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FACTORS INFLUENCING SHRINKAGE OF NATURAL RUBBER/EPDM BLEND

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งานวิจัยนี้ได้ศึกษาปัจจัยที่มีผลต่อการหดตัวของพอลิเมอร์ผสมของยางธรรมชาติและยางอีพีดีเอ็ม (สัดส่วน 70:30) และสมบัติทางกายภาพของยางวัลคาไนซ์ ปัจจัยที่ศึกษาได้แก่ปริมาณและชนิดสารตัวเติม และระบบการวัลคาไนซ์ พบว่ายางคอมปาวด์เติมด้วยเคลย์มีการหดตัวน้อยที่สุด และยางคอมปาวด์เติมด้วยแคลเซียมคาร์บอเนตมีการหดตัวมากที่สุด ขณะที่ยางคอมปาวด์เติมด้วยคาร์บอนแบล็กและซิลิกามีการหดตัวคล้ายคลึงกัน สำหรับยางวัลคาไนซ์ทั้งหมดพบว่าการเพิ่มปริมาณสารตัวเติมในคอมปาวด์ ทำให้การหดตัวของยางวัลคาไนซ์ลดลง เนื่องจากสัดส่วนยางลดลง การเปลี่ยนแปลงการหดตัวนี้สอดคล้องกับค่าสัมประสิทธิ์การขยายตัวเชิงความร้อนของแต่ละคอมปาวด์ นอกจากนี้ยังพบว่ายางคอมปาวด์ที่ใช้ระบบวัลคาไนซ์ประสิทธิภาพ มีการหดตัวน้อยกว่ายางคอมปาวด์ที่ใช้ระบบวัลคาไนซ์กึ่งประสิทธิภาพและระบบวัลคาไนซ์ปกติตามลำดับ เนื่องจากระบบวัลคาไนซ์ประสิทธิภาพทำให้เกิดพันธะเชื่อมขวางสูงที่สุด ยางวัลคาไนซ์มีความแข็งเหนียวมากทำให้มีการหดตัวต่ำ

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PRACHID SARAMOLEE : FACTORS INFLUENCING SHRINKAGE OF NATUAL RUBBER/EPDM BLEND. THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 90 pp. ISBN: 974-17-5537-6

In this research work, various factors influencing the shrinkage of natural rubber/EPDM blends (ratio of 70:30) and the physical properties of vulcanized rubber were studied. The types and concentrations of filler and vulcanization systems were also investigated. It was found that the shrinkage of the clay filled compound was the lowest, while the shrinkage of calcium carbonate filled compound was the highest. The results also showed that the carbon black filled compound and silica filled compound had similar trend. For all vulcanizates, the increased amount of filler resulted in decreasing shrinkage due to the decrease in rubber content. The change of shrinkage was consistent with the linear coefficient of thermal expansion of each filled compound. It was also found that the efficient vulcanized compound shrinkage was lower than semi-efficient and conventional vulcanized compound, respectively. This is due to the fact that the efficient vulcanized compound exhibited the highest crosslink density. The stiff vulcanizates yielded a low shrinkage value.

Field of Study…Petrochemistry and polymer science.. Student's signature………………………..

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CONTENTS

PAGE

PAGE

LIST OF TABLES

TABLES **PAGE**

TABLES **PAGE**

LIST OF FIGURES

FIGURES **PAGE**

FIGURES **PAGE**

LIST OF ABBREVIATIONS

^{0}C : Degree Celsius

g : gram

kg : Kilogram

mg : Milligram

MW : Molecular Weight

µm : Micrometer

%wt : Percent by weight

avg : Average

nm : Nanometer

phr : Part per hundred rubber

ASTM : The American Society for Testing and Material

TMA : Thermomechanical Analysis

CBS : N-Cyclohexyl-2-benzothiazolesulfenamide

TMTD : Tetramethylthiuram disulfide

DTDM : 4,4-Dithiodimorpholine

CV : Conventional Vulcanization

Semi-EV : Semi-Efficient Vulcanization

EV : Efficient Vulcanization

hr : Hour

CHAPTER I

INTRODUCTION

1.1 The Statement of Problem

The first automotive assembly plant of thailand was opened in 1961 and the industry has achieved significant milestones since then. Autos and auto parts generated the nation's second highest export earnings last year [1]. Today, Thailand is the largest automotive manufacturer in south-east Asia and ranks 15th worldwide with 2004 production of more than 900,000 vehicles. The Thai government has set a goal of producing 1.8 million vehicles by 2010 to become one of the world's top 10 automotive manufacturers. With this track record and the government's priority on further industry development, Thailand is poised to become the 'Detroit of Asia'. A car has more than 3000 parts and components – 20,000 if the small ones are counted. Currently, the auto parts industry in Thailand comprises over 1700 part suppliers providing engines, engine components, body parts, brake systems, steering systems, suspensions, transmissions and rubber parts. Both the domestic and export automotive markets are booming in Thailand. The Thai Automotive Institute (TAI) projects that the value of Thailand's total auto parts export will amount to $5 billion in 2006. $2 billion is expected to come from original equipment manufacturer (OEM) auto parts and $3 billion from replacement equipment manufacturer (REM) parts. Furthermore, the TAI forecasts that 800,000 units will be produced for export by 2010. As automotive assemblers expand production, parts and component suppliers benefit from higher demand. International parts suppliers as well as multinational auto assemblers are expanding their business operations in Thailand.

In traditional polymer material selection, designers consider part performance requirements in narrowing down, or pruning, a set of candidate materials. Typical issues include material cost, stiffness, creep, impact and fatigue resistance, dimensional stability, service temperature, chemical and UV resistance, hardness or abrasion resistance, regulation compatibility, flow characteristics, and surface finish.

Quantitative pruning of candidate materials occurs on several levels. For instance, aesthetic, regulation, and service environment requirements can immediately eliminate certain materials. The detailed structural and process analysises, mechanical, thermal, cost and processing property requirements will narrow the search even further. For critical applications, or for part requirements for which no adequately predictive models may exist (e.g., long term creep, or abrasion resistance), engineers must often resort to prototype and testing to arrive at a final material choice.

Molding rubber parts that meet dimensional tolerances in a cost-effective manner poses several challenges to the designer who must understand the reasonable tolerance limits for candidate materials, molders, and particular molding process control [2]. Typically, designers or molder will use shrinkage data of material to estimate achievable part tolerances. While mold shrinkage data provide a qualitative comparison of material dimensional stability, they do not explicitly capture the effects of process variables (packing pressure, mold and temperature). At advanced stages of design, molding process simulation can estimate part shrinkage and out of plan distortion. However, the results from this level of analysis are used to design process in which it is more difficult to make the changes that simulation may suggest.

1.2 Objective of the Research Work

The objective of this work is to study the effect of type and amount of fillers and vulcanization systems on the shrinkage and physical properties of natural rubber/EPDM blend.

1.3 Scope of the Research Work

The natural rubber/EPDM blends at ratio of 70/30 were prepared at various loading levels of fillers with different vulcanization systems. The shrinkage properties of rubber blends filled with carbon black, silica, clay and calcium carbonate were investigated.

The experimental procedures were carried out as follows:

1. Literature survey and study the research work.
2. Prepare the natural rubber/EPDM compound filled with carbon black, silica, clay and calcium carbonate at 0-50 phr. Two-roll mills was used to mix compounds.
3. Study the cure characteristics of natural rubber/EPDM blends using rheometer (MDR2000).
4. Prepare the vulcanizates by compression molding at temperature of 170^{0}C, cure time of 7 minutes and pressure of 120 kg/cm^2.
5. Investigate the mechanical properties and the crosslinking density of rubber compounds.
6. Investigate the shrinkage properties of rubber compounds for 240 h and study the thermomechanical properties using TMA technique.
7. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Elastomers [3-5]

There are hundreds of commercially graded elastomers which are available. These elastomers are mainly synthetic. However, natural rubber is the prototype of all elastomers since it is the first rubber that was commercially used. Due to many reasons, the large numbers of developments have been made on synthetic elastomers rather than natural rubber. So far, a lot of successful achievements have been made to compete the synthetic elastomers with the natural rubber, and in some cases, the synthetic one is superior to the natural one.

In general, the molecule of rubber is a long hydrocarbon chain composed of many repeating units, each of which normally has, at least, one reactive site. The reactive sites or functional groups can be double bond, hydroxyl group, halide group, amine group, etc., which can react with other substances i.e. curing agents. These sites are the most important for the vulcanization and degradation of rubbers. In the case of the vulcanization, the rubber becomes tough, strengthened and hard, while it turns to a soft, sticky or brittle material in the case of degradation.

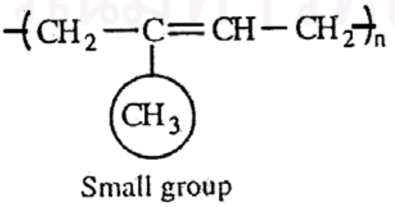
The length of the molecule is several thousand times of the cross section. Along the chain, the links are able to move laterally and freely depending upon the thermodynamic state of the rubber. Thus, many conformations of the molecule could be possible to happen. Statistically, at a constant temperature, there is the most probable distance between the ends of the chains or between any two points along the chain. If the chains are very long, they become tangled and thus they cannot slide by each other easily. It is these entropy and entanglement effects that explain the elastic recovery of raw rubber.

It is well understood that all elastomers have the glass transition temperature (T_g) below an ambient temperature and some elastomers can crystallize under stretching but some cannot. The ability to form crystallites when being stretched is dependent on the intensity of the interchain forces, which is related to chemical structure and regularity of the rubber molecules. The elastomers with high regularity and strong interchain forces have high tendency to crystallize.

2.1.1 Natural Rubber (NR) [6]

Any review of the major rubbers fittingly starts with the natural rubber. It was the first rubber and was unique until the development of polysulfide rubber in 1927. It supplies about one-third of the world demand for elastomers and is the one by which other are judged. Again, it was Charles Goodyear and Thomas Hancock's experiments with natural rubber, sulfur, and heat led to the discovery of vulcanization and was the birth as were of compounding.

In chemical structure, natural rubber is cis-1,4-polyisoprene, a linear long chain polymer with repeating isoprene unit ($C_5 H_8$). The molecular unit structure of natural rubber is illustrated below.



$$\left(CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2 \right)_n$$

Figure 2.1 Natural rubber.

Because of its structure, which is of remarkable regularity, NR is a crystallisable elastomer, especially under stretching. This effect renders high gum tensile strength to NR. There are several commercial grades of NR. Most grades mainly base on the purity and final form of the elastomer.

Table 2.1 Typical analysis of natural rubber [3]

Component	%
Moisture	0.6
Acetone extract	2.9
Protein (calculated from nitrogen)	2.8
Ash	0.4
Rubber hydrocarbon	93.3
Total	100.0

2.1.2 Ethylene Propylene Diene Rubber (EPM/EPDM) [7]

Polymers based on olefinic monomers represent a large commercial industry today, including polyethylene and polypropylene in their many forms. These polymers are considered to be thermoplastic, as they have significant levels of crystallinity present at processing temperatures, allowing repeatable forming operations. However, a copolymer of ethylene and propylene does exhibit a level of strength, flexibility, and elasticity that allows them to be classified as elastomer. These materials are commonly known as EPDM or EPM.

EPM represents copolymers of ethylene and propylene only. These polymers are completely saturated, and as such are crosslinked using peroxide curing systems.

EPM grade are available with different molecular weights (MW), and also with different ethylene/propylene (E/P) ratios. These two factors represent the two availabities that need to be considered when choosing the appropriate grade for specific application.

EPDM, on the other hand, contains ethylene and propylene, and also the third monomer that is incorporated into the polymer for the purpose of enabling a sulfur crosslinking. The third monomer contains a double bond that can then be accessed by the sulfur. Therefore, when choosing a grade of EPDM, it is important to consider the MW and E/P ratio as mentioned above, but in addition the amount and type of the third monomer must also be known. The molecular unit structure of EPM/EPDM rubber is illustrated below.

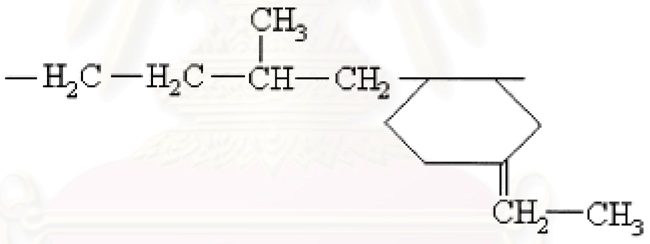


Figure 2.2 Ethylene Propylene Diene rubber.

2.2 Vulcanization [6]

The ASTM definition for vulcanization reads as follows: “An irreversible process during which a rubber compound though a change in its chemical structure (for example, cross-linking) becomes less plastic and more resistant to swelling by organic liquids while elastic properties are conferred, improved, or extended over a greater range of temperature.” This change can be brought about by variety of agents including irradiation. Since the last method at present requires expensive equipment and works best on thin rubber section, this section will deal only with the conventional vulcanization materials. The terms curing and vulcanizing will be used interchangeably.

There are four curing agents or systems in widespread use. They are:

1. Sulfur system
2. Peroxides
3. Urethane crosslinkers
4. Metallic oxides (used in vulcanizing neoprene only)

By far the most common vulcanizing methods are those depending on sulfur. Practically, all rubber products are vulcanized by one or more of five methods. There are:

1. Press curing (including injection and transfer molding)
2. Open steam curing
3. Lead press curing
4. Fluidized bed curing
5. Salt bath curing

Before considering specific vulcanizing agent, two aspects of the curing process should be touched on. A common problem in rubber goods factories is a scorch which is a tendency of a compound to start curing before it is the right form and right place to be cured. There is a vicious circle here: for cost reasons the quicker the compound can be cured and at the lowest temperature the better; yet compounding to this aim alone means more stock will be rejected because of scorch. Apart from careful compounding, scorch is lessened by mixing, storing, and processing the stock at the lowest temperature possible (yet breaking down and dispersing ingredients satisfactorily). So that heat history is at a minimum master batch of sulfur and accelerators were added at the end of the mixing cycle to help speeding up the reaction. Stocks should be cooled after mixing and should not be held for long times on warm-up mills prior for extruding or calendaring.

Another point to be remembered is that few rubber goods items are fully cured when they were made. A Full cure means a state when hardness is at maximum, modulus is fully developed, and further curing might result in a reversion, e.g., with natural rubber stocks. The reasons for not going to a full cure are that rubber properties develop at different rates of curing processes. For example, tear resistance usually peaks before tensile strength, as does abrasion. On the other hand, swelling resistance is the greatest when a compound is fully cured. The highest tear resistance is wanted, the best product cure might be what would be considered an under cure. The curing may be again finished in service giving a longer life. For example, steam hose tubes are made with some under cure as the curing will be completed in service.

2.2.1 Theory of Sulfur Vulcanization [8]

Sulfur vulcanization has been treated in an essentially empirical manner, and in fact the chemistry of sulfur vulcanization is so complex that it is only within the last few years that a coherent theoretical treatment has been possible. Even today, only the main stages are proven and there is still much to be learned about the effect of additives of various types.

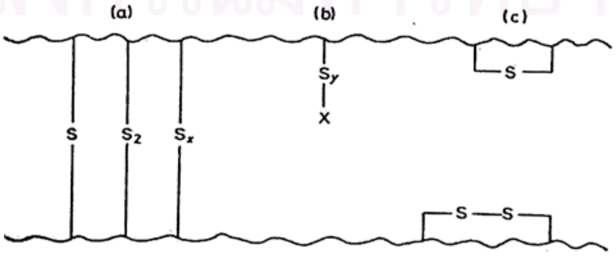


Figure 2.3 Structure features of vulcanisate network [8].

Sulfur is combined in the vulcanization network in a number of ways (Figure 2.3). As crosslink, it may be present as monosulphide and disulphides (Figure 2.3a), but it may also be present as pendant sulphides (Figure 2.3b), or cyclic monosulphides and disulphides (Figure 2.3c). An estimation of the number of sulfur atoms for each crosslinking formation has been made: an unaccelerated rubber-sulfur vulcanization may give a figure of 40-45, whilst in conventional accelerated sulfur vulcanization this “inefficiency” figure may drop to 10-50. Special “efficient” vulcanizing systems can further reduce to 4 or 5, but for even lower values, so-called “non-sulfur” vulcanization systems must be used.

By the use of chemical probes, the relative amounts of mono-, di-, and polysulphide materials can be assessed, and by measuring the degree of cross-linking as well, the dependant and intramolecular sulfur can be estimated. From this information and the amounts of nitrogen and sulfur combined with the rubber at various stages of vulcanization, it is possible to reduce the general course of the vulcanization reaction.

The initial step in vulcanization seems to be the reaction of sulfur with the zinc salt of the accelerator to give a zinc perthio-salt XS_xZnS_xX, where X is a group derived from the accelerator (e.g. thiocarbamate or benzothiazyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bond intermediate as shown in Eq. 2.1

$$XS_xZnS_x + RH \longrightarrow XS_xR + ZnS + HS_{x-1}X \qquad (2.1)$$

A perthio-accelerator group which, further reacts with zinc oxide will form a zinc perthio-salt of lower sulfur content; this may, nevertheless again be an active sulphurating agent, forming intermediates $XS_{x-1}R$. In this way, each molecule of accelerator gives rise to a series of intermediates of varying “degrees of polysulphidity”. The hydrogen atom, which is removed, is likely to be attached to a methylene group in the alpha position to the double bond, i.e. in natural rubber the hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction.

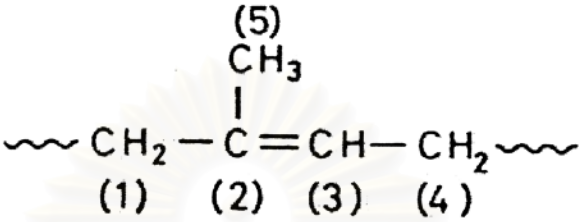


Figure 2.4 Position of hydrogen atoms in natural rubber [8].

The intermediate XS_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslinking decline. This process is catalyzed by XS_xZnS_xX and can result in additional crosslinks. It is also evident that the crosslinks, which were initially at positions 4 and 5, undergo an allylic shift, with the result of new configuration appearance:

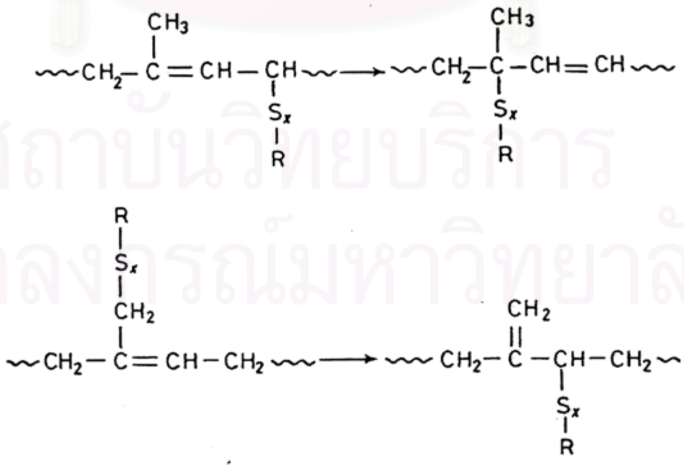


Figure 2.5 The crosslinks, which were initially at positions 4 and 5 [8].

At the same time, a disappearance of crosslinks of the disulphide and polysulphide types occurs, with formation of conjugated trienes:

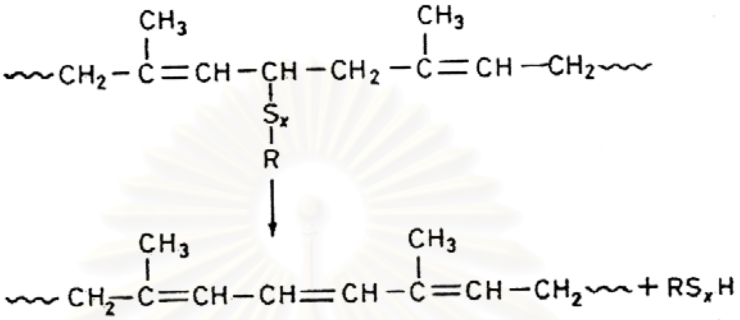


Figure 2.6 Formation of conjugated trienes [8].

This destruction of crosslinks is apparent associated with the formation of the cyclic sulphides (Figure 2.3c), but this has not been investigated in detail.

A consideration of the above reactions leads to the conclusion that, if desulphuration proceeds rapidly as in the case of the mix depicted in Figure 2.7, the final network will be highly crosslinked with mainly monosulphidic bonds, and there will be relatively few modifications of the cyclic sulphide or conjugated triene type: such a network is termed “efficiently crosslinked”.

On the other hand, desulphuration proceeds slowly as in the case of the compound depicted in Figure 2.8. There will be opportunities for thermal decomposition, leading to reversion or loss of crosslinks and network containing modifications. The crosslinks which do survive will be di- or poly-sulphidic and hence will be liable for further decomposition. These networks are inefficiently crosslinked.

Examination of a system containing high abrasion furnace (HAF) black shows that the remarks made above for a pure gum, generally hold for a natural rubber compound containing active black. The presence of HAF black increases the overall rate of reaction of the rubber and sulfur, and promotes the sulphuration reaction, thus leading to an increase in crosslink efficiency.

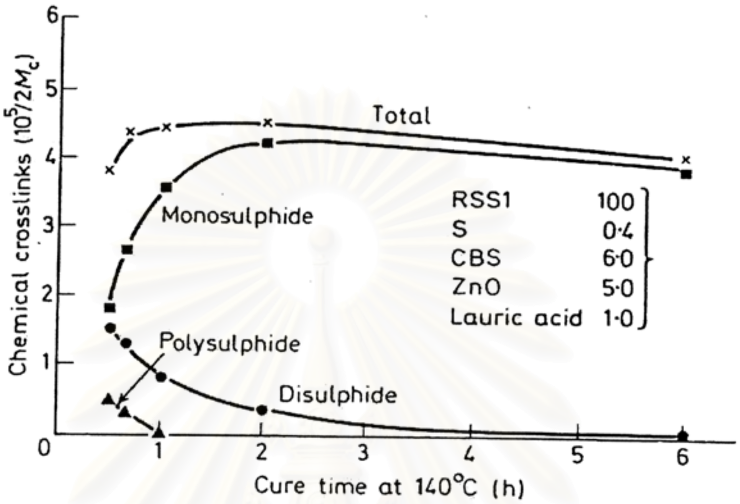


Figure 2.7 Feature of NR vulcanization produced by an efficient crosslinking system (M_c = number average molecular weight between crosslinks) [8].

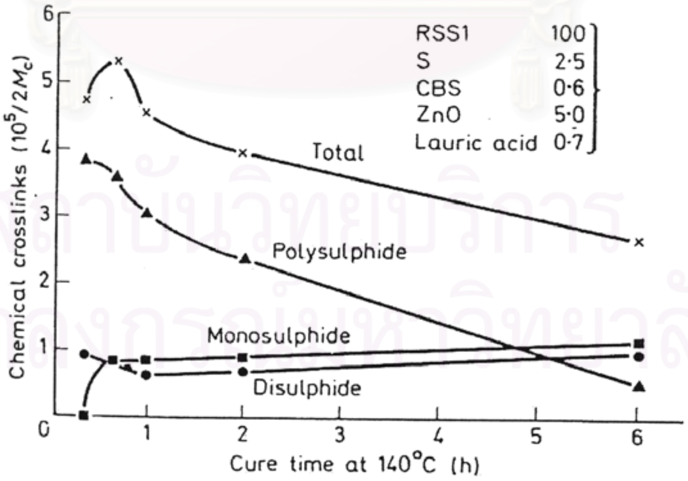


Figure 2.8 Features of NR vulcanization produced by a conventional crosslinking system (M_c = number average molecular weight between crosslinks) [8].

2.2.2 Sulfur Vulcanization Systems [9]

For conventional and most frequently used systems, one uses for example roughly 1.5-2.5 phr sulfur with 1.0-0.5 phr accelerator. When accelerator dosage is increased (for example 1.5-2.5 phr), the sulfur content has to be lowered (for example 1.2-0.5 phr) to achieve the same crosslink density; the consequence is formulation of crosslinks with less sulfur content. Such semi-efficient (semi-EV) systems produce, as expected, heat- and reversion-resistant vulcanizates.

Because a high accelerator content leads to a more effective use of the sulfur and thus to a shorter sulfur link as well as to a reduction of sulfur which is not used for crosslinking. When the amount of accelerator is drastically increased, small amounts of sulfur are sufficient to obtain a satisfactory degree of crosslinking. When the amount of sulfur is reduced even further, the use of accelerators which are at the same time sulfur donors (e.g. TMTD) is called for. For example, when 2.5-3.5 phr TMTD are used, vulcanization takes place with only very small amounts of sulfur (e.g., 0.2 phr), or even in the absence of all elemental sulfurs. For these semi-EV or EV compounds the sulfur donors without any accelerator activity also play a certain important role. A so-called Efficient-Vulcanization (EV) leads to mono- and di-sulfidic crosslink structures. The consequence is very good heat stability and reversion stability, respectively a high temperature compression set.

Table 2.2 Sulfur and accelerator of different vulcanization systems for NR [9].

Cure Systems, Conventional versus Efficient Vulcanization			
	Conventional	**Semi-EV**	**EV**
Sulfur, phr	2.0-3.5	1.0-1.7	0.4-0.8
Accelerator, phr	1.2-0.4	2.5-1.2	5.0-2.0
S/A ratio	10-1.5	1.5-0.4	0.4-0.08

2.2.3 Cure Characteristics [10]

The vulcanization is a chemical reaction and generally considered as a first order reaction. The shape of the cure curve is an important aspect in the consideration of practical vulcanization time at a specific temperature and a determination has to be made in order to find the optimum time for the properties required. There is no precise definition for the optimum cure because it is a matter of individual choice. Three typical shapes of cure, marching, plateau and reversion cures can be encountered as shown in Figure 2.9. From the cure graph, it is however possible to describe the state of cure whether the vulcanizate is under-cure, good, optimum, etc.

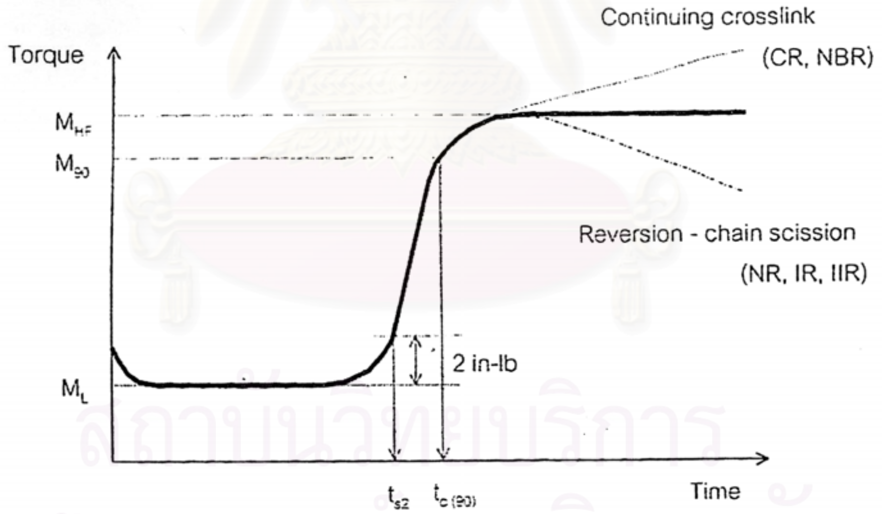


Figure 2.9 Typical cure curves [10].

2.3 Fillers [11]

Fillers are mostly in forms of both powders and compacted powders. They can be termed reinforcing and non-reinforcing, and also fall into black and non-black types.

2.3.1 Carbon Blacks

A few introductory remarks on carbon black will serve to make clear some of the observations discussed later. Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking.

In the now obsolete and virtually extinct channel process, natural gas is burned in small burners with a sooty diffusion flame and the carbon collected on a cool surface section of channel iron. Relatively, the free access of the hot product to air leads to oxidation of the surface, one of the unique features of this process. The surface oxygen complexes give channel black acidic character, manifesting itself in high adsorption capacity for bases and low pH of aqueous slurries. Surface acidity has a repressing effect on sulfur vulcanization.

At present, almost all rubber-reinforcing carbon blacks are manufactured by oil furnace processes. A fuel, either gas or oil, is burned in an excess of air, producing a turbulent mass of hot gases into which the conversion oil is injected. Reaction to finely divided carbon is complete within milliseconds and the hot smoke stream is quenched with water. Furnace blacks have low oxygen content (usually less than 1%) and their surface is neutral or alkaline.

In thermal process, oil or, more frequently, natural gas is cracked in the absence of oxygen at a hot refractory surface. The process produces un-oxidized blacks of relatively small specific surface area (6-15 m^2/g)(thermal blacks).

2.3.2 Non-Black and Mineral Fillers

In the rubber compounding field, naturally occurring mineral fillers are important in reducing cost and are usually classified on the basis of their origin.

They are usually classified as:

1. Fillers used mainly to reduce cost.
2. Certain unique properties required like thermal conductivity by the use of zinc oxide.
3. Reinforcing fillers used to achieve high performance in non-black products.

This classification is not rigid as materials derived from similar sources which may vary in function according to their methods of preparation and treatment. It has been considered expedient; therefore, to group them here according to their source (Figure 2.10).

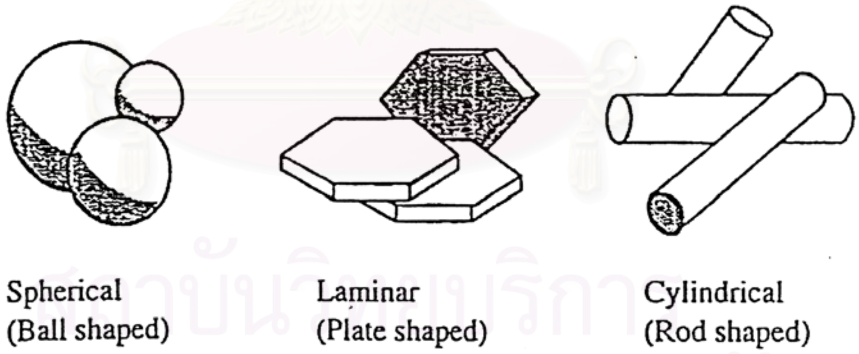


Figure 2.10 Basic Types of Mineral Filler shapes [11].

I) Silicas

Ground mineral silica, mineral silica or sand (silicon dioxide) grounded below 200 mesh is a cheap filler for heat resistant compounds. It has no effect on cure.

- Hydrated precipitated silicas: These silica are silicon dioxide containing 10-14 % water, with particle sizes in the range of 10-40 nm. They are reinforcing fillers giving compounds of high tensile strength, tear resistance, and good mechanical abrasion. In combination with reinforcing blacks, they improved tear resistance and adhesion of fabrics. Hydrated silicas retard cure and require increased dosage of accelerator or the addition of materials such as glycols or amines to promote curing. They respond to hot mixing techniques in a manner similar to reinforcing blacks giving increased modulus or resilience.

- Fume silica or pyrogenic silica: Fume or pyrogenic silica is silicon dioxide, containing less than 2% combined water, usually prepared by burning volatile silicon compounds. These silicas are highly reinforcing fillers of very small particle size, given high tensile strength, tear resistance, abrasion resistance, particularly to silicone rubbers. The retarding effect on cure in organic rubbers requires increased amounts of accelerators or the use of glycols or amines. The use of wax, polyethylene, or other lubricating materials is recommended to avoid sticking to rolls in processing and to moulds after cure.

II) Clays

Kaolin clay, also called kaolinite or china clay, is hydrous aluminum silicate ($Al_2Si_2O_5(OH)_4$), consisting of platelets with alternating layers of silica and alumina in its structure. The fine particles of clay are formed by the weathering of granite. Clay deposits are classified as primary, secondary, and tertiary. Primary deposits are mixtures of clay and granite that are found where the clay was originally weathered. Only 40 to 50 % of the particles contained in these deposits are less than 2 μm in diameter. Secondary deposits are formed when fine particles from primary deposits are carried by water flow and deposits in a new location. Tertiary deposits are the most important commercial deposits due to their fine particle sizes; more than 80% of the particles are less than 2 μm in diameter. Their high purity results when water carries the fine particles of a secondary deposit to a new location. Clays are commonly added to rubber compounds at levels of 20 to 150 phr.

- No reinforcement: Soft clay of surface area below 10 m^2/g, non active.
- Some reinforcement: Hard clay of surface area approximately 30 m^2/g, semi active.

III) Calcium Carbonates

Ground calcium carbonate ($CaCO_3$), also known as whiting, limestone, marble, chalk, and calcite, is added into rubber compounds to reduce cost and impart hardness and opacity to rubber articles. Particle sizes range from 2 to 80 μm for dry ground product and from 0.5 to 11 μm for wet ground product. The chemical composition and crystalline nature depend on the limestone deposit mined (for example, chalk or marble) and the color of the deposit.

The most important applications of calcium carbonate by the rubber industry are in electrical wire and cable insulation which the low moisture content and natural insulating properties make it a preferred filler. In the production of articles, low cost and smooth surface appearance are desired, such as footwear; and in extruded hoses and automotive sealing parts. Typical calcium carbonate levels in rubber compounds range from 20 to 300 phr.

IV) Synthetic Calcium Carbonates

Precipitated calcium carbonate is formed by dissolving limestone and precipitating $CaCO_3$ as very fine particles using carbon dioxide (Aroganite process) or sodium carbonate (Solvey process). Typical particle sizes range from 0.02 to 2 μm. Most commercially available, precipitated calcium carbonate consists of spherical, colloidal particles or aggregates consisting of a few spherical particles. Additional, shapes and aggregates varying morphology are possible and provide increased reinforcement. Precipitated calcium carbonate is used as semi-reinforcing filler in shoe products and industrial rubber goods, particularly when resistance to alkali solutions is needed. The low moisture content and good reinforcement allow precipitated calcium carbonate to be used in wire and cable insulation applications, as well.

2.4 Shrinkage during the Manufacture of Molded Articles [12]

An article molded from a rubber compound always ends up smaller than the mold in which it was vulcanized. The difference between the dimensions of the finished article and the mold, measured at room temperature and expressed in percent is called the degree of shrinkage. Since the dimensions of molded articles have to be very often within very close tolerances, it is important to know the degree of shrinkage so that it can be considered during the design of the mold.

On the one hand, the shrinkage of the rubber during cooling can be welcomed. To have the rubber and the mold in the same coefficient of expansion, removal of the part from the mold would be problematic. On the other hand, this phenomenon complicates the manufacture of articles of correct dimensions.

The degree of shrinkage is primarily determined by the difference of the coefficient of expansion between the vulcanizate and the mold materials as well as by the vulcanization temperature. The rubber part which fills in the mold completely during vulcanization contracts during cooling to room temperature more than the mold because it has a considerably higher coefficient of expansion than the latter. Thus, the degree of shrinkage increases with increasing the difference between the coefficients of expansion of the rubber compound and the mold materials as well as between vulcanization and room temperature. The difficulties during the calculation of degree of shrinkage arise mostly from the fact that the coefficient of expansion of vulcanizate changes with the compound composition.

The vulcanization time and the mastication time during the preparation of the compound are practically without influence on the degree of shrinkage, some of the coefficient of expansion is important for the calculation of the degree of shrinkage are summarized in Table 2.3. The temperature independent contraction which is a result of the chemical reaction between sulfur and the elastomer is of little consequence for the degree of shrinkage. It accounts for only 0.1% for sulfur dosages which are common for soft vulcanizates, but it is larger for hard rubber compound. Since the contraction is further reduced in filled compounds because of the reduced elastomer content. It might be within experimental error and can generally be neglected (Figure 2.11).

It is becoming increasingly difficult, with the number of compounds that are available to the trade, to be able to design a mold with any semblance of accuracy due to the lack of presenting a clear idea of what direction to take in regarding to mold shrinkage. Early laboratory work performed that covered a lot of the problems and this report has been taken and applied to present day compounds. There are several factors affecting shrinkage:

Table 2.3 Linear Expansion Coefficients of some Elastomer Types, Fillers and Mold Materials[12].

Material		**Linear expansion coefficient (10^{-6}in/in/^{0}F)**
Elastomers	: NR	220
	: SBR	221
	: NBR	195-199
	: CR	196-206
	: IIR	194
	: BR	224
	: EPDM	225
	: ECO	222
	: FKM	224
Filler		Order of Magnitude : 5-10
Mold Materials	: Steel	11
	: Light Metal	22

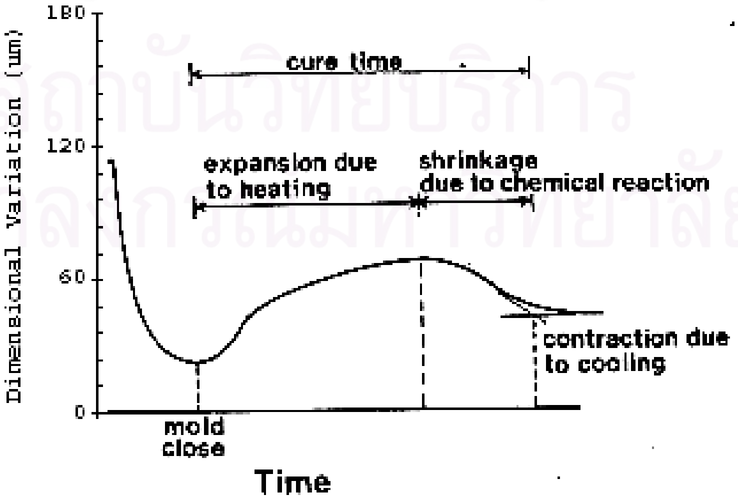


Figure 2.11 Shrinkage behavior of rubber vulcanization [13].

1. The principle reason for shrinkage is the thermal contraction resulting from cooling from the temperature of vulcanization to room temperature. Partly counteracting, this is the increase in dimensions of the mold cavity by heating from room temperature to vulcanizing temperature. A generally accepted figure for the coefficient of volume expansion for a high gum mix is 6.6 x $10^{-6}/^{0}$C.

2. A second factor affecting shrinkage is the change in volume resulting from vulcanization. Shrinkage due to vulcanization for a 3-part sulfur stock has been found to be about 0.0009 inch/inch. Thus, this would be reduced in proportion to the volume of rubber present for a compound stock.

3. Other factor affecting the shrinkage is the grain direction; i.e., parallel to and across the direction of the grain. This shrinkage is large along the direction of the grain and small across of the grain.

In general, linear shrinkage figures fall within the range of 1.5-3.0% depending on polymer type and filler loading (Figure 2.12). Fibrous materials such as cotton linters produce many complicating factors. Processing stocks with these materials will orient the fiber and often give much greater shrinkage perpendicular to the fiber than along the fiber.

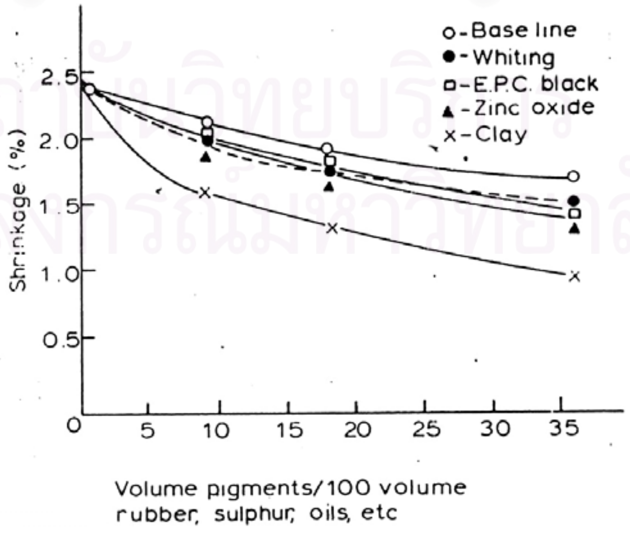


Figure 2.12 Effect of pigment volume on shrinkage of natural rubber [14].

2.5 Literature Review

Borrajo et al. [15] studied the effect of cure shrinkage on the miscibility of a polydisperse rubber with a trifunctional monomer. The use of a Flory-Huggins (FH) equation presented a thermodynamic analysis of phase separation for a rubber-modified cyanate ester system, for the uncatalysed cure of bisphenol A dicyanate at 200^0C. The volume contraction during polymerization (cure shrinkage) produces a slight decrease in the miscibility of the rubber in the thermosetting polymer, leading to a shift of cloud-point conversions to lower values. The reason for this effect is the reduction in the volume fractions of holes. This produces the decrease in the entropic contribution to the free energy of mixing and the increase in the value of the energetic term. Both factors act in the sense of decreasing rubber miscibility in the thermosetting polymer.

Chaturvedi and Shen [16] studied the thermal expansion response of particle-filled polymer matrix composites by micromechanical modeling. The model system used is the epoxy matrix filled with solid-sphere or hollow-sphere silica particles, which the coefficient of thermal expansion (CTE) value decreases with increasing the filler concentration. Within the range of heating rates considered, the viscous behavior of epoxy has essentially no effects on the overall CTE, because the CTE differences resulting from different heating rates and from the elastic and viscoelastic cases are negligible. The composite CTE values for the aligned fillers are greater than those for the staggered fillers. This difference due to the particle arrangement is; however, moderate. It is judged from the fact that there is an extremely large difference in CTE of the matrix phase and the filler phase.

Wu et al. [17] studied the polymer alloys with very low coefficient of linear thermal expansion (CLTE). The large reduction in CLTE is not based on an addition of low-thermal-expansion filler to suppress the bulk expansion. Rubber was used as an additive to tune the thermal expansion behavior of various plastics. The investigated influenced factors including rubber concentration, viscosity ratio, interfacial adhesion as well as the domain size. The thermal expansion for press-molded of polypropylene blend with 40 %wt ethylene-propylene rubber (PP/EPR, 40 %wt) was isotropic and its CLTE is 16.2 x $10^{-5}/^{0}$C. It is clear that the specimen formed by injection molding has a low CLTE in flow direction (FD) and transverse direction (TD). The very high CLTE in normal direction (ND) is compared with those of the press-molded samples. It can be seen that, compared to the linear increase in CLTE for press-molded of polyamide-6 blend with polyamide, maleic anhydride-grafted EPR (PA/m-EPR), the CLTE of the injection molded samples drastically decreases when the m-EPR concentration is higher than 40 %wt.

Tai and Chou [18] studied the cure kinetics of a highly filled epoxy molding compounds (EMCs). The epoxy molding compounds are transferred from a low temperature transferring pot to high temperature mold cavities wherein the crosslinking reaction take place. As the EMC reacts, gel and shrinks, the interfacial stress builds up. The interfacial stress grows further upon cooling down to 25 ^{0}C as each material shrinks to the different extent. The amount of linear stain contributed by chemical shrinkage is 1.18%, whereas the contribution obtained from physical shrinkage is only 0.18%, that even for a compound of low volumetric shrinkage. The shrinkage resulted from chemical reaction is considerably larger than that from thermal contraction.

Jansan *et al*. [19] studied the effect of processing conditions on mold shrinkage for common thermoplastic polymers such as polystyrene (PS), acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS), polycarbonate (PC), polybutadiene terephthalate (PBT), polybutadiene terephthalate which are filled with fiber glass 30% (PBT-GF30) and high density polyethylene (HDPE) and systematically varying holding pressure, injection velocity, mold temperature and melt temperature. The shrinkage of all polymers vary between 0.4% and 0.9%, whereas both increasing holding pressure and melt temperature decrease the product shrinkage. The addition of short glass fibers has a dramatic effect on the length of shrinkage (drop from about 3% to 0.2% shrinkage). The effect on width shrinkage is also considerable (decrease of about 0.7%). The holding pressure affects only width shrinkage, whereas length of shrinkage remains unaffected by the holding pressure. The injection velocity has only a small effect on the width of shrinkage and a negligible effect on length of shrinkage of fiber reinforced PBT.

Juve and Beatty [20] reported the shrinkage of molded rubber goods. The laboratory work on neoprene, natural rubber and nitrile compounds was performed in a mold with center pins varying in diameter from 1” to 5” and the outside diameter constant at 6”. With the constant height of 2”. Only the 1”, 3” and 5” I.D. pieces were made on each trial to reduce the time involved. Compounds were selected with varying elastomer content and each piece allowed standing over night before being measured. It is found that the inner and outer diameter shrinkages increase as the rubber contents increase. All rubbers are linear shrinkage and they have the nearly shrinkage value at the same rubber contents.

Khonakdar *et al*. [21] investigated the thermal shrinkage of stretched crosslinked high-density polyethylene (HDPE). With the aim to produce heat shrinkable materials and the effect of stretching ratio and stretching temperature on thermal and shrinkage behavior at varying peroxide contents. The shrinkage percentage (Sh%) as a function of temperature for crosslinked HDPE containing 0.5% and 1.5% di-*tert*-butyl cumyl peroxide (BCUP) at two different stretching temperatures (90 and 140^{0}C). The samples were elongated for four times at these temperatures and in the stretched state were cooled immediately to the room temperature. Therefore the induced stresses as a result of stretching are frozen in the samples. These stored stresses can be released by heating resulting the stretch of samples. It can be seen that the sample stretched at 140^0C as compared to the one stretched at 90^0C, shows a higher shrink temperature when heated.

Zarrelli *et al*. [22] studied the dimensional and mechanical property changes as a function of process parameters of epoxy resin compound. The glass transition temperature (T_g) of the material will expand due to the positive temperature change; on the other side, chemical shrinkage associated with post cure reaction of partially cured samples will tend to reduce the resin volume as the reaction proceeds. At a constant temperature, an elastic material or any structure made from elastic materials, show no deformation. When one of the components has viscoelastic behavior, as in the case of polymer based composites, the complex interactions between the viscoelastic component (matrix) and the elastic part (reinforcement mat) induce a residual stress state affecting both the material integrity and the final component shape.

Postawa and Koszkul [23] studied the effects of dependent variables on the longitudinal shrinkage (S_w), perpendicular shrinkage (S_p) and weight (m) of injection moldings made of semi-crystalline polyoxymethylene (POM) or amorphous polystyrene (PS). The increase in the clamp pressure causes the increase in molded piece mass, while the mold temperature is of little influence on the molded piece mass. The value of both longitudinal and transverse processing shrinkage depends significantly on the clamp pressure value. The shrinkage in each place on molded piece made of POM is 8-10%. In case of polystyrene, the diversity of molded pieces shrinkage is little lower than for the molded piece made of POM.

Chowdhury and Das [24] studied the heat shrinkagable polymer blends in the form of an elastomeric phase and through subsequent crosslinking. Blends of ethylene vinyl acetate and carboxylated nitrile rubber with different curative systems were studied. With increasing in the cure time i.e. crosslinking, shrinkability decreased, increasing in elastomer content beyond which shrinkability decreased. With the increase in temperature of stretching, the orientation is increased due to the greater flow of the plastic phase to enchance the shrinkability. The amount of crystallinity becomes more important than the amount of crosslinking in determining the thermal stability. Elastomer rich blend with higher crosslinks shows lower stability. It is probably due to the higher amount of elastomer phase with lower crystallinity. With increasing in orientation obtained from the increase in effectiveness of intermolecular interaction, the thermal stability of increases.

Ruffier *et al.* [25] investigated the shrinkage and exothermic peak of polymerization of the unsaturated polyester resin blend with polyvinylacetate (PVAc) by the Plastoreactomat (PRM). The influence of the pressure and temperature on these phenomena and on the morphology for various PVAc contents was also investigated. It was found that the shrinkage increases when the temperature and pressure increase. The shrinkage of the 7 wt% PVAc composition is 4% which is lower than that of the system without PVAc. The 10 and 15 wt% PVAc mixtures have also intermediate shrinkages. The behavior for 0.4 MPa is independent of the PVAc content. At the higher pressures, 1.6 and 5.0 Mpa with an optimum PVAc proportion are corresponding to the minimum shrinkage. Therefore, this optimum in %PVAc seems to be lower and less defined as pressure is increased. However the general trend of shrinkage decreases with increasing PVAc proportion.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Table 3.1 Rubber and chemicals used in this study

Chemicals		**Commercial name**	**Supplier**
NR	Rubber	STR 20CV	Sritrang Agro-Industry Co., Ltd.
EPDM	Rubber	KELTAN 312	DSM Idemitsu Co., Ltd.
Carbon black	Filler	HAF N-330	TCB
Silica	Filler	NIPSIL VN3	Nippon Silica Industry Co., Ltd
Clay	Filler	Eckafine BDF	Imerys Minerals Australia Ltd.
Calcium Carbonate	Filler	NOVELLIGHT TT	Sand and Soil Industry Co., Ltd.
DEG	Dispersing agent	D.E.G.	Mitsubishi Corporation
ZnO	Activator	ZnO White Seal	P.T. Indo Lysaght
Stearic acid	Activator	Stearic acid	Imperial Industrial Chemicals
TMTD	Accelerator	Perkacit TMTD	Flexsys Antwerp Belgium
DTDM	Accelerator	Sanfasan DTDM	Flexsys America L.P.
CBS	Accelerator	ACCEL CZ-R	Kawaguchi Chemical Industry
Sulfur	Vulcanizing agent	CURAGENT-OS	Chemmin Corporation Ltd.

3.2 Instruments

1) Two roll mill mixer : Yi Tzung Precision Machinery, Taiwan

2) Compression machine : Hong Yow Thai, Thailand

3) Rheometer : Alpha Technology, USA

4) Tensile testing machine : Lloyd Instruments, England

5) Hardness Tester : Teclock, Japan

6) Auto-Specific Gravity Tester : YMC Chyo Balance, Japan

7) Hot Air Oven : Memmert, Germany

8) DMA 7e Instrument : Perkin Elmer Instrument, USA

3.3 Procedure

Natural rubber STR 20CV (70 phr) and EPDM KELTAN 312 (30 phr) were masticated for 5 min by two-roll mill. Then activator additives such as zinc oxide (5 phr), stearic acid (1 phr) and fillers (0, 20, 40 and 50 phr) was added. The rubber compound was mixed by cut-and-fold technique for 10 min until the surface of compound was smooth. The compound was mixed with accelerators and sulfur. The cure time of sheet was determined by using moving die rheometer (MDR2000). The rubber compounds were then pressed into the preheated mold of compression molding at temperature of 170 ^{0}C, cure time for 7 min and pressure at 120 kg/cm^{2}.

After pressing, the rubber sheet of the specified size (Table 3.2) was transferred to an air cooled press for 5 min. The sheet was cut into the standard specimens according to the ASTM test method. The rubber sheets filled with fillers (carbon black, silica, clay and calcium carbonate) were prepared in the same manner. The summarized procedure for preparation of natural rubber/EPDM compound is shown in Figure 3.1. The compositions of compound formulation are shown in Tables 3.3-3.6.

Table 3.2 Mould Dimensions

Properties	Mould dimension (length x width x thickness, mm.)
Tensile	160 x 160 x 2
Hardness and Compression set	ɸ29 x 12.5 (cylinder)
Shrinkage test	150 x 150 x 3

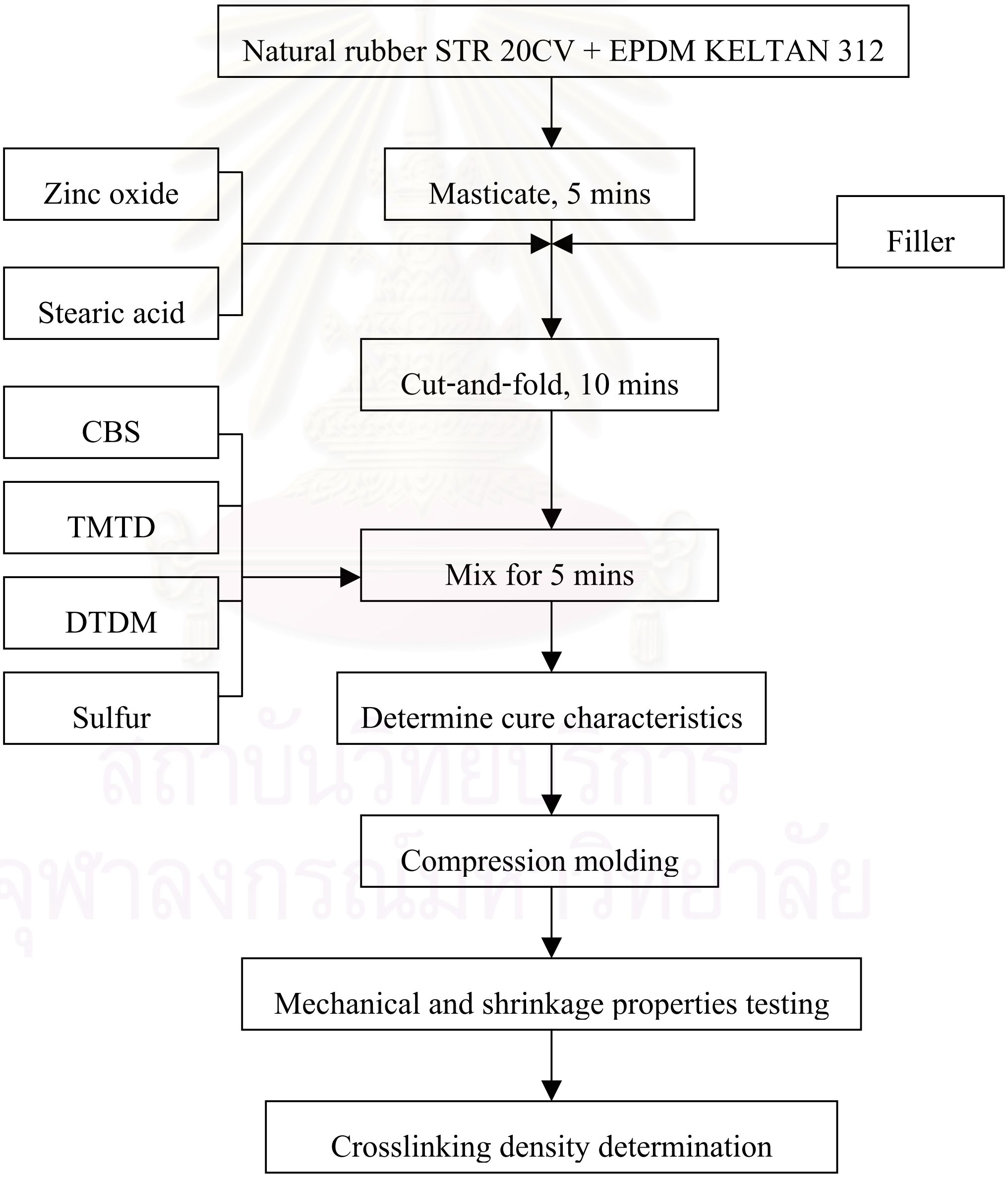


Figure 3.1 The Overall Schematic Experiment Process.

3.4 Formulation of the Compounds in the Experiments

In this experiment, the following formulations are used,

Table 3.3 Compound Formulation.

Ingredients*	**Composition, phr (part per hundred rubber)**		
	CV	**Semi-EV**	**EV**
STR 20CV	70	70	70
KELTAN 312	30	30	30
Stearic acid	1.5	1.5	1.5
Zinc oxide	3	3	3
Sulfur	3	0.6	-
CBS	1	2	1.5
TMTD	-	1	1.5
DTDM	-	-	1.5

* For compound filled silica add DEG for dispersing agent 0.3 phr.

CBS = N-Cyclohexyl-2-benzothiazolesulfenamide

TMTD = Tetramethylthiuram disulfide

DTDM = 4, 4’-Dithiodimorpholine

Table 3.4 Formulation of rubber compounds with various filler types for conventional vulcanization (CV) system.

Ingredient*	CT 00	CB 20	CB 40	CB 50	SIL 20	SIL 40	SIL 50	CC 20	CC 40	CC 50	CL 20	CL 40	CL 50
Carbon Black	-	20	40	50	-	-	-	-	-	-	-	-	-
Silica	-	-	-	-	20	40	50	-	-	-	-	-	-
$CaCO_3$	-	-	-	-	-	-	-	20	40	50	-	-	-
Clay	-	-	-	-	-	-	-	-	-	-	20	40	50

Table 3.5 Formulation of rubber compounds with various filler types for semi-efficient vulcanization (semi-EV) system.

Ingredient*	SCB 20	SCB 40	SCB 50	SSIL 20	SSIL 40	SSIL 50	SCC 20	SCC 40	SCC 50	SCL 20	SCL 40	SCL 50
Carbon Black	20	40	50	-	-	-	-	-	-	-	-	-
Silica	-	-	-	20	40	50	-	-	-	-	-	-
$CaCO_3$	-	-	-	-	-	-	20	40	50	-	-	-
Clay	-	-	-	-	-	-	-	-	-	20	40	50

Table 3.6 Formulation of rubber compounds with various filler types for efficient vulcanization (EV) system.

Ingredient*	ECB 20	ECB 40	ECB 50	ESIL 20	ESIL 40	ESIL 50	ECC 20	ECC 40	ECC 50	ECL 20	ECL 40	ECL 50
Carbon Black	20	40	50	-	-	-	-	-	-	-	-	-
Silica	-	-	-	20	40	50	-	-	-	-	-	-
$CaCO_3$	-	-	-	-	-	-	20	40	50	-	-	-
Clay	-	-	-	-	-	-	-	-	-	20	40	50

* Other chemical ingredients according to Table 3.3 and CT00 is rubber compound without fillers.

3.5 Testing

3.5.1 Determination of Cure Characteristics

A moving die rheometer, MDR2000 model, was used to obtain the torque-time curve at temperature 170 ^{0}C, 7 minute with 1 ^{0}amplitude.

- M_L – Minimum torque, lb_f*in
- M_H – Highest torque, lb_f*in attained during specified period of time when on plateau or maximum torque is obtained.
- Cure time (TC90) in minute is the time taken for attaining 90% of the maximum torque.
- Scorch time (TS2) in minute is the time taken for a two unit rise above the maximum torque.

3.5.2 Tensile Properties

Tensile strength, tensile modulus and elongation at break of specimen were measured in a universal testing machine (Lloyd LR5K). Dumbbell specimens were required according to ASTM D 412-00 (Figure 3.2). The specimens were placed in the grips at a specified grip separation and pulled until failure. Three specimens were required for each measurement. The test speed was 500 mm/min for measuring strength and elongation.

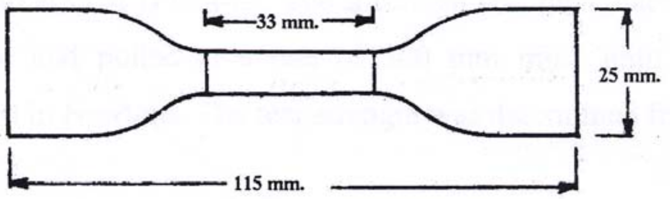


Figure 3.2 Dumbbell shape specimen for tensile property testing.

The tensile strength and % elongation at break were determined from Eq.3.1 and 3.2.

$$\text{Tensile strength (MPa)} = \frac{\text{Force at rupture (N)}}{\text{Cross-section area (m}^2\text{)}} \qquad (3.1)$$

$$\text{\%Elongation at break (\%)} = \frac{\text{(Length at rupture-original length)}}{\text{Original length}} \times 100 \qquad (3.2)$$

3.5.3 Hardness Measurement

The test specimen is at least 3 mm in thickness. The lateral dimensions of the specimen are sufficient to permit measurements at least 12 mm from any edge. The specimen is flat and parallel over a sufficient area to permit the pressure foot to contact the specimen.

The specimen was placed on a hard and horizontal surface. The pressure was held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The pressure was applied to the specimen. After the pressure foot was in firm to contact with the specimen, the scale reading was taken within 30 s. One measurement was made in 3 samples and the average of these measurements was used as hardness value.

3.5.4 Determination of Specific Gravity

The vulcanized rubber specific gravity was determined by using Electronic Densimeter, Auto-Specific Gravity Tester adopted from Archimedes' principle. The determination of (relative) density value was based on the density of water at 4 ^{0}C: 1g/cm per electronic densimeter instruction manual.

3.5.5 Determination of Crosslink Density

Specimen of approximately 15 mm in diameter and 2.5 mm in thickness were allowed to swell in toluene. The density of each specimen was determined according to section 3.5.4. Specimen was then placed in a vial containing toluene. The vial was always kept covered to prevent evaporation. Periodically, over a period of 1-3 days, the specimens were removed from the toluene, blotted dry on a paper towel, and then weighed quickly and accurately. The swelling index, which is defined as the grams of solvent per gram of rubber hydrocarbon, is calculated according to the Flory-Huggins Theory.

3.5.6 Compression Set

Compression set testing is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the somewhat permanent deformation of the specimen after it has been exposed to compressive stress for a set time period. This test is particularly useful for applications in which elastomers would be in a constant pressure/release state.

The thickness of the original specimen was measured. The specimen was then placed between spacers and in the compression device. The specimen was compressed to 25% of its original height, using spacers to accurately measure the compression. Within two hours of assembly, the compression device was placed in an oven at a specified temperature for the suggested time periods of 22 hours and 70 hours. After removing the sample from the oven, the specimen was allowed to cool for 30 minutes before measuring the final thickness.

Cylindrical disk specimen sizes, thickness is 12.5 mm +/- 0.5 mm. Diameter is 29.0 mm +/- 0.5 mm. Compression set was determined from Eq.3.3.

$$CS\ (\%) = [(t_o - t_i)/(t_o - t_n)]\ x100 \qquad (3.3)$$

where;

CS = Compression set ; %

t_o = Original thickness of the specimen; mm

t_i = Final thickness of the specimen; mm

t_n = thickness of the space bars used; 9.5 mm

3.5.7 Shrinkage Measurement

Mold shrinkage is the shrinkage of the polymer as it cools after the molding process. A flat, square, 150 mm test plaque with different thickness was used for generating the shrinkage data. Two width and two length measurements were made on each plaque 48 and, in some cases, 240 hours after molding. These width and length measurements were made between the cross hairs molded onto the plaque in each corner, all being 130 mm from each other (Figure 3.3).

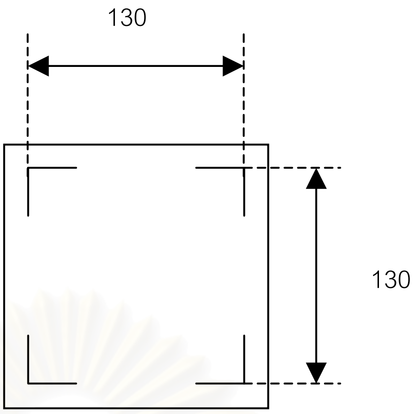


Figure 3.3 130 mm between cross hairs on all sides

All calculations are in mm/mm. The decimal point can be moved two places to the right if percent calculations are required. This calculation is a dimensional and corresponds equally to inch/inch calculations and the values obtained for a particular grade of material are dependent on processing conditions and mould design. A component is molded from a cavity of known dimensions (at 25°C) and allowed to cool to 25°C. Measurements are made after a specified time.

Compression mold for a 150 x 150 x 3 mm plaque have been measured and can be used for mold shrinkage evaluations. The shrinkage were determined from Eq. 3.4

$$\text{Mold Shrinkage (\%)} = \frac{L_0 - L_1}{L_0} \times 100 \qquad (3.4)$$

where;

L_0 = Length in mm of cavity mold

L_1 = Length in mm of rubber specimen

3.5.8 Thermomechanical Analysis (TMA)

The thermal expansion coefficients of the partially cured rubber samples could be measured using Dynamic Mechanical Analyser (Perkin Elmer), which gives an output proportional to the displacement caused by the temperature variations. Thermo-mechanical tests have been performed according to the principles stated in the final draft of ISO11359.

Specimens sized 3x3x15 mm were cut and shaped from partially cured rubber plates. After placing the specimen in the cell and equilibrating the temperature at 30 ^{0}C, the linear dimension of the sample was monitored up to 120 ^{0}C at a heating rate of 5 ^{0}C/min. with used loading as 0.1 N; The curves of the linear strain ε_l versus temperature can be easily obtained according to the following Eq. 3.5

$$\varepsilon_l\,(T,\alpha) = (\,l - l_0) = \gamma^{CTE}\,(\alpha)\Delta T \qquad (3.5)$$

where;

ε_l = the thermal linear strain

l = the final sample length

l_0 = the initial sample length, respectively;

$\gamma^{CTE}(\alpha)$ = the coefficient of linear thermal expansion

ΔT = the temperature variation

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Cure Characteristics

The cure characteristics of filler filled compound are presented in Tables 4.1-4.4. For three curing systems, the maximum torque of N330-filled (fillers loading 20 phr) and silica-filled (fillers loading more than 20 phr) compound are higher than that of the $CaCO_3$-filled compound because of lower crosslink density. This can be explained that the carbon black has carboxyl, lactone quinone and other organic function groups, which promote a high affinity of rubber to filler. Another reason is due to the high surface area of carbon black, which resulted in the intimate elastomer-carbon black contact. The carbon black also has a limited number of chemically active sites, which arise from broken carbon-carbon-bonds as a consequence of the methods used to manufacture the carbon black. The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The carbon black particles effectively become a crosslink. The non-black ($CaCO_3$, clay) fillers generally offer less affinity and less surface activity toward the common elastomer [26].

For conventional vulcanization system, the cure curve of silica filled rubber compound yielded high cure time because of the surface silica (SiO_2) groups, which were hydrolyzed to silanols (-SiOH). These silanol groups behave as acids ($-SiO\text{-}H^+$) and chemically active [26]. The sulfur vulcanization was also accelerated by alkaline material but it was also retarded with acids. For semi-EV and EV systems, the cure time is the same for various filler types because these curing systems had high content of accelerators. The reversion phenomenon was observed for compounds with the $CaCO_3$ filled compound (SCC40, 50 and ECC40, 50). This was due to the breakdown of poly-sulfidic crosslinks at high temperature [27].

Table 4.1 Effect of curing system and loading on cure properties of carbon black filled rubber compounds.

Properties	**CT00**	**CB20**	**SCB20**	**ECB20**	**CB40**	**SCB40**	**ECB40**	**CB50**	**SCB50**	**ECB50**
Minimum Torque;lb-in	0.62	1.02	1.00	0.71	1.59	1.54	1.23	2.07	1.93	1.42
Maximum Torque; lb-in	3.90	7.08	5.90	5.63	10.10	7.73	7.12	13.28	10.12	9.14
Scorch time; min	1.68	1.18	0.89	1.26	0.88	0.75	1.01	1.04	0.84	1.14
Cure time; min	3.97	3.22	2.69	3.80	2.90	2.06	3.32	3.23	2.33	3.58

Table 4.2 Effect of curing system and loading on cure properties of silica filled rubber compounds.

Properties	**CT00**	**SIL20**	**SSIL20**	**ESIL20**	**SIL40**	**SSIL40**	**ESIL40**	**SIL50**	**SSIL50**	**ESIL50**
Minimum Torque;lb-in	0.62	0.98	0.93	0.77	3.66	2.98	3.34	7.62	5.96	6.48
Maximum Torque; lb-in	3.90	3.43	4.01	4.13	11.78	11.75	12.88	19.39	19.18	17.21
Scorch time; min	1.68	1.72	1.09	0.84	0.31	0.09	0.16	0.26	0.05	0.46
Cure time; min	3.97	6.17	2.47	3.42	5.54	1.74	2.97	5.82	2.63	3.70

Table 4.3 Effect of curing system and loading on cure properties of calcium carbonate filled rubber compounds.

Properties	**CT00**	**CC20**	**SCC20**	**ECC20**	**CC40**	**SCC40**	**ECC40**	**CC50**	**SCC50**	**ECC50**
Minimum Torque;lb-in	0.62	0.60	0.54	0.53	0.61	0.52	0.55	0.75	0.65	0.71
Maximum Torque; lb-in	3.90	4.75	3.60	3.42	3.46	2.96	2.85	3.52	2.58	3.49
Scorch time; min	1.68	1.53	1.11	1.46	1.30	1.11	1.67	1.48	1.31	1.71
Cure time; min	3.97	3.73	2.97	4.87	3.86	1.53	2.88	3.22	1.88	2.91

Table 4.4 Effect of curing system and loading on cure properties of clay filled rubber compounds.

Properties	**CT00**	**CL20**	**SCL20**	**ECL20**	**CL40**	**SCL40**	**ECL40**	**CL50**	**SCL50**	**ECL50**
Minimum Torque;lb-in	0.62	0.77	0.62	0.54	0.91	0.89	0.72	1.25	0.92	0.76
Maximum Torque; lb-in	3.90	4.81	3.65	3.47	4.81	4.71	4.63	6.44	3.18	4.29
Scorch time; min	1.68	1.71	1.17	1.39	1.63	1.14	1.09	1.76	1.03	0.95
Cure time; min	3.97	4.32	3.14	4.54	4.32	2.83	3.92	4.31	3.07	3.53

4.2 Mechanical Properties

The mechanical properties of the rubber composites with different filler types (carbon black, silica, clay, $CaCO_3$) at various filler loading (20, 40 and 50 phr) and vulcanization systems (conventional, semi-EV and EV) were investigated. The tensile properties, compression set, specific gravity and hardness of rubber composites are also presented in Table 4.4-4.8 and Figure 4.1-4.3.

From Figure 4.1a, the tensile strength increase with increasing filler loading. It also indicates that the incorporation of all fillers into the rubber matrix improved the stiffness of the vulcanizates. The increase in tensile properties of carbon black filled compound is higher than that of silica filled compound, clay filled compound and $CaCO_3$ filled compound respectively, since tensile strength represented the material stiffness. As expected, the smaller size of the carbon black (0.024-0.028 μm) and silica (0.01-0.04 μm) give higher strength than the large filler size of the $CaCO_3$ (0.95-1.2 μm) and clay (2.0-6.0 μm). Carbon black and silica are good reinforcing fillers due to the good filler-rubber interaction which increase the effectiveness of the stress transferred from rubber matrix to filler particles dispersed in the rubber matrix. Clay and $CaCO_3$ are semi-reinforcing filler and non-reinforcing filler, respectively due to the insertion between polymer chain segments. Therefore, the tensile properties of clay and $CaCO_3$ filled rubber was lower than that of carbon black filled rubber.

Tensile strength of rubber compounds with efficient curing system (EV) is much higher than that of compounds with conventional (CV) and semi-efficient curing system (semi-EV). This is probably due to the fact that the majority of crosslink density of the EV system are mono-sulfidic crosslinks (C-S energy bond = 285 KJ) which are higher than di-sulfidic and polysulfidic crosslinks (S-S energy bond = 155-278 KJ) [27]. The break elongation of compounds with EV system is the lowest among these three curing systems. The effect of filler loading on break elongation is illustrated in Figure 4.1b. It can be seen that the break elongation for all fillers decreased steadily with increasing filler loading. The cause explained that the increment in filler content resulted in the reduction of the deformability of rigid interface between the filler and rubber matrix. The addition of filler tends to impose extra resistance of rubber to flow and, thus, lower the elongation at break value.

Table 4.5 Effect of curing system and loading on mechanical properties of carbon black filled rubber compounds.

Properties	**CT00**	**CB20**	**SCB20**	**ECB20**	**CB40**	**SCB40**	**ECB40**	**CB50**	**SCB50**	**ECB50**
Tensile strength; MPa	4.4	10.8	11.1	12.2	12.0	12.5	14.3	12.2	12.5	15.9
Elongation at break; %	430	380	410	380	350	360	360	260	270	280
Hardness; Shore A	44	56	56	58	67	67	67	73	72	71
Specific gravity	0.94	1.02	1.01	1.02	1.08	1.07	1.08	1.12	1.11	1.11
Compression set; %	51.75	52.92	26.42	27.94	53.64	30.51	28.08	51.42	27.74	26.18

Table 4.6 Effect of curing system and loading on mechanical properties of silica filled rubber compounds.

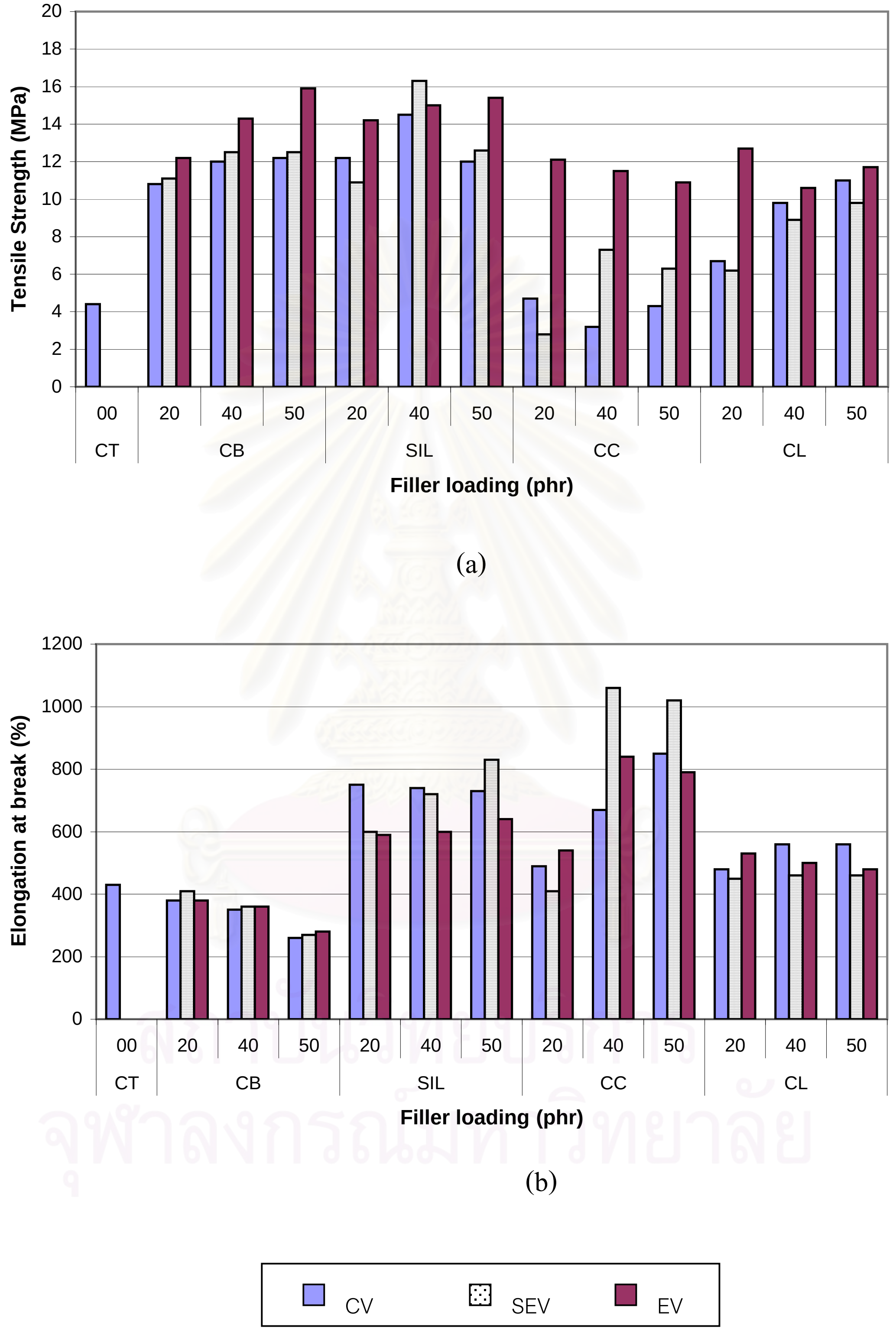
Properties	**CT00**	**SIL20**	**SSIL20**	**ESIL20**	**SIL40**	**SSIL40**	**ESIL40**	**SIL50**	**SSIL50**	**ESIL50**
Tensile strength; MPa	4.4	12.2	10.9	14.2	14.5	16.3	15.0	12.0	12.6	15.4
Elongation at break; %	430	750	600	590	740	720	600	730	830	640
Hardness; Shore A	44	50	50	52	60	60	66	74	70	73
Specific gravity	0.94	1.03	1.01	1.02	1.09	1.09	1.10	1.13	1.12	1.13
Compression set; %	51.75	57.67	32.79	25.25	75.82	42.19	32.92	86.57	73.53	46.87

Table 4.7 Effect of curing system and loading on mechanical properties of calcium carbonate filled rubber compounds.

Properties	**CT00**	**CC20**	**SCC20**	**ECC20**	**CC40**	**SCC40**	**ECC40**	**CC50**	**SCC50**	**ECC50**
Tensile strength; MPa	4.4	4.7	2.8	12.7	3.2	7.3	11.5	4.3	6.3	10.9
Elongation at break; %	430	490	410	530	670	1060	840	850	1020	790
Hardness; Shore A	44	49	49	51	45	40	40	45	40	42
Specific gravity	0.94	1.03	1.04	1.04	1.14	1.11	1.12	1.18	1.16	1.16
Compression set; %	51.75	55.25	28.25	33.90	70.85	60.40	42.52	71.33	63.09	44.75

Table 4.8 Effect of curing system and loading on mechanical properties of clay filled rubber compounds.

Properties	**CT00**	**CL20**	**SCL20**	**ECL20**	**CL40**	**SCL40**	**ECL40**	**CL50**	**SCL50**	**ECL50**
Tensile strength; MPa	4.4	6.7	6.2	12.7	9.8	8.9	10.6	11.0	9.8	11.7
Elongation at break; %	430	480	450	530	560	460	500	560	460	480
Hardness; Shore A	44	53	51	51	57	56	59	61	56	60
Specific gravity	0.94	1.06	1.05	1.04	1.15	1.14	1.13	1.19	1.17	1.17
Compression set; %	51.75	59.52	40.33	33.90	65.42	49.15	44.62	63.27	44.07	42.37



(a)

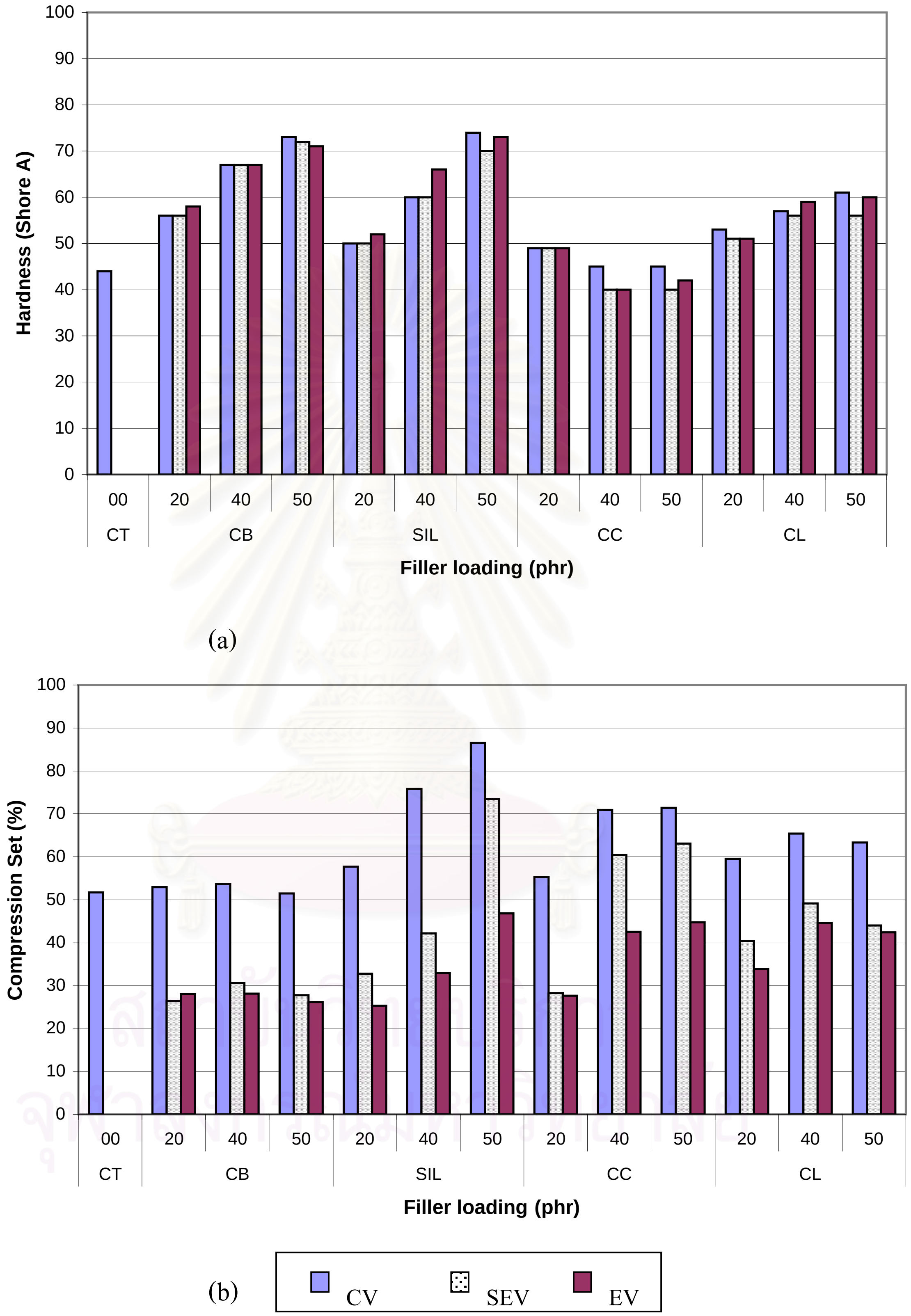
(b)

Figure 4.1 Effect of curing system and filler types and loading on; a) tensile strength and b) elongation at break.

The compound hardness is the most effectively controlled by adjusting the filler loading and types. The effect of filler loading and types on hardness of rubber vulcanizates is shown in Figure 4.2a. It can be seen that the hardness for all rubbers gradually increases with increasing filler loading. As more filler is incorporated into the rubber matrix, the elasticity and flexibility of the rubber chain is reduced, resulting in more rigid rubber vulcanizates [28]. Increase in the hardness can also be due to the reinforcement effect of the filler as well as higher extents of crosslinking of polymeric materials. It is also found that the curing system does not show any influence on compound hardness. The hardness of carbon black filled compounds are higher than silica filled compound, clay filled compound, and $CaCO_3$ filled compound respectively, because carbon black and silica are reinforcing filler, clay and $CaCO_3$ are non-reinforcing filler.

From Figure 4.2b, the compression set of filled rubber composite increases with increasing filler loading. Compounds with the conventional curing system exhibited much higher compression set than the compound with the semi-EV and EV curing systems. Compounds with efficient curing system have the lowest compression set among the three curing systems. This implies that the mono-sulfidic crosslinks are much more stable than the polysulfidic crosslinks under dynamically thermal aging conditions. In general, the compression set increases with increasing filler loading due to the high degree of compactness of the filler-filler networks [29].

From Figure 4.3, the specific gravity of the filled rubber composites increases with increasing filler loading. Furthermore the curing system does not affect the compound specific gravity.



(a)

(b)

Figure 4.2 Effect of curing system and filler types and loading on; a) hardness b) compression set.

Figure 4.3 Effect of curing system, filler types and loading on specific gravity.

Crosslinking density of filled rubber composites are presented in Table 4.9 and Figure 4.4. At a similar filler loading and equilibrium state, it can be seen that the crosslink density of the carbon black filled compound is significantly higher than that of clay filled compound, silica rubber filled compound and $CaCO_3$ filled compound, respectively. Compound with the efficient curing system (EV) shows a much higher crosslink density than the ones with CV and SEV systems. The decrease in swelling with increasing filler loading was proportional to the increase in tensile modulus, hardness and tensile strength for rubber filled vulcanizates. This can be because of the formulation of more interfacial regions between the filler and rubber matrix, and consequently, increased the crosslink density. Since the crosslink density is increased, it can restrict the molecular movement of the rubber and make it more difficult for toluene to penetrate through the rubber and decrease the swelling percentage.

Table 4.9 Effect of curing system and filler types on crosslink density.

Compound		Crosslink density (mol/cm^{3}x10^5)		
		CV	SEV	EV
Carbon black	20	7.12	6.95	11.60
	40	9.29	10.84	12.98
	50	15.47	15.14	17.36
Silica	20	4.31	5.20	6.75
	40	4.44	5.40	7.33
	50	6.33	3.43	6.87
Clay	20	3.80	5.95	6.99
	40	4.42	2.77	3.88
	50	5.12	2.86	3.64
$CaCO_3$	20	6.03	5.71	7.08
	40	6.97	7.17	10.41
	50	8.04	8.71	9.96

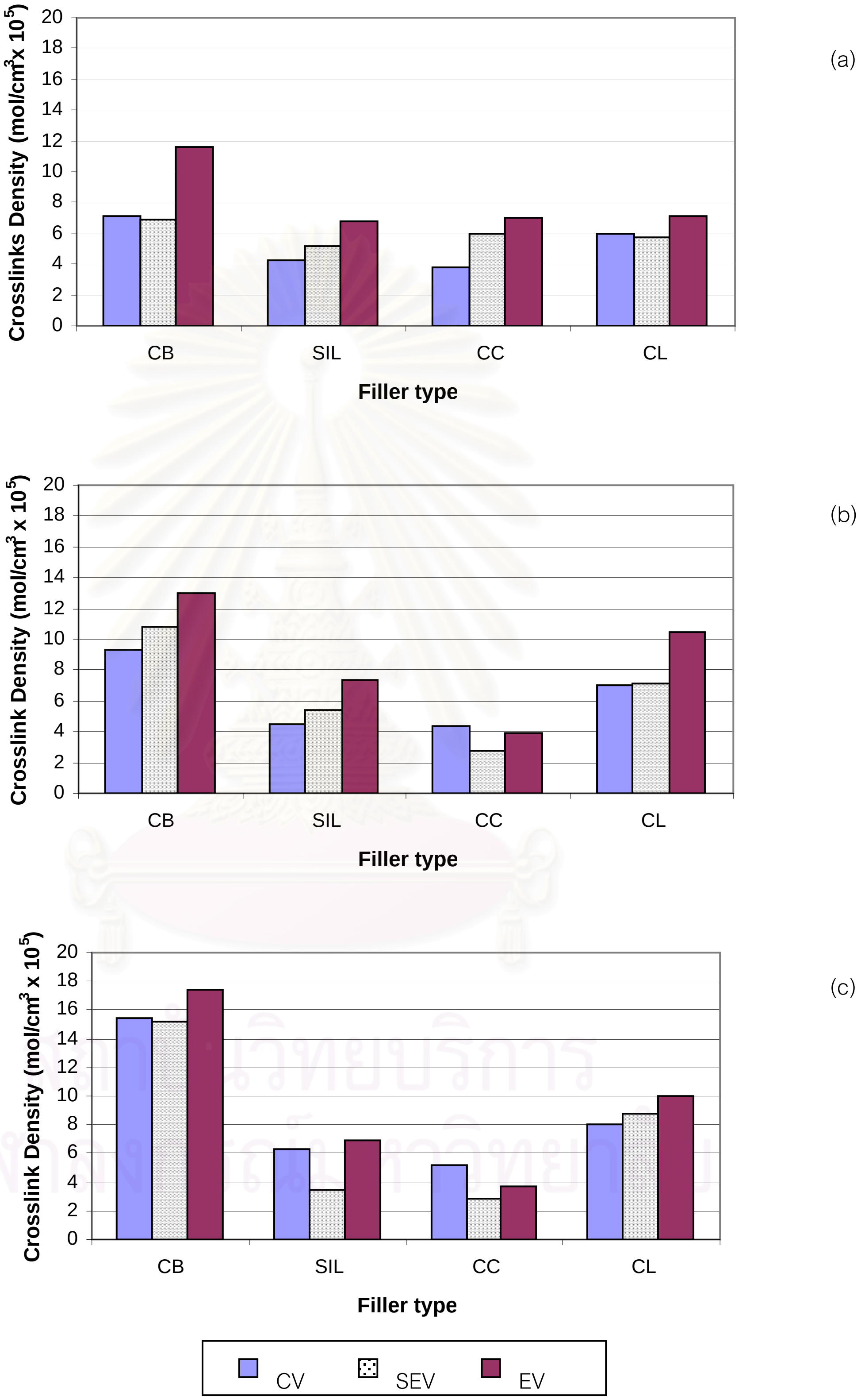


Figure 4.4 Effect of curing system and filler types on crosslink density at various filler loadings; a) 20 phr b) 40 phr and c) 50 phr.

4.3 Shrinkage Studies

4.3.1 Shrinkage Measurement

The shrinkage behaviors of filled rubber compound are presented in Tables 4.10-4.12 and Figures 4.5-4.9. The shrinkage increased with increasing time after cooling. The shrinkage remained constant at cooling time above 168 hrs. From Figure 4.8, it is also found that the shrinkage decreases with the increasing filler loading. At high filler loadings, a combination of polymer-filler linkages and chain entanglements within the polymer products. The three-dimensional network structures with long relaxation of the structures are compressed vertically (equivalent to lateral stretching) and a part or all of the network chains are permanently fixed by chemical crosslink during the press cure. The net result is two types of elastically effective network chains; the first-stage network chains present before and during deformation, and the second-stage network chains formation after complete filling of the cavity upon release of the pressure. The first-stage network chains will relax partially, according to the theory of composite networks, leading to a decrease in vertical shrinkage [30].

For various filler types, it was found that the clay filled rubber has the lowest shrinkage (1-2%), where as the rubbers filled with silica, carbon black and $CaCO_3$ exhibit higher shrinkage (2-3%), due to the plate-like particles of clay, which is known to be rather easily oriented and the larger particle size of clay than $CaCO_3$, silica and carbon black, respectively. For silica and carbon black filled compound, when sufficient amount of reinforcing filler is added into rubber, filler-filler interactions take place as a result of the decrease in the distance between the filler aggregates. Since as silica contains a large number of silanol groups on its surface, the strong filler-filler interaction exists through the hydrogen bonds. These interactions are particularly obvious when deformations are small. The $CaCO_3$ filled compound showed the highest shrinkage, due to particle insertion between polymer chain segments. The bonding between filler-filler or filler-rubber interaction did not occur.

Table 4.10 Variation of shrinkage with time after cooling for CV rubber compound.

Compound	Shrinkage (%)/hr										
	1	24	48	72	96	120	144	168	192	216	240
CT00	2.80	2.87	2.99	2.88	2.89	2.89	2.91	2.91	2.92	2.92	2.88
CB20	2.67	2.85	2.94	2.88	2.92	2.92	2.91	2.90	2.89	2.89	2.91
CB40	2.57	2.71	2.64	2.72	2.70	2.68	2.68	2.65	2.66	2.66	2.65
CB50	2.40	2.56	2.60	2.61	2.59	2.58	2.58	2.58	2.59	2.59	2.57
SIL20	2.68	2.78	2.82	2.83	2.83	2.83	2.83	2.83	2.83	2.83	2.83
SIL40	2.62	2.65	2.68	2.67	2.67	2.67	2.66	2.67	2.67	2.67	2.67
SIL50	2.40	2.49	2.47	2.47	2.47	2.47	2.48	2.48	2.48	2.48	2.48
CC20	2.88	3.10	3.11	3.11	3.07	3.07	3.08	3.08	3.09	3.09	3.09
CC40	2.80	3.01	3.06	3.06	3.01	3.01	3.00	3.00	3.00	3.00	3.00
CC50	2.59	2.60	2.58	2.58	2.62	2.62	2.63	2.63	2.63	2.63	2.63
CL20	2.38	2.51	2.51	2.51	2.40	2.40	2.42	2.42	2.41	2.41	2.41
CL40	1.94	1.96	1.96	1.96	1.99	1.99	2.00	2.00	1.98	1.98	1.98
CL50	1.93	1.94	1.97	1.97	1.94	1.94	1.98	1.98	1.96	1.96	1.96

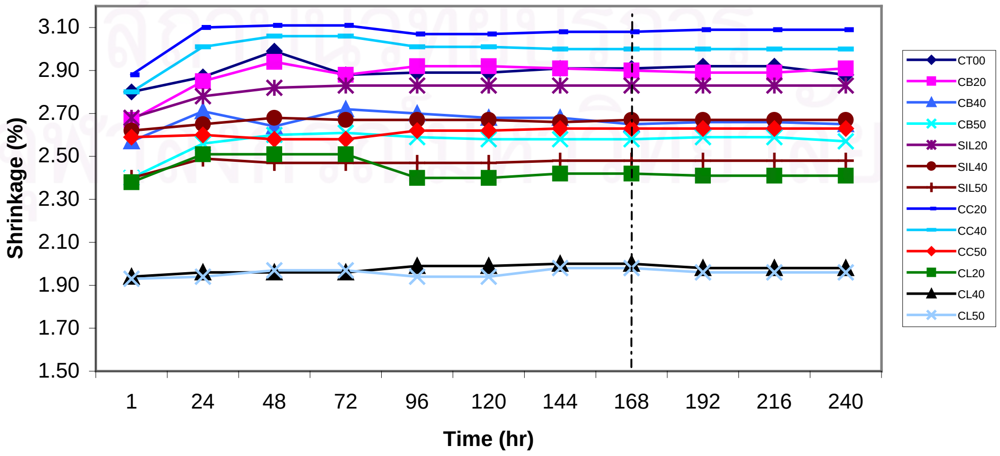


Figure 4.5 Variation of shrinkage with time after cooling for CV rubber compound.

Table 4.11 Variation of shrinkage with time after cooling for semi-EV rubber compound.

Compound	Shrinkage (%)/hr										
	1	24	48	72	96	120	144	168	192	216	240
SCB20	2.85	2.89	2.97	2.98	2.97	2.97	2.97	2.97	2.97	2.93	2.92
SCB40	2.66	2.69	2.78	2.70	2.70	2.70	2.71	2.71	2.71	2.69	2.59
SCB50	2.58	2.70	2.70	2.68	2.67	2.68	2.68	2.68	2.67	2.67	2.68
SSIL20	2.80	2.89	2.82	2.82	2.84	2.84	2.84	2.84	2.84	2.84	2.84
SSIL40	2.24	2.36	2.29	2.31	2.31	2.31	2.31	2.31	2.31	2.31	2.31
SSIL50	2.30	2.30	2.25	2.24	2.25	2.25	2.26	2.26	2.26	2.26	2.26
SCC20	2.90	3.07	3.01	3.01	3.02	3.02	3.05	3.05	3.06	3.06	3.06
SCC40	2.75	2.94	2.95	2.95	2.94	2.94	2.95	2.95	2.95	2.95	2.95
SCC50	2.80	2.85	2.88	2.88	2.90	2.90	2.90	2.90	2.90	2.90	2.90
SCL20	2.23	2.24	2.25	2.28	2.26	2.26	2.27	2.27	2.26	2.26	2.26
SCL40	2.11	2.10	2.12	2.15	2.12	2.12	2.13	2.13	2.13	2.13	2.13
SCL50	1.66	1.73	1.73	1.73	1.76	1.76	1.75	1.75	1.76	1.76	1.76

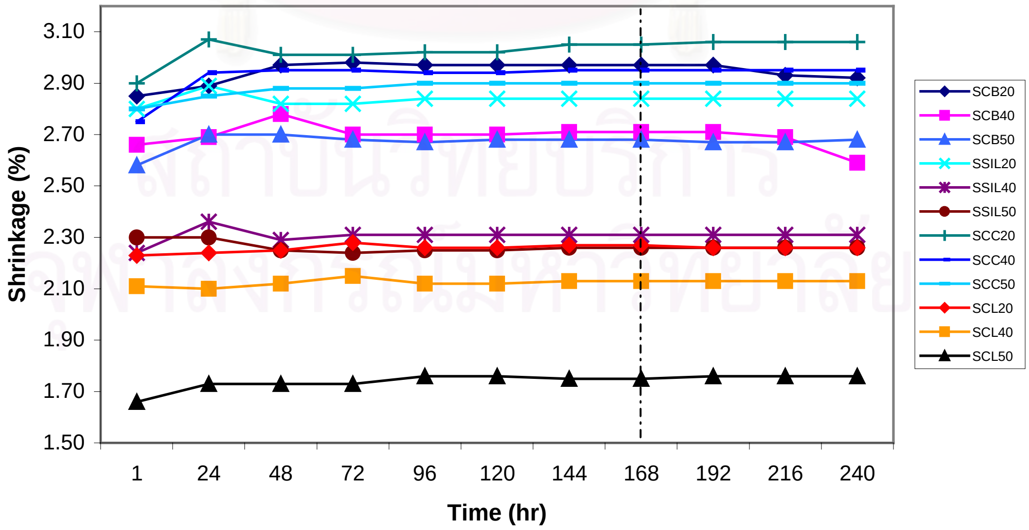


Figure 4.6 Variation of shrinkage with time after cooling for semi-EV rubber compound.

Table 4.12 Variation of shrinkage with time after cooling for EV rubber compound.

Compound	Shrinkage (%)/hr										
	1	24	48	72	96	120	144	168	192	216	240
ECB20	2.76	2.82	2.83	2.83	2.83	2.83	2.83	2.83	2.83	2.83	2.83
ECB40	2.43	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47
ECB50	2.17	2.18	2.20	2.20	2.19	2.19	2.19	2.19	2.19	2.19	2.19
ESIL20	2.70	2.78	2.75	2.84	2.84	2.83	2.83	2.83	2.83	2.83	2.83
ESIL40	2.37	2.41	2.44	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
ESIL50	2.28	2.31	2.36	2.37	2.37	2.36	2.36	2.36	2.36	2.36	2.36
ECC20	2.76	2.87	2.91	2.92	2.92	2.91	2.89	2.89	2.89	2.89	2.89
ECC40	2.70	2.76	2.78	2.78	2.78	2.79	2.79	2.79	2.79	2.79	2.79
ECC50	2.48	2.59	2.59	2.60	2.60	2.60	2.61	2.61	2.61	2.61	2.61
ECL20	2.34	2.36	2.35	2.36	2.36	2.36	2.36	2.36	2.36	2.36	2.36
ECL40	1.92	1.97	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ECL50	1.70	1.78	1.77	1.79	1.79	1.79	1.78	1.78	1.78	1.78	1.78

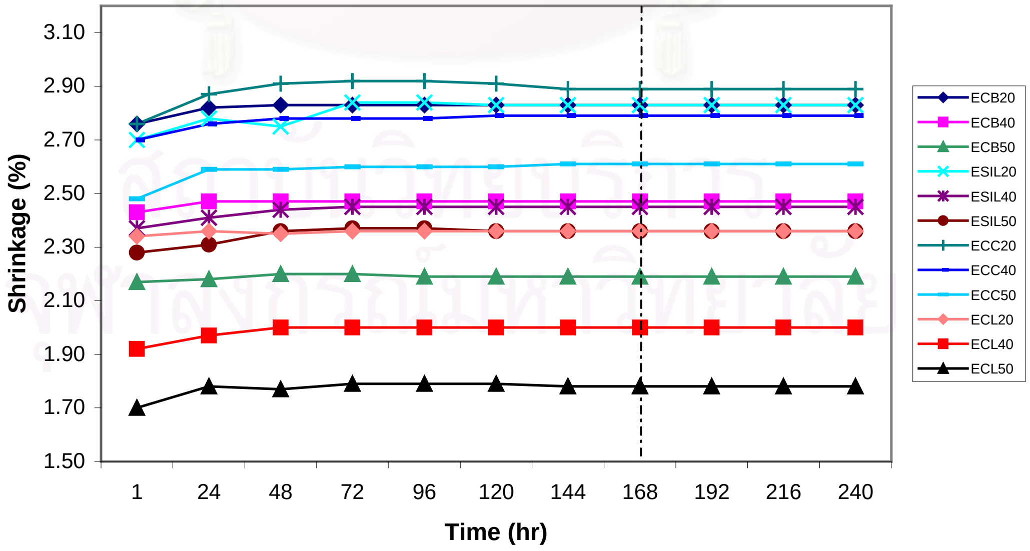


Figure 4.7 Variation of shrinkage with time after cooling for EV rubber compound.

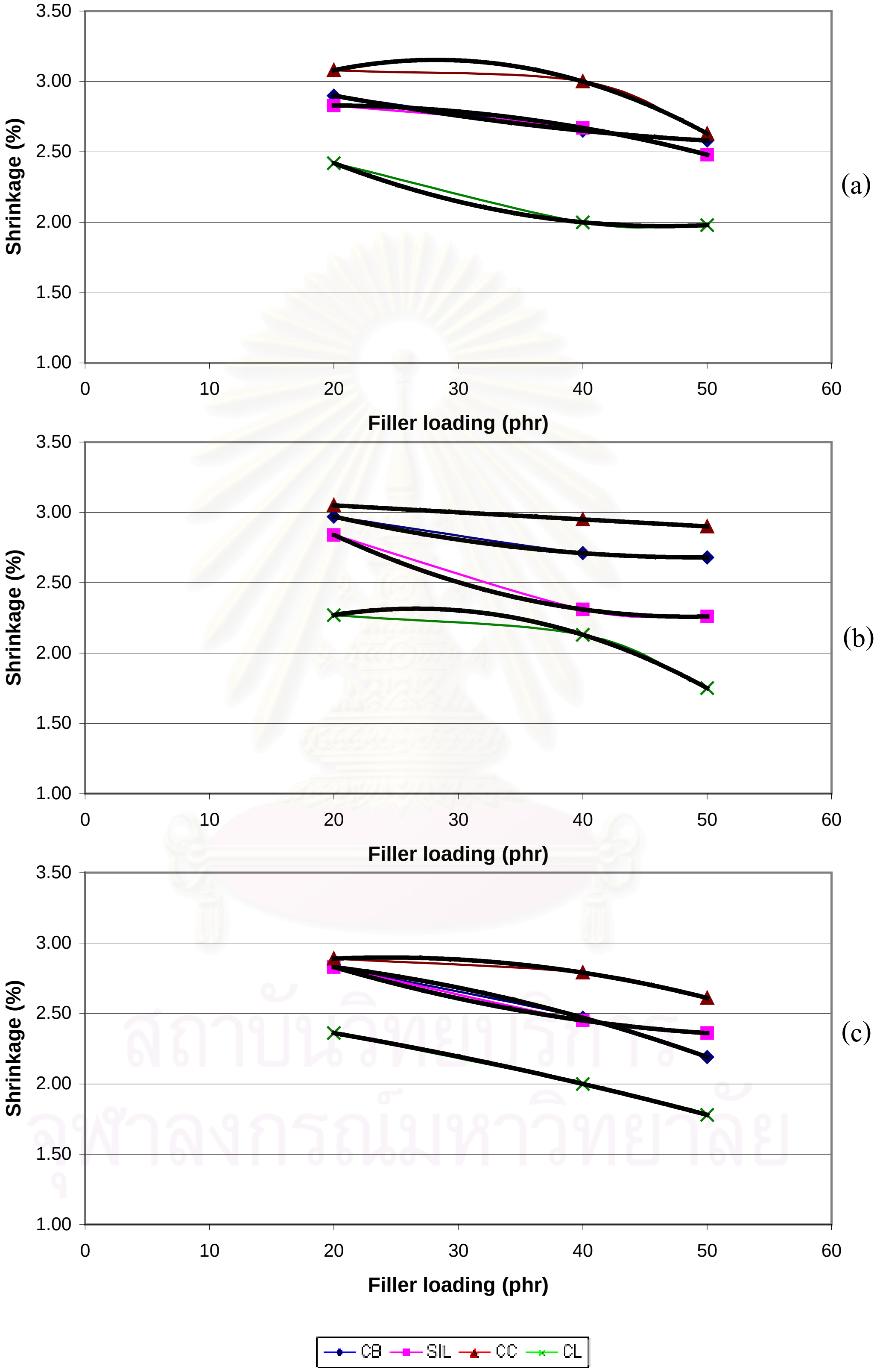
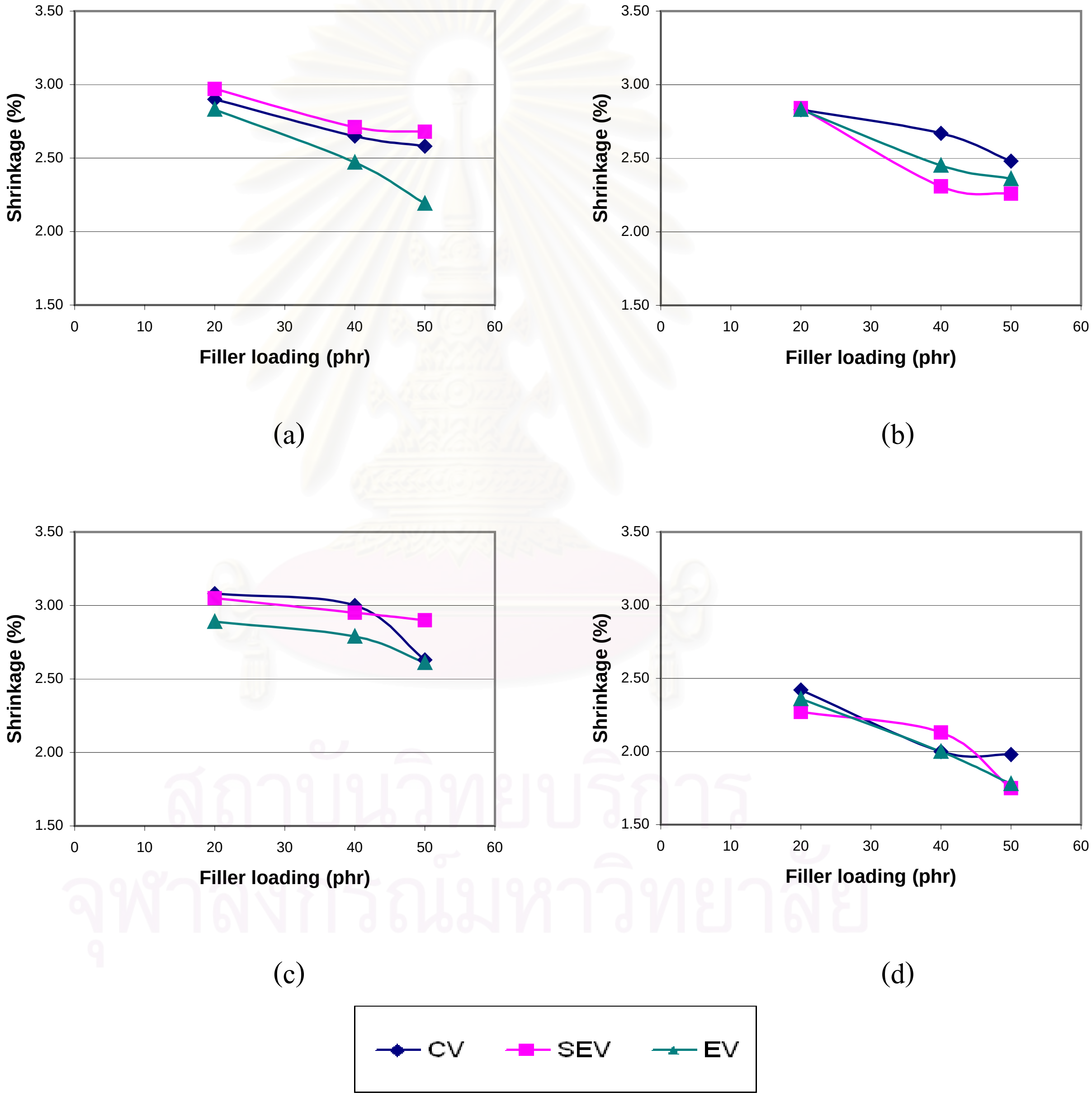


Figure 4.8 Effect of filler loading on shrinkage after cooling for 168 hrs; a) CV, b) semi-EV and c) EV system.

]

From Figure 4.9, the efficient curing system shows a much lower shrinkage than semi-EV and conventional curing system, due to the high crosslink density of EV system. The mono-sulfidic crosslink in EV system has lower flexibility than di-sulfidic and polysulfidic crosslink in conventional and semi-EV curing systems.



(a) (b)

(c) (d)

Figure 4.9 Effect of filler loading on shrinkage after cooling for 168 hrs; a) carbon black, b) silica, c) $CaCO_3$ and d) clay.

4.3.2 Shrinkage Equation

The shrinkage equation of filled rubber compound as a function of filler content in phr was proposed. In Figures 4.8, the plots of the percentage of shrinkage versus amount of filler loading after cooling for 168 hrs are shown. The continuous line obtained yielded a good relationship fitted by using the polynomial equation of filler content in phr. Therefore, the shrinkage data can be fitted very well by Eq. 4.1

$$S = a + bx + cx^2 \tag{4.1}$$

S is the percentage of shrinkage of filled rubber compounds (%), x is the filler content in phr. The shrinkage equations for carbon black, silica, $CaCO_3$ and clay filled rubber compound for three curing systems are as follows;

For carbon black,

CV system : $S = 3.2967-0.024x+0.0002x^2$ (4.2)

SEV system : $S = 3.4967-0.033x+0.0003x^2$ (4.3)

EV system : $S = 2.9233+0.002x-0.0003x^2$ (4.4)

For silica,

CV system : $S = 2.6967+0.014x-0.0004x^2$ (4.5)

SEV system : $S = 3.9433-0.070x+0.0007x^2$ (4.6)

EV system : $S = 3.4767-0.039x+0.0003x^2$ (4.7)

For $CaCO_3$,

CV system : $S = 2.2800+0.062x-0.0011x^2$ (4.8)

SEV system : $S = 3.1500-0.005x$ (4.9)

EV system : $S = 2.6433+0.021x-0.0004x^2$ (4.10)

For clay,

CV system : $S = 3.3467-0.059x+0.0006x^2$ (4.11)

SEV system : $S = 1.5833+0.055x-0.0010x^2$ (4.12)

EV system : $S = 2.6133-0.010x-0.0001x^2$ (4.13)

4.3.3 Thermomechanical Analysis

The linear coefficients of thermal expansion (CTE) of rubber compounds are presented in Figures 4.10-4.12. From Figure 4.10, the CTE decreased with increasing carbon black loading (CV system). A decrease in the fractional free volume occurred, which implied an increased packing density in rubbery phase. From Figure 4.11, the CTE of clay filled compound is lower than that of silica, carbon black and $CaCO_3$ filled compound, respectively. From Figure 4.12, compound with the EV system exhibited a lower CTE than the compound with the other two curing systems, because EV system yielded higher crosslink density than CV and SEV systems. Because of increasing crosslink density of rubber compound, a decrease in the fractional free volume occurs, which means an increased packing density in the rubbery phase. It can also explained that the larger constraints on the polymer are because the network hinder the thermal mobility of the chains. However, this effect is not so pronounced in the glassy region, since the thermal mobility is almost frozen, and the reduced effects are expected in the free volume [31]. The CTE equation of carbon black filled compound as a function of the carbon black content in phr is proposed. Figure 4.10 also shows the plot of CTE continuous line fitted by using polynomial equation. The CTE versus amount of carbon black loading for CV vulcanized compound can be fitted by Eq. 4.14

$$\mathrm{CTE} = 504.85 - 123.96x + 14.551x^2 \qquad (4.14)$$

$$R^2 = 0.9602$$

Where CTE is the linear coefficients of thermal expansion of filled rubber compounds and x is the carbon black content in phr.

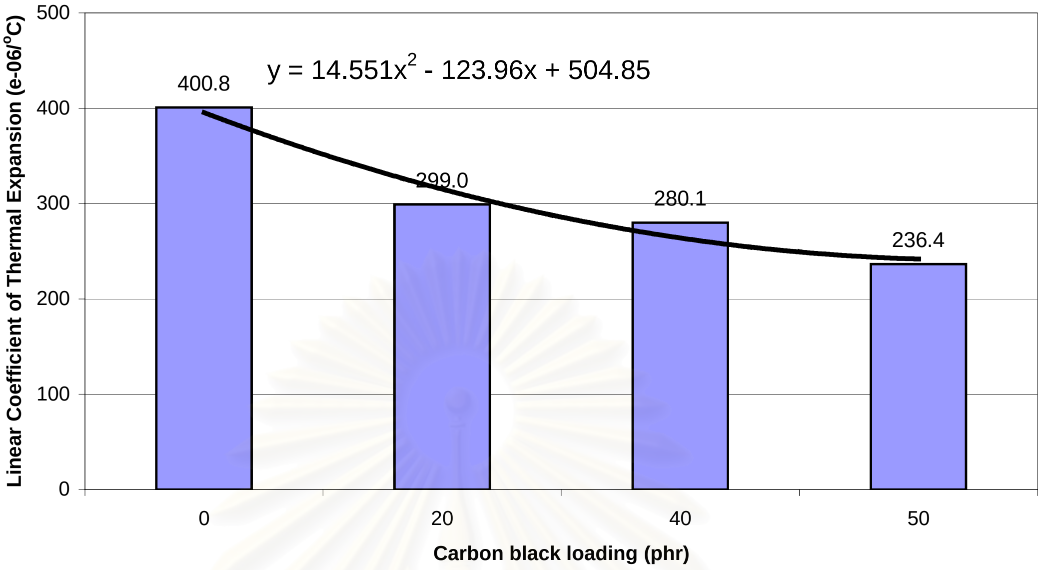


Figure 4.10 Effect of carbon black loading on linear coefficient of thermal expansion of rubber compound (CV system).

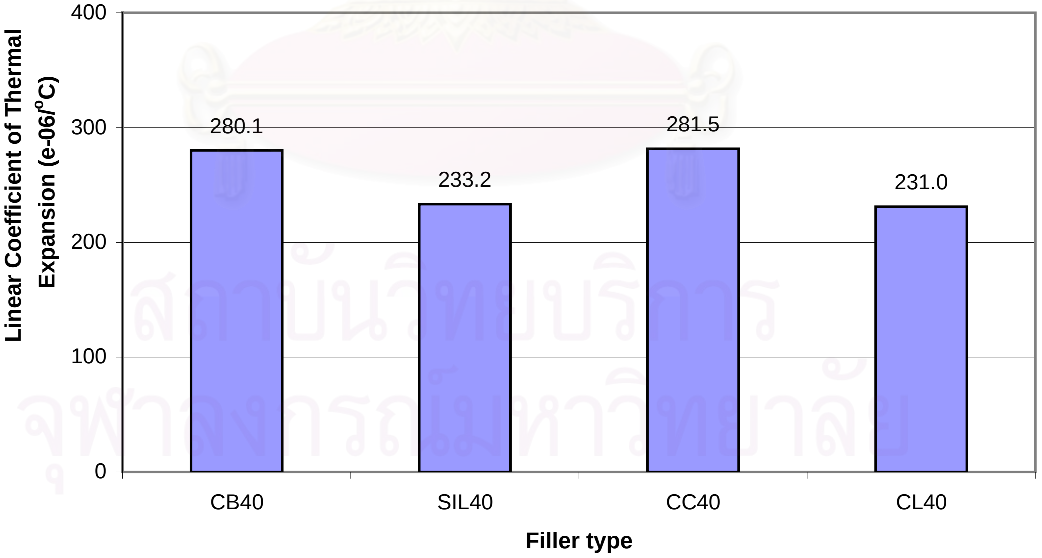


Figure 4.11 Effect of filler types on linear coefficient of thermal expansion of rubber compound at 40 phr loading (CV system).

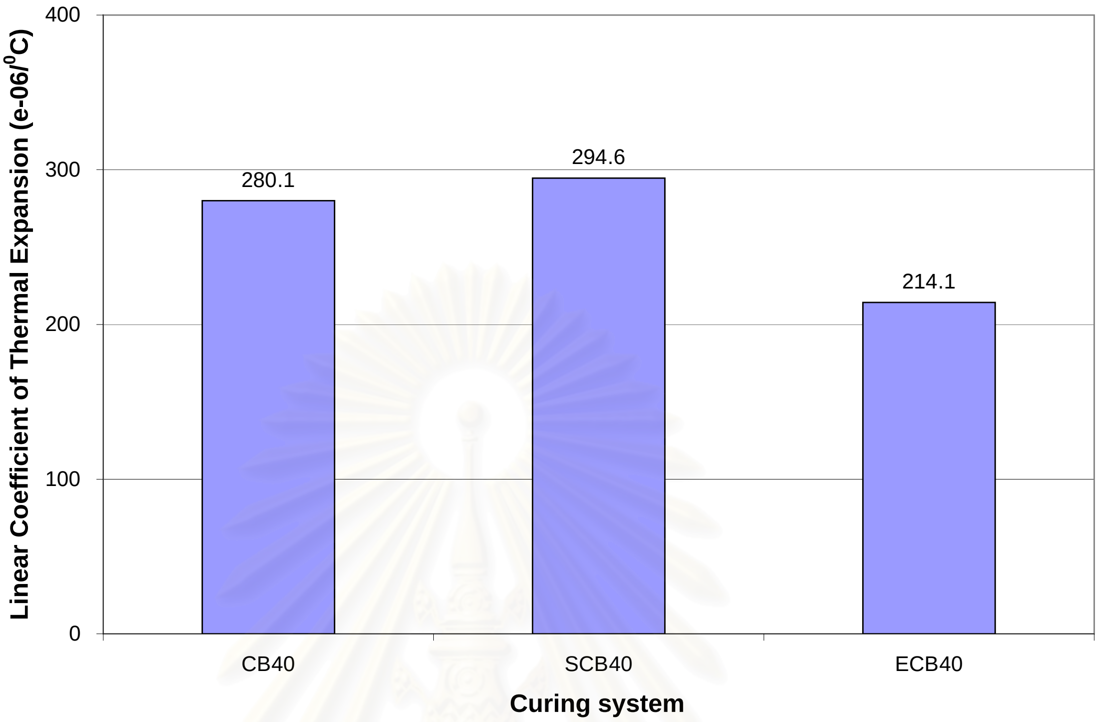


Figure 4.12 Effect of curing systems on linear coefficient of thermal expansion of rubber compound at 40 phr loading.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The effects of type and amount of fillers and vulcanization systems on shrinkage properties of natural rubber/EPDM blend were studied. In this work, the natural rubber/EPDM filled with carbon black, silica, clay and calcium carbonate were prepared. The shrinkage properties of various rubber compounds were investigated and compared as follows:

1. The mechanical properties of carbon black filled compound were higher than those of silica filled compound, clay filled compound and $CaCO_3$ filled compound, respectively. Increasing filler loading in the rubber compound could also increase the mechanical properties, except $CaCO_3$ filled compound, due to the strong interaction of functional group on carbon black, silica and clay with rubber. For $CaCO_3$ filler insertion between polymer chain segments was occurred.
2. The shrinkage and the linear coefficient of thermal expansion decreased with increasing filler loading because of decreasing rubber content.
3. The shrinkage and the linear coefficient of thermal expansion of clay filled compound were lower than those of silica filled compound, carbon black filled compound, and $CaCO_3$ filled compound.
4. The shrinkage and the linear coefficient of thermal expansion of efficient vulcanized compound were lower than those of semi-efficient and

conventional vulcanized compound because the crosslink density of EV compound was the highest.

5. The shrinkage equations were proposed to predict the correct value of the shrinkage. If other loadings of filler are desired, the appropriate shrinkage value can be determined by using the shrinkage equations described in this work.

5.2 Future work

Future study on other factors affecting the shrinkage mold parts will be carried out as follows:

- To study the various shape and thickness of mold geometry.
- To study the conditions, temperature, pressure of curing process.
- To study the shrinkage of injection molded rubber compounds.

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APPENDICES

APPENDIX A

Table A-1 Natural rubber STR 20CV properties.

Characteristic	**unit**	**tolerance**
Dirt Content	%Max	0.16 Max
Ash Content	%Max	0.80 Max
Volatile Matter	%Max	0.80 Max
Nitrogen	%Max	0.60 Max
PRI	-	40 Min
Mooney viscosity; ML(1+4) 125	-	60(+7,-5)

Table A-2 EPDM KELTAN312 properties.

Characteristic	**unit**	**tolerance**
Mooney viscosity; ML(1+4) 125	-	28-38
Ethylene content	wt%	45.4-52.6
ENB content	wt%	3.70-4.90
Oil	wt%	n.a.
Volatile Matter	wt%	0.7 Max

Table A-3 Carbon black properties.

Characteristic	**unit**	**tolerance**
DBP absorption	cc/100g	97-107
Iodine NO.	mg/g	77-87
Sieve residue #325	% MAX	0.100
Sieve residue #35	% MAX	0.001
pH value	-	6-10
Heat loss	% MAX	2.5
Ash content	% MAX	1.0

Table A-4 Calcium Carbonate properties.

Characteristic	**unit**	**tolerance**
Average particle size	micron	0.95-1.20
Residue on 325 mesh	%	0.10 Max
Surface coating	%	1.80 Min
DOP absorption	g/100g	16.00-18.00
Bulk density	g/cc	0.85±0.05
Moisture content	%	0.20 Max
Whiteness (Paste)	-	67.0 Min

Table A-5 Silica properties.

Characteristic	unit	tolerance
Moisture	%	4.7
pH value (4% Suspension)	-	6.0
Loss weight	g/l	154
Specific surface Area	m^2/g	203
Sieve residue (150 μm)	%	0.2

Table A-6 Clay properties.

Characteristic	unit	tolerance
Brightness (ISO 457)	nm	74
Moisture content	%	1.0 Max
pH value	-	4.5-5.5
Specific gravity	-	2.6
Surface area (BET)	m^2/g	21
Oil absorption	g/100g	48

APPENDIX B

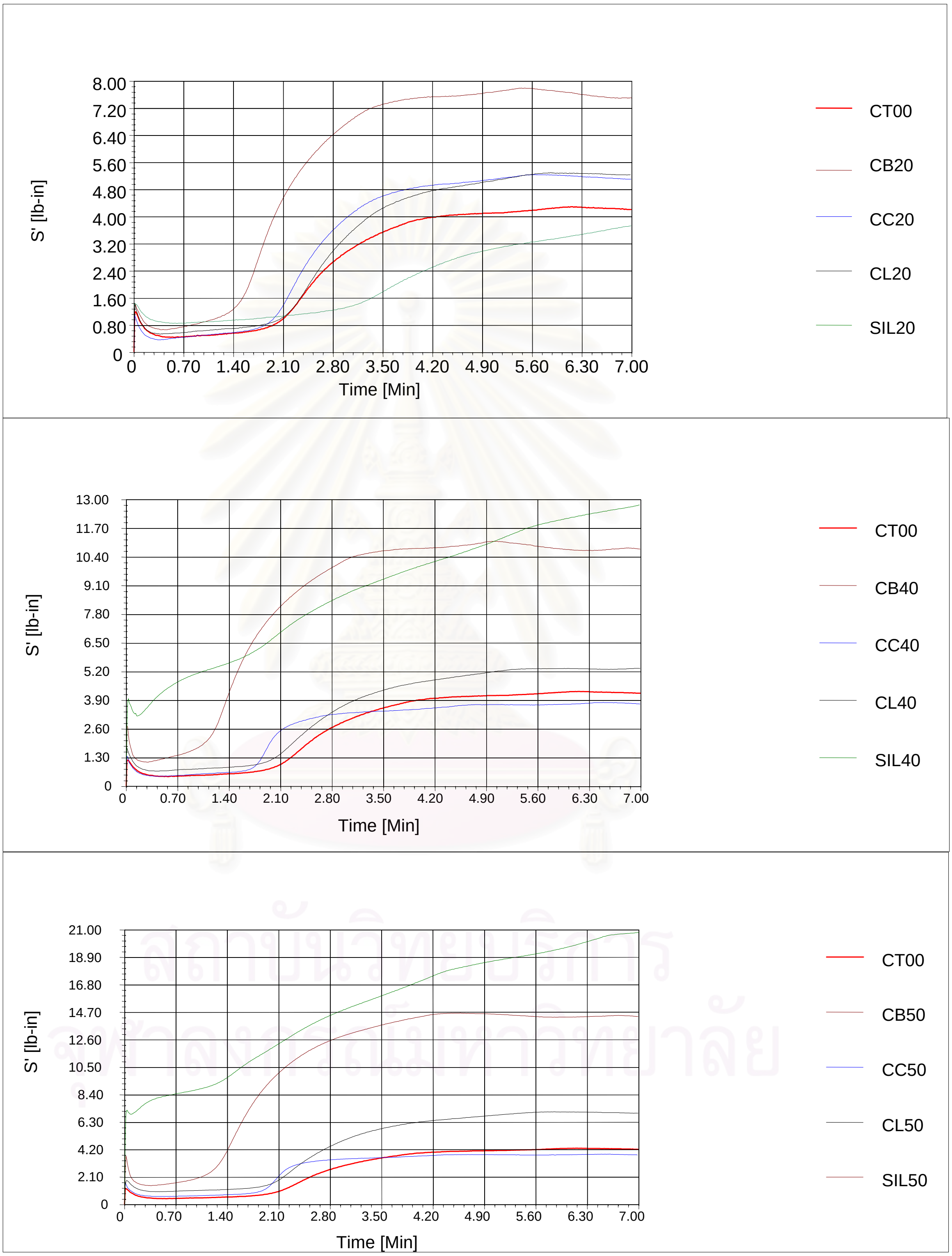


Figure B-1 Cure curves of rubber compounds with various filler types and loading for CV system.

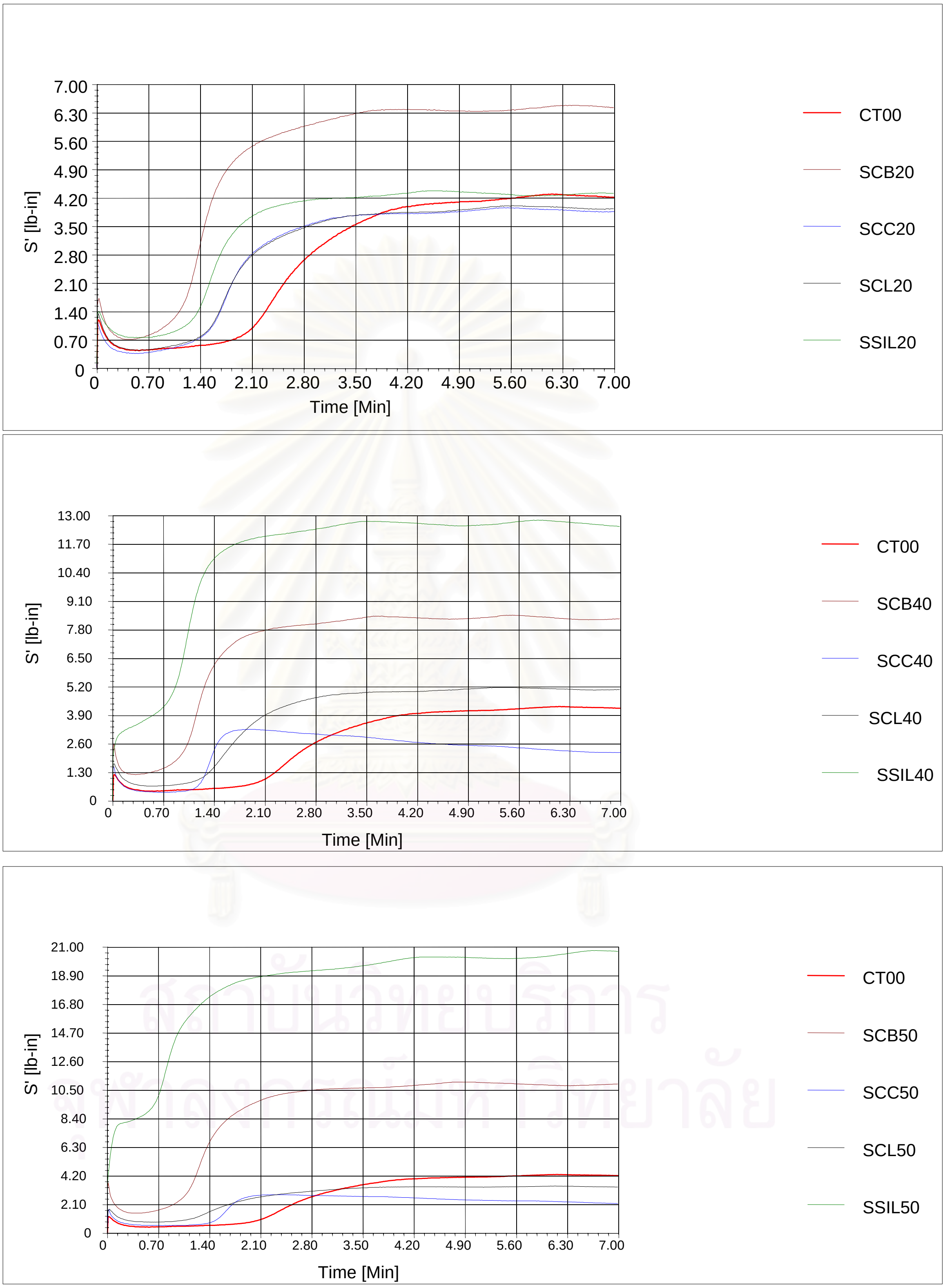


Figure B-2 Cure curves of rubber compounds with various filler types and loading for semi-EV system.

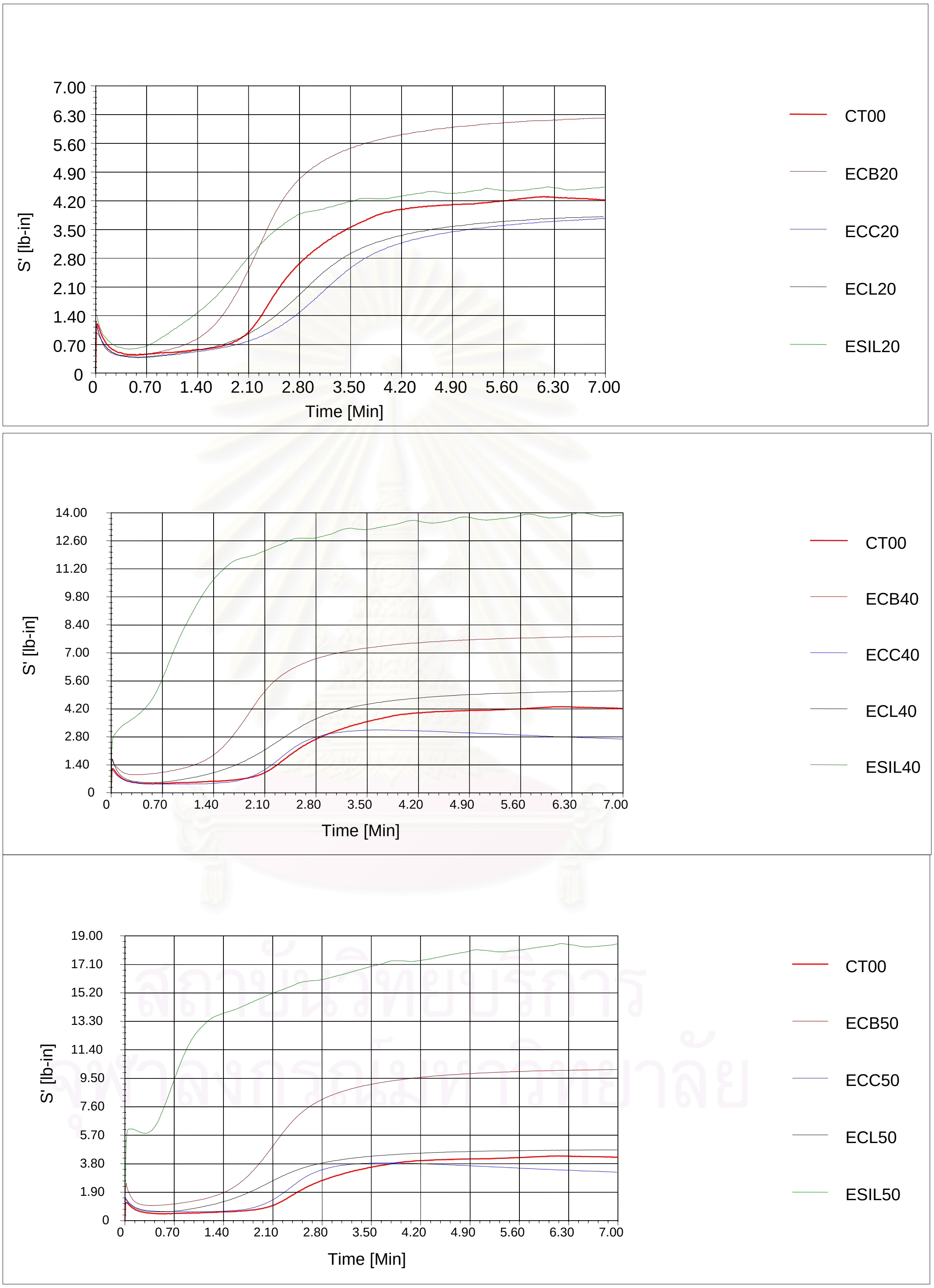


Figure B-3 Cure curves of rubber compounds with various filler types and loading for EV system.

APPENDIX C

Table C-1 Tensile Strength of Compound according to ASTM D412-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Tensile	CV1	3.8	10.4	11.9	12.1	12.1	13.1	11.7	5.6	9.2	10.7	3.8	2.9	3.7
strength	CV2	2.8	9.6	11.5	10.8	11.9	12.7	11.5	4.8	9.0	9.1	3.3	2.8	2.9
(Mpa)	CV3	4.8	11.1	12.7	12.3	12.2	13.2	12.2	7.3	10.1	11.4	5.1	3.4	4.6
	Mean*	4.4	10.8	12.4	12.1	12.2	13.1	12.0	6.7	9.8	11.0	4.7	3.2	4.3
	SD.	1.0	0.8	0.6	0.8	0.2	0.3	0.4	1.3	0.6	1.2	0.9	0.3	0.9
	SEV1	-	10.0	12.1	12.2	9.0	14.5	12.6	5.7	8.2	9.7	2.4	7.1	6.5
	SEV2	-	9.5	11.9	12.1	5.7	13.1	12.5	4.4	7.7	9.3	2.0	6.8	6.3
	SEV3	-	11.6	12.3	12.6	12.2	15.4	12.6	6.6	9.2	9.9	3.0	7.4	6.9
	Mean*	-	11.1	12.2	12.5	10.9	15.0	12.6	6.2	8.9	9.8	2.8	7.3	6.8
	SD.	-	1.1	0.2	0.3	3.3	1.2	0.1	1.1	0.8	0.3	0.5	0.3	0.3
	EV1	-	11.4	14.6	12.8	13.6	14.9	15.4	11.9	10.5	11.5	11.5	11.3	11.0
	EV2	-	10.8	13.8	12.8	12.0	13.8	14.6	11.7	10.3	11.4	10.7	10.2	9.9
	EV3	-	13.1	17.6	14.0	14.7	15.2	15.5	13.0	10.7	11.8	12.5	11.7	11.1
	Mean*	-	12.5	16.6	13.6	14.2	15.0	15.4	12.7	10.6	11.7	12.1	11.5	11.0
	SD.	-	1.2	2.0	0.7	1.4	0.7	0.5	0.7	0.2	0.2	0.9	0.8	0.7

Table C-2 Elongation at break of Compound according to ASTM D412-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Elongation	CV1	460.0	370.0	350.0	270.0	730.0	760.0	740.0	450.0	570.0	550.0	470.0	660.0	830.0
at break	CV2	440.0	360.0	330.0	250.0	720.0	750.0	730.0	430.0	570.0	510.0	470.0	650.0	800.0
(%)	CV3	550.0	390.0	370.0	270.0	760.0	760.0	740.0	500.0	550.0	580.0	510.0	680.0	870.0
	Mean*	521.0	383.0	362.0	268.0	750.0	759.0	739.0	483.0	556.0	567.0	498.0	673.0	855.0
	SD.	58.6	15.3	20.0	11.5	20.8	5.8	5.8	36.1	11.5	35.1	23.1	15.3	35.1
	SEV1	-	420	350	280	600	730	830	450	430	470	390	1030	1020
	SEV2	-	380	340	270	550	690	800	410	440	460	380	1030	1010
	SEV3	-	420	360	280	650	750	840	460	470	470	430	1080	1030
	Mean*	-	416.0	356.0	279.0	630.0	740.0	834.0	453.0	459.0	469.0	417.0	1065.0	1026.0
	SD.	-	23.1	10.0	5.8	50.0	30.6	20.8	26.5	20.8	5.8	26.5	28.9	10.0
	EV1	-	360	360	250	590	610	650	530	500	480	540	830	790
	EV2	-	350	350	230	570	590	630	530	500	480	530	810	770
	EV3	-	390	400	280	600	610	650	540	500	490	550	850	800
	Mean*	-	380.0	387.0	269.0	595.0	608.0	648.0	537.0	500.0	487.0	546.0	842.0	795.0
	SD.	-	20.8	26.5	25.2	15.3	11.5	11.5	5.8	0.0	5.8	10.0	20.0	15.3

Mean* = 0.7S1+0.3S2+0.1S3 ; S1>S2>S3

Table C-3 Hardness of Compound according to ASTM D2240-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Hardness	CV1	44	56	67	70	50	61	73	51	55	57	48	44	43
(Shore A)	CV2	45	57	66	70	50	60	71	51	56	56	49	45	42
	CV3	44	57	66	69	51	60	71	50	55	57	49	44	43
	Mean	44	57	66	70	50	60	72	51	55	57	49	44	43
	SD.	0.6	0.6	0.6	0.6	0.6	0.6	1.2	0.6	0.6	0.6	0.6	0.6	0.6
	SEV1	-	56	65	71	50	60	71	50	55	56	49	35	35
	SEV2	-	56	67	70	51	61	71	51	55	56	50	36	36
	SEV3	-	57	64	71	50	60	72	50	54	57	49	36	35
	Mean	-	56	65	71	50	60	71	50	55	56	49	36	35
	SD.	-	0.6	1.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	EV1	-	56	67	70	50	66	74	51	56	60	45	40	40
	EV2	-	56	65	70	51	67	75	51	55	61	44	40	40
	EV3	-	57	64	71	50	67	75	50	56	60	46	41	40
	Mean	-	56	65	70	50	67	75	51	56	60	45	40	40
	SD.	-	0.6	1.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.0	0.6	0.0

Table C-4 Specific gravity of Compound according to ASTM D1817-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Specific gravity	CV1	0.9428	1.0195	1.0835	1.1165	1.0251	1.0995	1.1281	1.0561	1.1471	1.1889	1.0344	1.1371	1.1812
	CV2	0.9453	1.0187	1.0835	1.1153	1.0281	1.0925	1.1265	1.0615	1.1491	1.1716	1.0321	1.1354	1.1826
	CV3	0.9438	1.0214	1.0814	1.1157	1.028	1.0921	1.1285	1.0612	1.1499	1.1855	1.0329	1.1339	1.1818
	Mean	0.9440	1.0199	1.0828	1.1158	1.0271	1.0947	1.1277	1.0596	1.1487	1.1820	1.0331	1.1355	1.1819
	SD.	0.0013	0.0014	0.0012	0.0006	0.0017	0.0042	0.0011	0.0030	0.0014	0.0092	0.0012	0.0016	0.0007
	SEV1	-	1.01	1.0715	1.1075	1.0122	1.0888	1.11	1.0446	1.1391	1.1775	1.0447	1.112	1.162
	SEV2	-	1.0125	1.0728	1.1086	1.0107	1.092	1.1214	1.0457	1.135	1.1717	1.0449	1.1153	1.1597
	SEV3	-	1.005	1.0757	1.1073	1.0148	1.0874	1.1196	1.0456	1.1292	1.1645	1.0437	1.1117	1.1614
	Mean	-	1.0092	1.0733	1.1078	1.0126	1.0894	1.1170	1.0453	1.1344	1.1712	1.0444	1.1130	1.1610
	SD.	-	0.0038	0.0022	0.0007	0.0021	0.0024	0.0061	0.0006	0.0050	0.0065	0.0006	0.0020	0.0012
	EV1	-	1.016	1.0738	1.1093	1.0136	1.0958	1.1281	1.0374	1.1336	1.1727	1.0425	1.1158	1.161
	EV2	-	1.0177	1.0751	1.1095	1.0158	1.0945	1.1316	1.0402	1.1343	1.1716	1.0577	1.1174	1.1576
	EV3	-	1.0154	1.0753	1.1099	1.0152	1.0957	1.1314	1.0394	1.1371	1.1727	1.0408	1.1178	1.159
	Mean	-	1.0164	1.0747	1.1096	1.0149	1.0953	1.1304	1.0390	1.1350	1.1723	1.0470	1.1170	1.1592
	SD.	-	0.0012	0.0008	0.0003	0.0011	0.0007	0.0020	0.0014	0.0019	0.0006	0.0093	0.0011	0.0017

Table C-5 Compression set of Compound according to ASTM D395-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
CV	t_0 (mm)	12.65	12.75	12.8	12.67	12.5	12.85	12.85	12.39	12.45	12.44	12.45	12.45	12.5
	t_1 (mm)	11.02	11.03	11.03	11.04	10.77	10.31	9.95	10.67	10.52	10.58	10.82	10.36	10.36
	t_n (mm)	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50
	*C/S (%)	51.75	52.92	53.64	51.42	57.67	75.82	86.57	59.52	65.42	63.27	55.25	70.85	71.33
SEV	t_0 (mm)	-	12.49	12.81	12.6	12.5	12.85	12.85	12.39	12.45	12.44	12.45	12.45	12.5
	t_1 (mm)	-	11.7	11.8	11.74	10.77	10.31	9.95	10.67	10.52	10.58	10.82	10.36	10.36
	t_n (mm)	-	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50
	*C/S (%)	-	26.42	30.51	27.74	57.67	75.82	86.57	59.52	65.42	63.27	55.25	70.85	71.33
EV	t_0 (mm)	-	12.65	12.67	12.67	12.55	12.75	12.85	12.45	12.75	12.45	12.5	12.44	12.45
	t_1 (mm)	-	11.77	11.78	11.84	11.78	11.68	11.28	11.45	11.3	11.2	11.67	11.19	11.13
	t_n (mm)	-	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50	9.50
	*C/S (%)	-	27.94	28.08	26.18	25.25	32.92	46.87	33.90	44.62	42.37	27.67	42.52	44.75

C/S* = Compression set (%)

Table C-6 Original Polymer Weight for crosslink density Calculation.

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Original	CV1	0.2026	0.2056	0.2514	0.2031	0.2465	0.2172	0.2369	0.2254	0.2443	0.2554	0.2461	0.2304	0.226
weight (g)	CV2	0.2056	0.2225	0.242	0.2044	0.2262	0.214	0.2329	0.2198	0.2404	0.2347	0.2124	0.2289	0.2306
	CV3	0.202	0.227	0.248	0.2118	0.2194	0.2103	0.2282	0.2276	0.2464	0.2364	0.2338	0.2356	0.2255
	Mean	0.2034	0.2184	0.2471	0.2064	0.2307	0.2138	0.2327	0.2243	0.2437	0.2422	0.2308	0.2316	0.2274
	SD.	0.0019	0.0113	0.0048	0.0047	0.0141	0.0035	0.0044	0.0040	0.0030	0.0115	0.0171	0.0035	0.0028
	SEV1	-	0.2115	0.2096	0.2438	0.2298	0.2251	0.2372	0.2064	0.2236	0.2363	0.218	0.2411	0.235
	SEV2	-	0.2159	0.2256	0.2313	0.2278	0.2218	0.2407	0.2261	0.2254	0.2435	0.2068	0.2497	0.2376
	SEV3	-	0.2217	0.2154	0.2387	0.2496	0.2032	0.229	0.2078	0.2324	0.2269	0.2058	0.2419	0.238
	Mean	-	0.2164	0.2169	0.2379	0.2357	0.2167	0.2356	0.2134	0.2271	0.2356	0.2102	0.2442	0.2369
	SD.	-	0.0051	0.0081	0.0063	0.0121	0.0118	0.0060	0.0110	0.0046	0.0083	0.0068	0.0048	0.0016
	EV1	-	0.2093	0.2144	0.212	0.2108	0.2408	0.243	0.207	0.2395	0.2425	0.2051	0.2358	0.2516
	EV2	-	0.2102	0.2334	0.2088	0.204	0.2293	0.2396	0.2105	0.2279	0.2256	0.2323	0.2413	0.253
	EV3	-	0.2245	0.2198	0.224	0.2145	0.2347	0.244	0.2276	0.2331	0.2384	0.2239	0.2425	0.2518
	Mean	-	0.2147	0.2225	0.2149	0.2098	0.2349	0.2422	0.2150	0.2335	0.2355	0.2204	0.2399	0.2521
	SD.	-	0.0085	0.0098	0.0080	0.0053	0.0058	0.0023	0.0110	0.0058	0.0088	0.0139	0.0036	0.0008

Table C-7 Swollen Polymer Weight for crosslink density Calculation.

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Swollen weight (g)	CV1	1.0480	0.8292	0.849	0.5485	1.1648	0.9244	0.8428	0.9676	0.8851	0.8432	1.2980	1.0341	0.9237
	CV2	1.0500	0.8964	0.8185	0.5483	1.0681	0.9036	0.8468	0.9416	0.8721	0.7664	1.1251	1.046	0.9375
	CV3	1.0372	0.9224	0.8478	0.5741	1.0481	0.9091	0.8147	0.9735	0.8921	0.753	1.2406	1.0895	0.9302
	Mean	1.0451	0.8827	0.8384	0.5570	1.0937	0.9124	0.8348	0.9609	0.8831	0.7875	1.2212	1.0565	0.9305
	SD.	0.0069	0.0481	0.0173	0.0148	0.0624	0.0108	0.0175	0.0170	0.0101	0.0487	0.0881	0.0292	0.0069
	SEV1	-	0.8606	0.6695	0.6657	1.0075	0.8796	1.1251	0.8695	0.8116	0.7558	0.9510	1.3648	1.2604
	SEV2	-	0.8768	0.7210	0.6326	0.9898	0.9010	1.1379	0.9673	0.8161	0.7765	0.8995	1.4029	1.2603
	SEV3	-	0.8979	0.6863	0.6488	1.0920	0.7908	1.0931	0.8893	0.8364	0.7249	0.9005	1.359	1.2483
	Mean	-	0.8784	0.6923	0.6490	1.0298	0.8571	1.1187	0.9087	0.8214	0.7524	0.9170	1.3756	1.2563
	SD.	-	0.0187	0.0263	0.0166	0.0546	0.0584	0.0231	0.0517	0.0132	0.0260	0.0294	0.0238	0.0070
	EV1	-	0.6845	0.6345	0.5518	0.8320	0.8500	0.8415	0.8120	0.7518	0.7432	0.8231	1.127	1.1880
	EV2	-	0.6874	0.6915	0.5823	0.8086	0.8101	0.8435	0.8270	0.7132	0.6907	0.9400	1.1485	1.1768
	EV3	-	0.7380	0.6530	0.5394	0.8532	0.8278	0.8462	0.8970	0.7325	0.7282	0.9031	1.1506	1.1547
	Mean	-	0.7033	0.6597	0.5578	0.8313	0.8293	0.8437	0.8453	0.7325	0.7207	0.8887	1.1420	1.1732
	SD.	-	0.0301	0.0291	0.0221	0.0223	0.0200	0.0024	0.0454	0.0193	0.0270	0.0598	0.0131	0.0169

Table C-8 Shrinkage of Compound at 168 hr after cooling according ASTM D955-00

		Control	Carbon black			Silica			Clay			CaCO3		
		0	20	40	50	20	40	50	20	40	50	20	40	50
Shrinkage*	CV1	2.91	2.90	3.07	2.58	2.90	2.67	2.51	2.49	2.01	1.98	2.80	2.60	2.73
(%)	CV2	2.88	2.91	2.65	2.80	2.83	2.83	2.48	2.27	1.91	1.73	3.08	3.00	2.56
	CV3	3.13	2.89	2.68	2.56	2.80	2.57	2.45	2.42	2.00	2.05	3.40	3.06	2.63
	Mean	2.98	2.90	2.80	2.65	2.84	2.69	2.48	2.39	1.97	1.92	3.09	2.89	2.64
	SD.	0.14	0.01	0.23	0.13	0.05	0.13	0.03	0.12	0.06	0.17	0.30	0.25	0.08
	SEV1	-	2.97	2.71	2.69	2.84	2.12	2.82	2.27	2.13	2.03	3.05	2.87	2.90
	SEV2	-	2.98	2.71	2.46	2.83	2.42	2.21	2.05	2.06	1.68	2.93	2.96	2.83
	SEV3	-	2.87	2.83	2.68	3.08	2.31	2.26	2.28	2.59	1.75	3.17	2.95	3.14
	Mean	-	2.94	2.75	2.61	2.92	2.28	2.43	2.20	2.26	1.82	3.05	2.93	2.96
	SD.	-	0.06	0.07	0.13	0.14	0.15	0.34	0.13	0.29	0.19	0.12	0.05	0.16
	EV1	-	2.83	2.47	2.19	2.83	2.45	2.24	2.33	2.07	1.75	2.95	2.67	2.98
	EV2	-	2.84	2.49	2.32	2.83	2.41	2.36	2.36	2.00	1.80	2.89	2.83	2.61
	EV3	-	2.75	2.36	2.10	2.76	2.54	2.39	2.47	1.69	1.78	2.79	2.79	2.46
	Mean	-	2.81	2.44	2.20	2.81	2.47	2.33	2.39	1.92	1.78	2.88	2.76	2.68
	SD.	-	0.05	0.07	0.11	0.04	0.07	0.08	0.07	0.20	0.03	0.08	0.09	0.27

* Data from average 4 point check per 1 piece

APPENDIX D

The crosslinkink density of natural rubber/EPDM blend was calculated according to Flory-Huggins Theory [32]. Swelling can be determined gravimetrically, by weighting the polymer sample before the experiment (w_0) and subtracting this value from the solvent swollen polymer weight (w_s) as in Eq.C.1

$$V_{equil} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \qquad \text{(C.1)}$$

and

$$V_{2m} = \frac{w_0}{V_{equil} \times \rho_2} \qquad \text{(C.2)}$$

where ρ_2 = polymer density = 0.940 g/cm^3 (Table C-4)

ρ_1 = solvent density (toluene) = 0.860 g/cm^3 (COA)

w_0 = original polymer weight = 0.2034 g (Table C-6)

w_s = swollen polymer weight = 1.0250 g (Table C-7)

$$V_{equil} = \frac{0.2034}{0.940} + \frac{1.0250 - 0.2034}{0.870} = 1.1607$$

Substituting V_{equil} = 1.1607 in Eq. C.2

$$V_{2m} = \frac{0.2034}{1.1607 \times 0.940} = 0.1864$$

The molecular weight per crosslinking unit, M_c is calculated using Eq. C.3

$$M_c = \frac{V_1 \rho_2 \left[V_{2m}^{1/3} - V_{2m}/2 \right]}{-[\ln(1 - V_{2m}) + V_{2m} + \chi_1 V_{2m}]} \qquad \text{(C.3)}$$

Where V_1 is molar volume of solvent and χ_1 is polymer-solvent interaction parameter.

In chemistry, the molar volume of a substance is the volume of one mole of that substance. It can be computed as the substance's atomic or molecular weight, divided by its density.

Hence,

$$V_1 = 107.10 \text{ cm}^3/\text{mol}$$

Substituting the known value V_1 , ρ_2 , V_{2m} and $\chi_1 = 0.393$ [33] for rubber/toluene in Eq. C.3

$$M_c = 7722.78 \text{ g/mol}$$

Thus, the crosslinking density of natural rubber/EPDM compound is,

$$n_c = \frac{\rho_2}{7722.78}$$

$$= 1.217 \times 10^{-4} \text{ mol/cm}^3$$

APPENDIX E

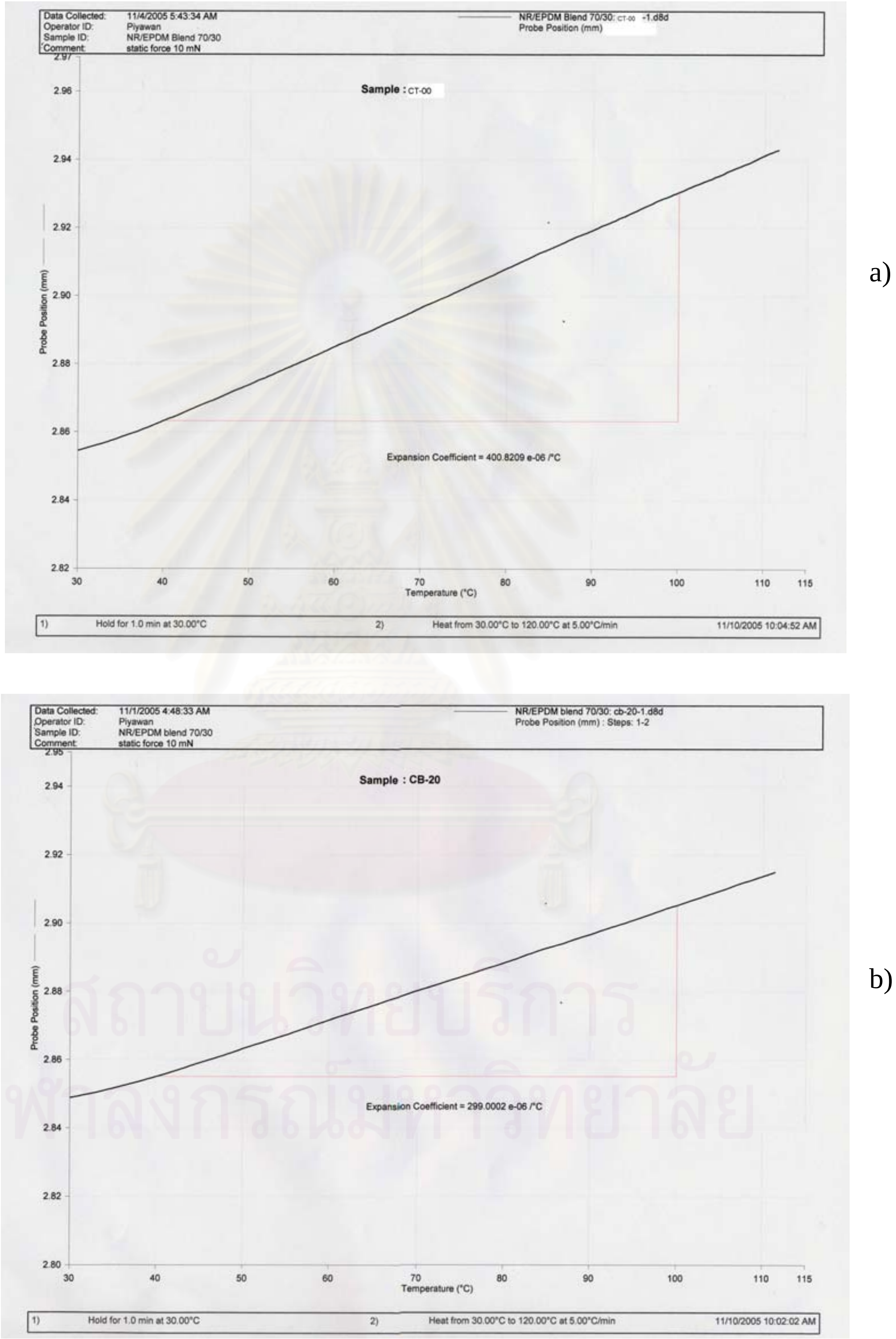
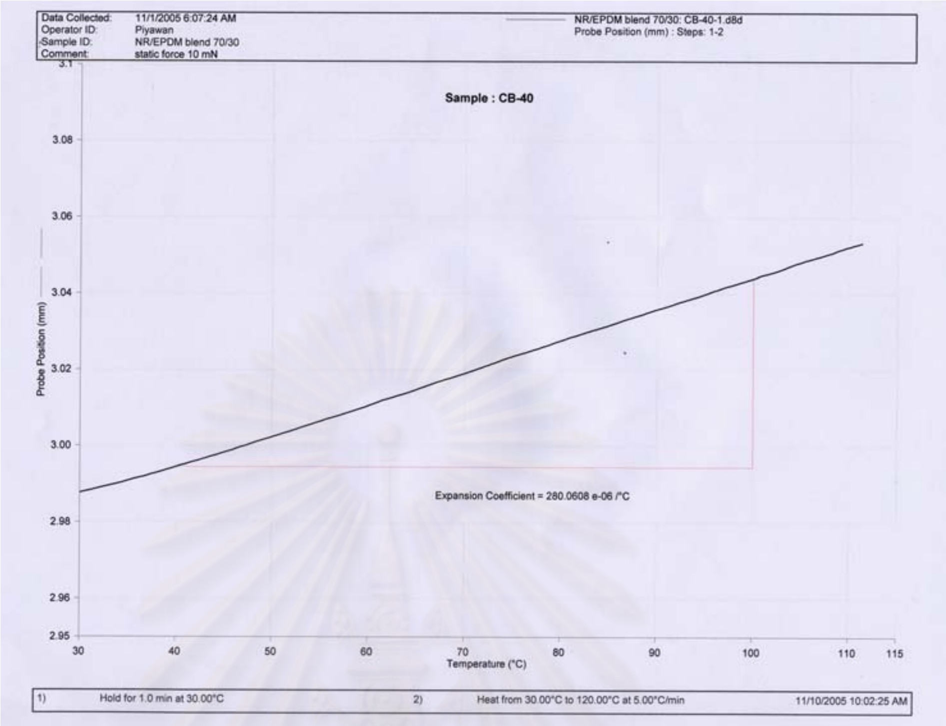


Figure E TMA thermogram of filled rubber compound; a) CT00, b) CB20, c) CB40, d) CB50, e) SIL40, f) CC40, g) CL40, h) SCB40 and i) ECB40).



Data Collected: 11/1/2005 6:07:24 AM
Operator ID: Piyawan
Sample ID: NR/EPDM blend 70/30
Comment: static force 10 mN

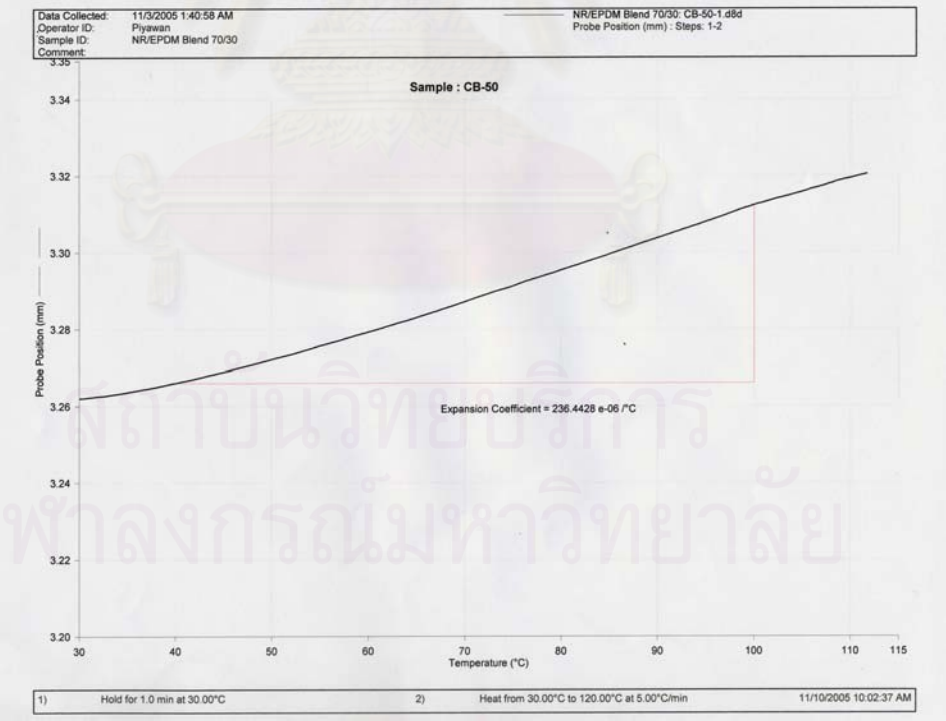
NR/EPDM blend 70/30: CB-40-1.d8d
Probe Position (mm) : Steps: 1-2

Sample : CB-40

Expansion Coefficient = 280.0608 e-06 /°C

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:02:25 AM

c)



Data Collected: 11/3/2005 1:40:58 AM
Operator ID: Piyawan
Sample ID: NR/EPDM Blend 70/30
Comment:

NR/EPDM Blend 70/30: CB-50-1.d8d
Probe Position (mm) : Steps: 1-2

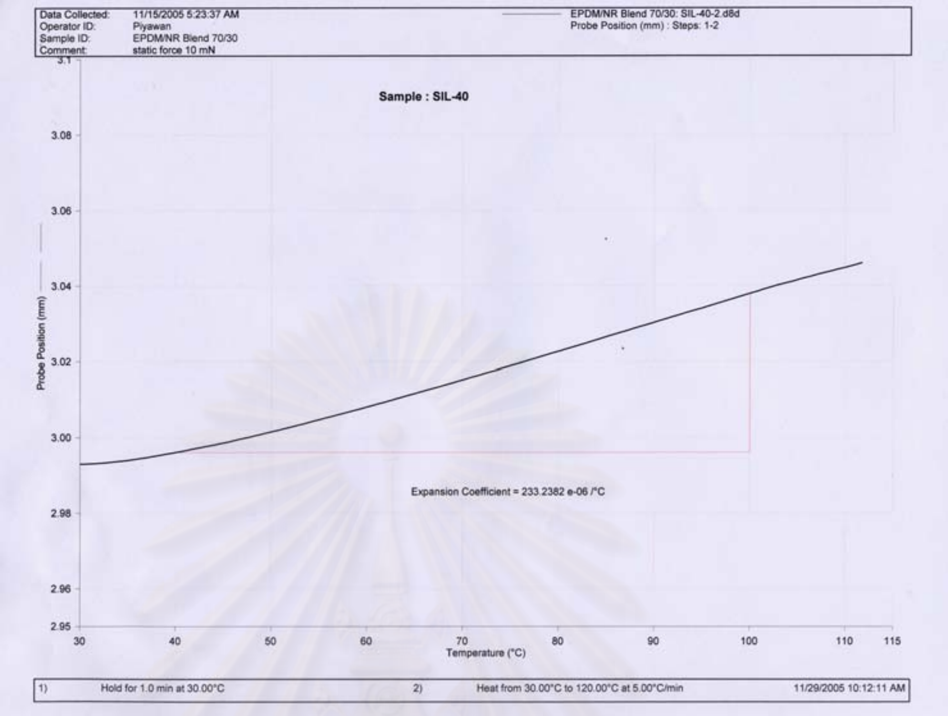
Sample : CB-50

Expansion Coefficient = 236.4428 e-06 /°C

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:02:37 AM

d)

Figure E (Continue)



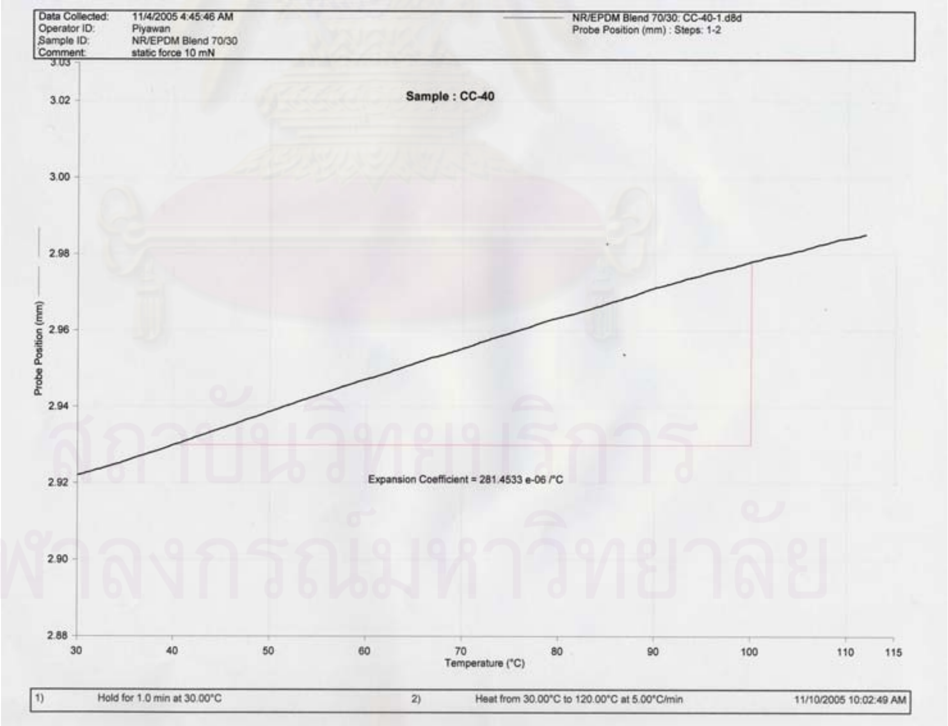
Data Collected: 11/15/2005 5:23:37 AM
Operator ID: Piyawan
Sample ID: EPDM/NR Blend 70/30
Comment: static force 10 mN

EPDM/NR Blend 70/30: SIL-40-2.d8d
Probe Position (mm) : Steps: 1-2

Expansion Coefficient = 233.2382 e-06 /°C

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/29/2005 10:12:11 AM

e)



Data Collected: 11/4/2005 4:45:46 AM
Operator ID: Piyawan
Sample ID: NR/EPDM Blend 70/30
Comment: static force 10 mN

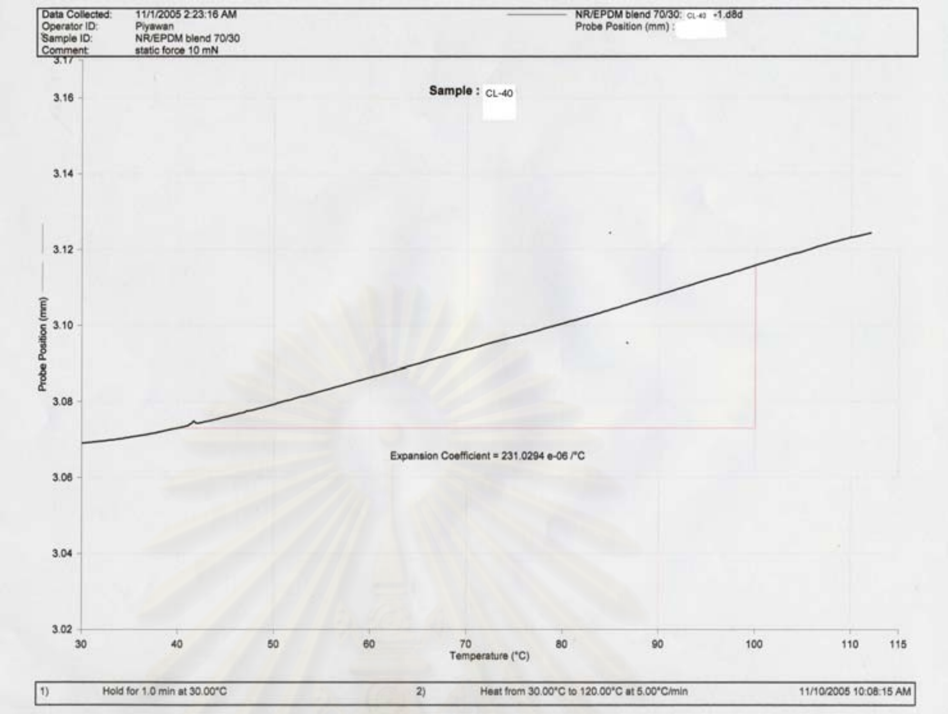
NR/EPDM Blend 70/30: CC-40-1.d8d
Probe Position (mm) : Steps: 1-2

Expansion Coefficient = 281.4533 e-06 /°C

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:02:49 AM

f)

Figure E (Continue)

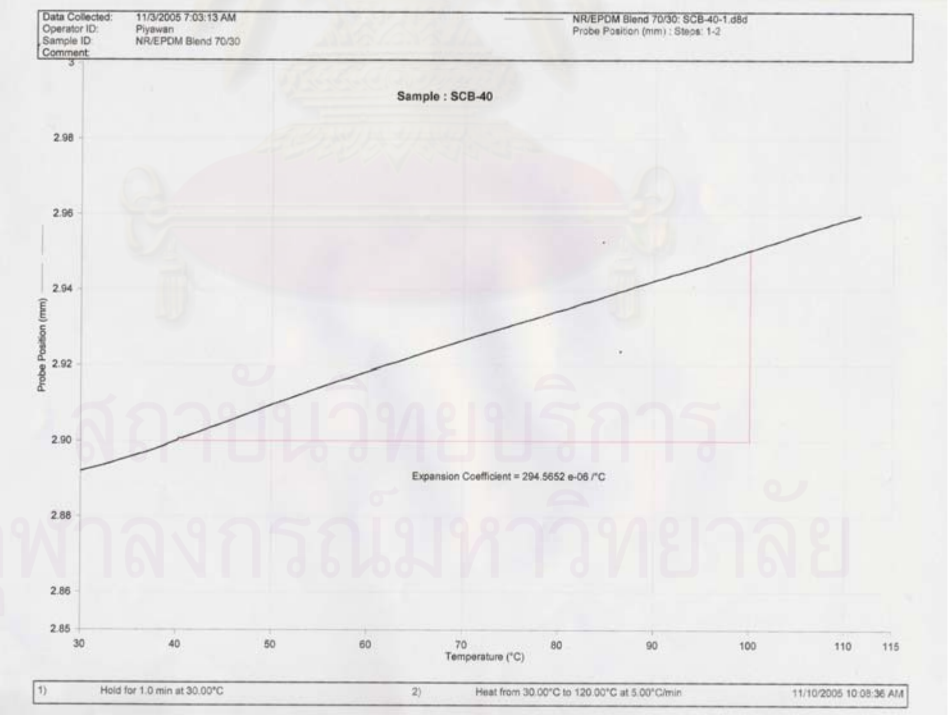


Data Collected: 11/1/2005 2:23:16 AM
Operator ID: Piyawan
Sample ID: NR/EPDM blend 70/30
Comment: static force 10 mN

NR/EPDM blend 70/30: CL-40 +1.d8d
Probe Position (mm) :

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:08:15 AM

g)



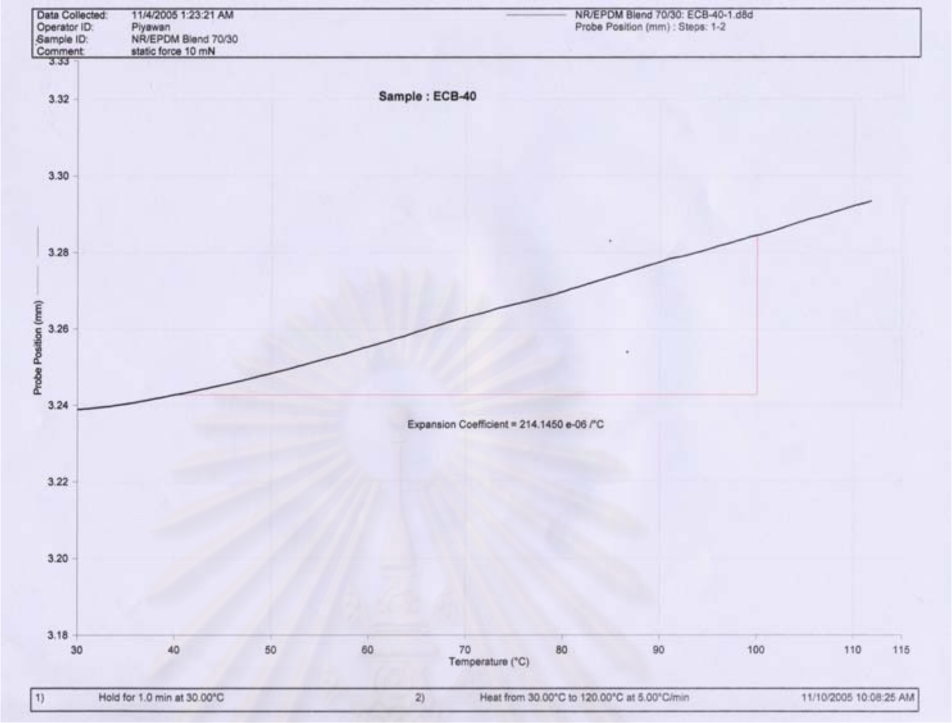
Data Collected: 11/3/2005 7:03:13 AM
Operator ID: Piyawan
Sample ID: NR/EPDM Blend 70/30
Comment:

NR/EPDM Blend 70/30: SCB-40-1.d8d
Probe Position (mm) : Steps: 1-2

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:08:36 AM

h)

Figure E (Continue)



i)

Data Collected: 11/4/2005 1:23:21 AM
Operator ID: Piyawan
Sample ID: NR/EPDM Blend 70/30
Comment: static force 10 mN

NR/EPDM Blend 70/30: ECB-40-1.d8d
Probe Position (mm) : Steps: 1-2

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 120.00°C at 5.00°C/min
11/10/2005 10:08:25 AM

Figure E (Continue)

VITAE

Mr.Prachid Saramolee was born on August 8, 1979, in Phutthalung, Thailand. He received his Bachelor's degree in Rubber Technology, from the Faculty of Science and Technology, Prince of Songkla University in 2002. He has pursued Master's Degree in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2004 and finished his study in 2006.