_g

value while T_m changed to lower temperature while the DCP increased from 2 to 3 phr. The unchanged of T_g value mean that NR was fully crosslinked. Therefore, excess DCP crosslinked the EVA instead. Increasing DCP content in TPV samples led to increase of gel content and decrease of swelling ratio, indicating the more crosslinking part and denser 3D network. The TPV samples with 2 phr of DCP showed the best mechanical properties and good processability in capillary extrusion. Therefore, this method was used to prepare the sample to fabricate the TPV film with various gel content.

In the second part, the package was fabricated from TPV with various gel content. The gel content of TPV was varied by varying DCP content in the TPV. According to the different size of internal mixer, the formulation of TPV should be defined again because the 2 phr of DCP from previous section resulted in the excess crosslink. The DCP content was varied at 0, 0.5, 1, 1.5 phr and the gel content value of TPV at each DCP content were 0.0%, 23.9%, 41.7%, and 42.6%, respectively. All of package from TPV can endure hot asphalt at 150 °C. Then, asphalt was improved by blending of EVA/NR TPVs. The properties of polymer modified asphalt (PMA) were studied in terms of microstructure as well as physical and rheological properties. It was found that appearances of neat asphalt and asphalt blended with uncrosslinked EVA/NR blend (PMAD0) exhibited smooth surface while other PMA exhibited rough surface. The physical properties such as penetration and softening temperature were affected by gel content of TPV. The higher gel content of TPV in PMA resulted in better PMA properties such as lower penetration value (higher degree of hardness) and higher softening temperature. Rheological properties of PMA at 60 °C increased with the increase of gel content of TPV blended with asphalt seeing that the material was more difficult to deform due to crosslinking point. The incorporation of TPV also made the temperature value for rutting parameter ($G^*/\sin\delta$) more than 1 shifted from 64 °C to 70 °C for all PMA formulation. Brookfield viscosity of asphalt blended with TPV contained DCP of 1.5 phr at 135 °C was lower than that of asphalt blended with non-crosslinked EVA/NR blend due to the more degree of entanglement of long-chain polymer contained in non-crosslinked EVA/NR blend, while the EVA/NR TPVs contained less amount of long-chain polymer. Increase of DCP resulted in the decrease of long-chain polymer in TPV. It is worth mentioned that the improvement of asphalt by blending with TPV which has higher gel content is recommended because the obtained asphalt exhibited better physical and rheological properties than those contained non-crosslinked EVA/NR blend. Whereas the Brookfield viscosity of asphalt blended with TPV contained DCP of 1.5 phr showed the lowest value compared with those of PMA contained the TPV with lower gel content. The samples were a suitable candidate for use as pavement material in hot climate regions.

6.2 Recommendations

6.2.1 The weight ratio of ethylene vinyl acetate copolymer and natural rubber in thermoplastic vulcanizate should be varied to study the processability of TPV because the more thermoplastic would provide good processability and increase more soluble part when incorporating with asphalt

6.2.2 Scale-up process for fabrication of zero-waste package should be investigated.

6.2.3 The effect of TPV content on properties of asphalt should be investigated.

6.2.4 The molecular weight of polymer with different gel content should be investigated to support the possible mechanism described in section 5.3.4.

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APPENDIX A Evaluation of Crosslinking Profiles of EVA and NR

The crosslink profiles are time dependence of storage shear modulus (G′) at constant temperature of neat polymer contained peroxide was investigated using a strain-controlled parallel-plate type rheometer (MR-500 model, UBM) in a time-sweep mode with a gap of 1 mm. The plate diameter was 25 mm. The measurement was performed at 190 °C with frequency of 1 Hz and constant strain of 0.1%). The polymer sample was prepared by blending the polymer with peroxide at 100 °C to prevent the crosslinking reaction and was compressed into a sheet with 1-mm thickness using a compression molding machine at 100 °C. It was cut into a circular shape with a diameter of 25 mm. First, the gap between two tested plate was calibrated by setting it to be zero as observing from the normal force shown when the plate contacted together. The chamber of rheometer was preheated to 190 °C and maintained for 5 minutes, then the sample was placed in between the parallel-plate and was immediately tested. The G′was recorded until the value remained constant.

The crosslinking profiles at 190 °C of neat EVA and neat NR contained DCP of 1 and 5 phr were evaluated as time dependence of shear storage modulus as shown in Figure A.1. The shear storage modulus (G') increased at the initial stage and subsequently constant after 1 minute for both EVA and NR at 1 and 5 phr DCP.

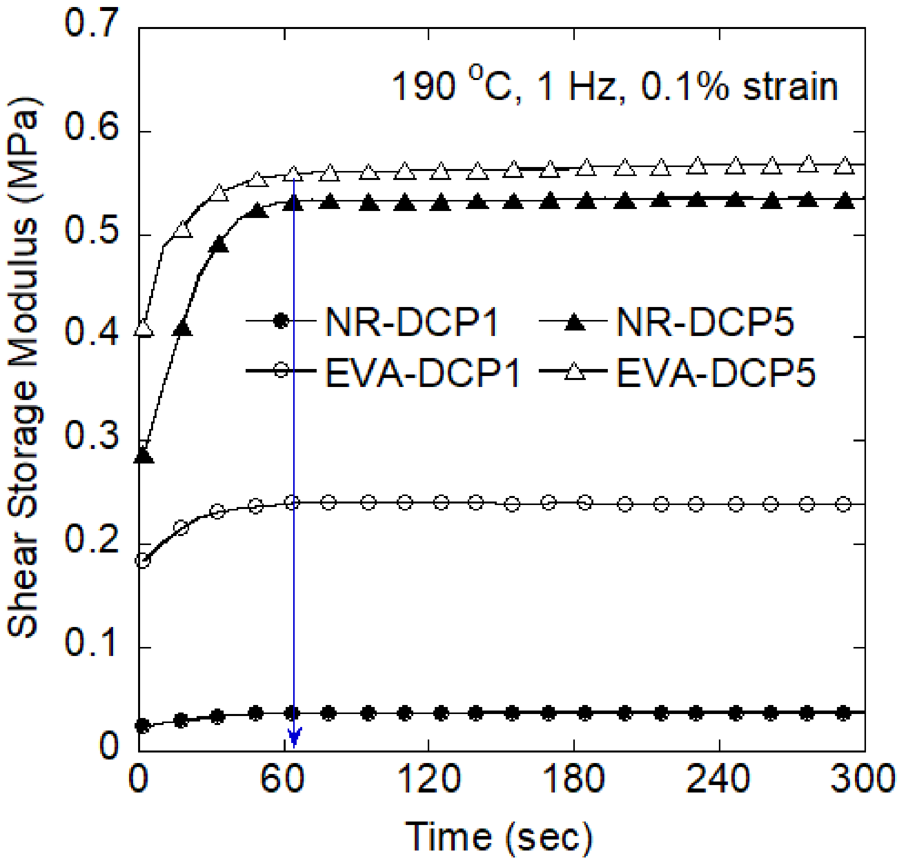

Figure A.1 Shear storage modulus (G') at 190 °C versus time of neat NR and neat EVA contained 1 and 5 phr DCP

The G' of each sample at t = 0 were different. The G' of EVA was higher than that of NR for both DCP content of 1 and 5 phr. As mentioned in the section 3.1 (evaluation of crosslinking profile), the sample sheet was placed into chamber at 190 °C and immediately started the test. The EVA in solid form was rigid than NR in solid form due to its crystallinity. Therefore, the EVA showed higher value G' at initial compared with the NR.

The difference between the G’ at initial and G’ at plateau (ΔG’) indicated the degree of crosslink in the vulcanized polymer. It was found that NR showed higher ΔG’ than that of EVA at DCP content of 5 phr, while the G’ of NR and EVA at DCP content of 1 phr showed the opposite results. According to Niu et al. [70], pre-cure or pre-crosslinking reaction can be occurred in the sample with higher DCP content which exhibited in the graph that the higher G’ at initial of sample contained more DCP was observed. From this result, it could suggest that the mixing time of 5 minutes in dynamic vulcanization process was enough to decompose all DCP in the blend.

APPEXDIX B Sample Preparation of EVA/NR TPV

The weight of EVA and NR in sample preparation using an internal mixer of 30 cm^3 and 60 cm^3 were shown in Table B.1 – Table B.2 and Table B.3 – Table B.4, respectively. According to the fill factor of mixer should be about 70 vol% and the density of EVA and NR was 0.93 and 0.92 g/cm^3, respectively, the recommended weight for each batch should be about 20 – 25 or 40 – 50 g for the internal mixer size of 30 and 60 cm^3, respectively.

Because the weight ratio of EVA/NR blend using Split-DV method was 1:2 (33.3/66.7 wt/wt), the total weight of polymer in the first step was fixed at 21 or 42 g for 30 and 60 cm^3, respectively, for easy calculation. The other sample was also fixed at the same polymer weight to achieve the same shear mixing. The total weight of polymer in the second step was fixed at 20 and 40 g, respectively.

The sample prepared using the internal mixer of 30 and 60 cm^3 chamber size was shown in Figure 2.1 and Figure 2.2, respectively. Due to the different size of mixer, the vulcanized sample from the dynamic vulcanization step showed different appearance even it has the same formula. Excess crosslinked sample showed light color and some part of obtained sample becomes powder. Therefore, the DCP content in TPV formulation was adjusted to achieve the sample that was suitable to prepare the TPV in this work.

Table B.1 Formulations of the sample obtained from the dynamic vulcanization step of EVA/NR thermoplastic vulcanizates using an internal mixer of 30 cm^3

Sample name	EVA		NR		DCP		**Total batch size**
	wt% of total	g	wt% of total	g	phr	g	g
Vulcanized NR/DCP2	0	0	50	21	2	0.42	21.42
Un-vulcanized EVA25/NR50/DCP0	25	7	50	14	0	0	21.00
Vulcanized EVA25/NR50/DCP1	25	7	50	14	0	0.21	21.21
Vulcanized EVA25/NR50/DCP2	25	7	50	14	0	0.42	21.42
Vulcanized EVA25/NR50/DCP3	25	7	50	14	3	0.63	21.63
Vulcanized EVA50/NR50/DCP2	50	10.5	50	10.5	2	0.42	21.42

Table B.2 Formulations of the sample obtained from the further blending step of EVA/NR thermoplastic vulcanizates using an internal mixer of 30 cm^3

Formula name	The sample from the first step		EVA		TS1		TS2		Total batch size
	Name	g	wt% of total	g	phr	g	phr	g	g
nTPVD2	Vulcanized NR/DCP2	10	50	10	0.5	0.1	0.5	0.1	20.2
sTPVD0	Un-vulcanized EVA25/NR50/DCP0	15	25	5	0.5	0.1	0.5	0.1	20.2
sTPVD1	Vulcanized EVA25/NR50/DCP1	15	25	5	0.5	0.1	0.5	0.1	20.2
sTPVD2	Vulcanized EVA25/NR50/DCP2	15	25	5	0.5	0.1	0.5	0.1	20.2
sTPVD3	Vulcanized EVA25/NR50/DCP3	15	25	5	0.5	0.1	0.5	0.1	20.2
aTPVD2	Vulcanized EVA50/NR50/DCP2	20	0	0	0.5	0.1	0.5	0.1	20.2

Table B.3 Formulations of the sample obtained from the dynamic vulcanization step of EVA/NR thermoplastic vulcanizates using an internal mixer of 60 cm^3

Sample name	EVA		NR		DCP		**Total batch size**
	wt% of total	g	wt% of total	g	phr	g	g
Vulcanized NR/DCP2	0	0	50	42	2	0.84	42.84
Un-vulcanized EVA25/NR50/DCP0	25	14	50	28	0	0	42.00
Vulcanized EVA25/NR50/DCP1	25	14	50	28	0	0.42	42.42
Vulcanized EVA25/NR50/DCP2	25	14	50	28	0	0.84	42.84
Vulcanized EVA25/NR50/DCP3	25	14	50	28	3	1.26	43.26
Vulcanized EVA50/NR50/DCP2	50	10.5	50	10.5	2	0.84	42.84

Table B.4 Formulations of the sample obtained from the further blending step of EVA/NR thermoplastic vulcanizates using an internal mixer of 60 cm^3

Formula name	The sample from the first step		EVA		TS1		TS2		Total batch size
	Name	g	wt% of total	g	phr	g	phr	g	g
nTPVD2	Vulcanized NR/DCP2	20	50	20	0.5	0.2	0.5	0.2	40.4
sTPVD0	Un-vulcanized EVA25/NR50/DCP0	30	25	10	0.5	0.2	0.5	0.2	40.4
sTPVD1	Vulcanized EVA25/NR50/DCP1	30	25	10	0.5	0.2	0.5	0.2	40.4
sTPVD2	Vulcanized EVA25/NR50/DCP2	30	25	10	0.5	0.2	0.5	0.2	40.4
sTPVD3	Vulcanized EVA25/NR50/DCP3	30	25	10	0.5	0.2	0.5	0.2	40.4
aTPVD2	Vulcanized EVA50/NR50/DCP2	40	0	0	0.5	0.2	0.5	0.2	40.4

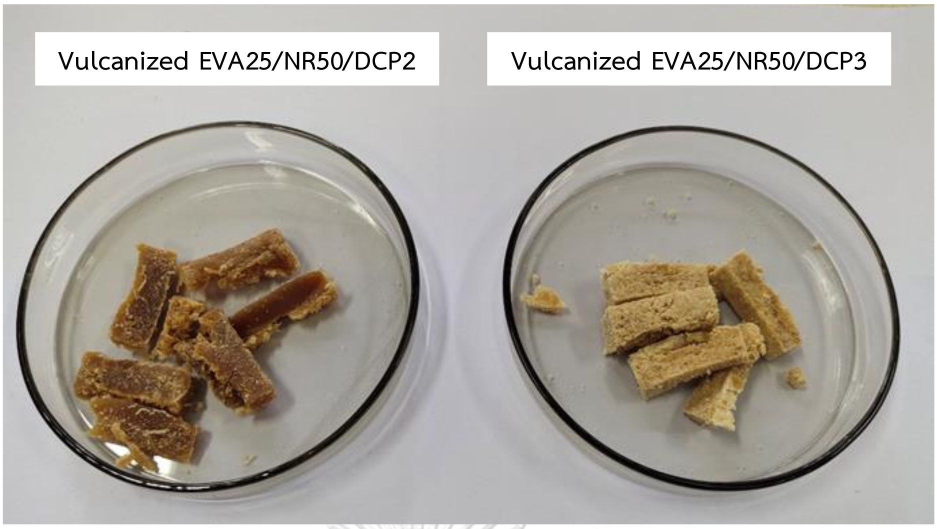

Figure B.1 Vulcanized sample from the internal mixer of 30 cm^3

(left) EVA25/NR50/DCP2 (right) EVA25/NR50/DCP3

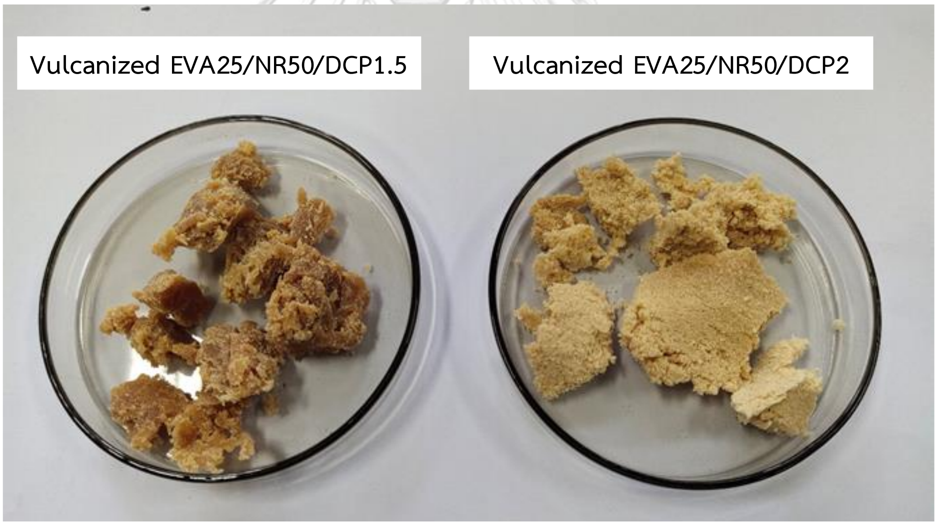

Figure B.2 Vulcanized sample from the internal mixer of 60 cm^3

(left) EVA25/NR50/DCP1.5 (right) EVA25/NR50/DCP2

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PUBLICATION	Journal articles: 1. Nappaphan Kunanusont, Chavakorn Samthong, Fan Bowen, Masayuki Yamaguchi, and Anongnat Somwangthanaroj, Effect of Mixing Method on Properties of Ethylene Vinyl Acetate Copolymer/Natural Rubber Thermoplastic Vulcanizates, Polymers, 2020, 12(8), 1739 2. Nappaphan Kunanusont, Boonchai Sangpetngam, and Anongnat Somwangthanaroj, Improvement on Asphalt by Blending with Ethylene Vinyl Acetate Copolymer and Natural Rubber Thermoplastic Vulcanizates (TPV) (Submitted) Presentations and Proceedings: 1. Nappaphan Kunanusont, Chavakorn Samthong, and Anongnat Somwangthanaroj, Effects of Blend Composition and Dynamic Vulcanization using Peroxide on Morphology, Dynamic Mechanical and Thermal Properties of Ethylene

Vinyl Acetate Copolymer and Natural Rubber Blends, presented at The International Rubber Conference 2016 (IRC2016), Kitakyushu, Fukuoka, Japan, October 24 – 28, 2016 (Poster presentation and proceedings)

2. Nappaphan Kunanusont, Anongnat Somwangthanaroj, and Masayuki Yamaguchi, Effect of Mixing Procedures on Rheological Properties of EVA/NR TPVs, presented at The Annual Technical Conference for Plastics Professionals 2017 (ANTEC2017), Anaheim, California, United States of America (USA), May 8 – 10, 2017 (Poster presentation)

3. Nappaphan Kunanusont, Masayuki Yamaguchi, and Anongnat Somwangthanaroj, Effect of Peroxide Content on Rheological and Mechanical Properties of EVA/NR TPVs, presented at The 43th Congress on Science and Technology of Thailand (STT43), Bangkok, Thailand, October 17 – 19, 2017 (Oral presentation)

4. Nappaphan Kunanusont, Chavakorn Samthong, Boonchai Sangpetngam, and Anongnat Somwangthanaroj, Ethylene Vinyl Acetate Copolymer and Natural Rubber Thermoplastic Vulcanizate Modified Asphalt: Effect of Crosslink Degree on Physical and Rheological Properties, presented at The Thailand Science Research and Innovation (TSRI) congress 2019, Bangkok, Thailand, August 8, 2019 (Poster presentation)

AWARD RECEIVED	1. Outstanding presentation of Research and Researchers for Industries Bangkok Forum 2019 (RRi BKK Forum 2019) 2. Travel award for oversea student (ANTEC2017)