

**İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

**CONTINUOUS COMPOUNDING OF SILICA LOADED RUBBER IN A  
TWIN SCREW EXTRUDER**

**M.Sc. Thesis by  
Eren DALGAKIRAN**

**Department : Polymer Science and Technology**

**Programme : Polymer Science and Technology**

**JUNE 2010**



**CONTINUOUS COMPOUNDING OF SILICA FILLED RUBBER IN A TWIN  
SCREW EXTRUDER**

**M.Sc. Thesis by  
Eren DALGAKIRAN  
(515081012)**

**Date of submission : 07 May 2010  
Date of defence examination : 07 June 2010**

**Supervisor (Chairman) : Prof. Dr. İ. Ersin SERHATLI (ITU)  
Members of the Examining Committee : Prof. Dr. Hulusi ÖZKUL (ITU)  
Prof. Dr. Hüseyin YILDIRIM (YTU)**

**JUNE 2010**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**ÇİFT VİDALI EKSTRUDER İLE SÜREKLİ SİLİKA  
DOLGULU ELASTOMER HAMUR ÜRETİMİ**

**YÜKSEK LİSANS TEZİ  
Eren DALGAKIRAN  
(515081012)**

**Tezin Enstitüye Verildiği Tarih : 07 Mayıs 2010**

**Tezin Savunulduğu Tarih : 07 Haziran 2010**

**Tez Danışmanı : Prof. Dr. İ. Ersin SERHATLI (İTÜ)  
Diğer Jüri Üyeleri : Prof. Dr. Hulusi ÖZKUL (İTÜ)  
Prof. Dr. Hüseyin YILDIRIM (YTÜ)**

**HAZİRAN 2010**



## FOREWORD

I would like to express my gratitude to my advisor Prof. Dr. İ. Ersin Serhatlı for his invaluable advice, guidance, and encouragement throughout my studies.

I sincerely thank Dr. Osman G. Ersoy for his invaluable help and academic advice and I extend my thanks to all members of the Material Technologies Department in the name of Sibel Odabaş.

I would like to express my thanks to Arçelik A.Ş. for invaluable support in the name of Cemil İnan and Fatih Özkadı.

I would like to thank to Adnan Çapar, Selami Doruk and Hüseyin Süleymanoğlu from PMR Ltd. Şti. for providing the laboratory equipments..

My very special thanks are to Nursel Karakaya, Mehmet Ali Oral, Fatih Kotan, Aylin Met, Deniz Erdinç, Turgay Gönül, Hamza Sancaklı, Hatice Yılmaz and Sevinç Mert for their contribution in this thesis in almost every possible way.

Last but definitely not least, I thank to my family and my lovely fiancée Dilek Kutsal who supported and encouraged me all my life

May 2010

Eren DALGAKIRAN

Polymer Science and Technology





## TABLE OF CONTENTS

	<u>Page</u>
<b>FOREWORD.....</b>	<b>v</b>
<b>TABLE OF CONTENTS.....</b>	<b>vii</b>
<b>ABBREVIATIONS .....</b>	<b>ix</b>
<b>LIST OF TABLES .....</b>	<b>xi</b>
<b>LIST OF FIGURES .....</b>	<b>xiii</b>
<b>SUMMARY .....</b>	<b>xv</b>
<b>ÖZET.....</b>	<b>xvii</b>
<b>1. INTRODUCTION.....</b>	<b>1</b>
<b>2. INGREDIENTS OF RUBBER COMPOUNDS .....</b>	<b>5</b>
2.1 Elastomers .....	5
2.1.1 Ethylene propylene diene rubber (EPM, EPDM) .....	5
2.2 Fillers.....	7
2.2.1 Silica.....	8
2.2.2 Carbon black .....	9
2.2.3 Other fillers .....	9
2.3 Coupling Agents.....	10
2.3.1 Silane coupling agent.....	10
2.3.2 Titanate and zirconate coupling agents .....	11
2.4 Activators .....	11
2.4.1 Zinc oxide and stearic acid.....	11
2.4.2 Iron oxide .....	12
2.4.3 Lead oxide.....	12
2.4.4 Magnesium oxide.....	13
2.5 Process additives .....	13
2.6 Vulcanizing Agents .....	13
2.6.1 Sulfur.....	13
2.6.2 Peroxide .....	15
2.7 Accelerators.....	15
2.8 Other Ingredients.....	17
2.8.1 Antioxidants .....	17
2.8.2 Antiozonants .....	17
2.8.3 Plasticizers .....	17
2.8.4 Pigments.....	17
2.8.5 Antistatic agents.....	18
2.8.6 Fire reterdants .....	18
2.8.7 Prevulcanization inhibitors .....	18
<b>3. PRODUCTION METHODS.....</b>	<b>19</b>
3.1 Open Mill .....	19
3.2 Internal Mixing Machines .....	20
3.3 Extruders .....	22

<b>4. SILICA – SILANE INTERACTION.....</b>	<b>25</b>
4.1 Silanisation Reaction .....	26
4.1.1 Discontinuous compounding in an internal mixer .....	28
4.1.2 Continuous compounding in a twin screw extruder.....	29
4.1.3 Continuous compounding of silica/silane compounds.....	29
<b>5. EXPERIMENTAL WORK.....</b>	<b>31</b>
5.1 Materials.....	31
5.2 Compounding Recipes.....	31
5.3 Manufacturing Process .....	33
5.3.1 Open mill operation.....	33
5.3.1.1 Compounding of the rubber by open mill .....	33
5.3.2 Banbury .....	35
5.3.2.1 Compounding of the rubber by banbury .....	35
5.3.3 Twin screw extruder.....	36
5.3.3.1 Compounding of the rubber by twin screw extruder.....	39
5.3.4 Compression molding .....	40
5.4 Testing and Characterization of Compounds .....	41
5.4.1 Rheological properties (Test on unvulcanized rubbers).....	41
5.4.1.1 Oscillating Disc Rheometer .....	41
5.4.1.2 Mooney Viscometer .....	43
5.4.2 Mechanical properties (Test on vulcanized rubbers) .....	45
5.4.2.1 Tensile test.....	45
5.4.2.2 Tear strength test .....	46
5.4.3 Physical properties (Test on vulcanized rubbers) .....	47
5.4.3.1 Hardness .....	47
5.4.3.2 Abrasion resistance test.....	48
5.4.3.3 Compression set test.....	50
5.4.3.4 Density .....	51
5.4.3.5 Determination of ash content .....	51
<b>6. RESULTS AND DISCUSSION.....</b>	<b>53</b>
6.1 Rheological Properties.....	53
6.2 Mechanical Properties .....	59
6.2.1 Tensile strength test.....	59
6.2.2 Tear strength test .....	62
6.3.1 Hardness .....	63
6.3.2 Abrasion resistance .....	64
6.3.3 Compression set .....	66
6.3.4 Density measurement .....	67
6.3.5 Ash content.....	68
<b>7. CONCLUSION.....</b>	<b>71</b>
<b>REFERENCES.....</b>	<b>73</b>
<b>CURRICULUM VITA.....</b>	<b>77</b>

## **ABBREVIATIONS**

<b>ASTM</b>	: American Society for Testing Materials
<b>CBS</b>	: N-cyclohexyl-2-benzothiazol sulfenamide
<b>DPG</b>	: Diphenyl guanidine
<b>ENB</b>	: Ethylidene norbornene
<b>EPM</b>	: Ethylene propylene monomer
<b>EPDM</b>	: Ethylene propylene diene monomer
<b>FC</b>	: Forward conveying
<b>ISO</b>	: International Organization for Standardization
<b>KB</b>	: Kneading block
<b>MBT</b>	: Mercaptobenzothiazole
<b>ODR</b>	: Oscillating disc rheometer
<b>PEG</b>	: Polyethylene glycol
<b>PHR</b>	: Parts per hundred of rubber
<b>S</b>	: Sulfur
<b>Si69</b>	: Bis[3-(triethoxysilyl) propyl] tetrasulfide
<b>TMTD</b>	: Tetramethylthiuram disulfide
<b>TSE</b>	: Twin screw extruder
<b>VIC</b>	: Variable intermeshing clearance
<b>ZDBC</b>	: Zinc dibutyl dithiocarbamate
<b>ZnO</b>	: Zinc oxide



## LIST OF TABLES

	<u>Page</u>
<b>Table 2.1</b> : Typical accelerators .....	16
<b>Table 5.1</b> : Recipes of experimental works .....	32
<b>Table 5.2</b> : Mixing cycles of open mill operation .....	34
<b>Table 5.3</b> : Mixing cycles of unreinforced recipe .....	34
<b>Table 5.4</b> : Mixing cycles of banbury operation .....	36
<b>Table 5.5</b> : Technical specifications of Prism TSE 24 HC 28:1 extruder .....	37
<b>Table 5.6</b> : Mixing cycles of extruder operation .....	39
<b>Table 5.7</b> : Dimension of test specimens .....	46
<b>Table 5.8</b> : Dimension of test specimens .....	47
<b>Table 6.1</b> : $M_L$ results .....	53
<b>Table 6.2</b> : $M_H$ results.....	54
<b>Table 6.3</b> : $t_{s1}$ results.....	56
<b>Table 6.4</b> : $t_{90}$ results .....	57
<b>Table 6.5</b> : Mooney viscosity results.....	58
<b>Table 6.6</b> : Tensile strength results .....	59
<b>Table 6.7</b> : Elongation at break results.....	61
<b>Table 6.8</b> : Tear strength results .....	62
<b>Table 6.9</b> : Hardness results .....	63
<b>Table 6.10</b> : Abrasion resistance results.....	65
<b>Table 6.11</b> : Compression set results.....	66
<b>Table 6.12</b> : Density measurement results .....	68
<b>Table 6.13</b> : Ash content results .....	69



## LIST OF FIGURES

	<b>Page</b>
<b>Figure 1.1</b> : Diagram of mastication and the addition of additives.....	2
<b>Figure 1.2</b> : A diagram of banbury.....	3
<b>Figure 2.1</b> : Terpolymer: dicyclopentadiene.....	6
<b>Figure 2.2</b> : Terpolymer: ethylidene norbornene.....	6
<b>Figure 2.3</b> : Terpolymer: 1,4-hexadiene.....	6
<b>Figure 2.4</b> : The general formula for a silane coupling agent.....	10
<b>Figure 2.5</b> : Structural features of a vulcanized rubber.....	14
<b>Figure 2.6</b> : Properties after vulcanization.....	15
<b>Figure 3.1</b> : Conceptual view of rubber mill rolls.....	19
<b>Figure 3.2</b> : Conceptual cross-section through an internal mixing machine, with tangential rotors.....	22
<b>Figure 3.3</b> : Conceptual view of a basic extruder.....	22
<b>Figure 4.1</b> : Payne effect.....	26
<b>Figure 4.2</b> : Silanisation reaction – primary reaction.....	27
<b>Figure 4.3</b> : Silanisation reaction – secondary reaction.....	27
<b>Figure 5.1</b> : Met-Gür MG/H-300 open mill.....	33
<b>Figure 5.2</b> : Met-Gür MG-15 banbury.....	35
<b>Figure 5.3</b> : Prism TSE 24 HC 28:1 extruder.....	37
<b>Figure 5.4</b> : Barrel profile.....	38
<b>Figure 5.5</b> : Screw configuration (KB: Kneading block, FC: Forward conveying)..	39
<b>Figure 5.6</b> : Laboratory compression press.....	40
<b>Figure 5.7</b> : Test specimens (a: tensile strength; b: tear strength; c: hardness; d: abrasion resistance; e: compression test specimen).....	40
<b>Figure 5.8</b> : Principles of oscillating disc rheometers.....	41
<b>Figure 5.9</b> : Oscillating disc rheometer trace.....	42
<b>Figure 5.10</b> : Oscillating disc rheometer.....	43
<b>Figure 5.11</b> : Mooney geometry. A is usually the stator and B the rotor, C is the rotating shaft, xy indicates the mid-plane along which the chamber can be opened for filling.....	44
<b>Figure 5.12</b> : Mooney viscometer.....	44
<b>Figure 5.13</b> : Tensile test specimen.....	45
<b>Figure 5.14</b> : Tear strength test specimen.....	46
<b>Figure 5.15</b> : Indenter for type Shore A durometer (1: presser foot; 2: indenter).....	48
<b>Figure 5.16</b> : Schematic illustration of apparatus (1: Swivel arm; 2: Sledge; 3: Double sided adhesive tape; 4: Abrasive sheet; 5: Cylinder; 6: Gap < 2; 7: Test piece; 8: Test piece holder; 9: Rotational speed 40±1 rpm)....	49
<b>Figure 5.17</b> : Device for compression set test under constant deflection.....	50
<b>Figure 6.1</b> : $M_L$ results.....	54
<b>Figure 6.2</b> : $M_H$ results.....	55
<b>Figure 6.3</b> : $t_{s1}$ results.....	56
<b>Figure 6.4</b> : $t_{90}$ results.....	57

<b>Figure 6.5 : Mooney viscosity results .....</b>	<b>58</b>
<b>Figure 6.6 : Tensile strength results .....</b>	<b>60</b>
<b>Figure 6.7 : Elongation at break results .....</b>	<b>61</b>
<b>Figure 6.8 : Tear strength results.....</b>	<b>62</b>
<b>Figure 6.9 : Hardness results .....</b>	<b>64</b>
<b>Figure 6.10 : Abrasion resistance results .....</b>	<b>65</b>
<b>Figure 6.11 : Compression set results .....</b>	<b>67</b>
<b>Figure 6.12 : Density measurement results .....</b>	<b>68</b>
<b>Figure 6.13 : Ash content results.....</b>	<b>69</b>



## **CONTINUOUS COMPOUNDING OF SILICA LOADED RUBBER IN A TWIN SCREW EXTRUDER**

### **SUMMARY**

Open mill and banbury are the most popular mixer for rubber compounding around the world. Although these two mixer are used for many years, a new method to compound the rubber has developed in recent years. Due to its advantages like; high automation level dosage and compounding, screw element and barrel configuration flexibility, high mixing efficiency, and continuity of the process, compounding of rubber by a twin screw extruder is an interesting alternative to compounding with an internal mixer. With respect to the compounding of silica filled rubber, there is a further advantage in comparison to the compounding in the internal mixer.

Together with carbon black, silica is one of the most important reinforcing fillers for rubber compounds. The untreated silica particles feature high filler-filler interactions and tend to build agglomerates with strong internal bonding forces. Compared to the filler-filler interaction, the polymer-filler interaction is small and the reinforcing effect is limited. The improvement of the mechanical properties can only be achieved through the addition of the coupling agent silane to the rubber compound. The silane bonds to the silica in the so-called silanisation reaction and chemically modifies the surface of the silica particles. Due to the reaction of the silica and the silane, the filler-filler interaction of the silica particles decreases and the interaction of the silica and a nonpolar rubber polymer increases. A better dispersion of the additives and therefore better material properties can be achieved.

The aim of this study is to compare the compounding of rubber within the twin screw extruder with well-known classical compounding methods; i.e. open mill or banbury mixing. The effect of silanisation reaction within the twin screw extruder is also investigated according to reaction temperature. Nine recipes were prepared with open mill, banbury-open mill and twin screw extruder-open mill combinations. Curing characteristics and mooney viscosity were measured with uncured rubber. Mechanical properties such as tensile strength and tear strength and physical properties such as hardness, abrasion resistance and compression set which were measured after preparation of samples by hot press during 6 minutes at 180°C.



# ÇİFT VİDALI EKSTRUDER İLE SÜREKLİ SİLİKA DOLGULU ELASTOMER HAMUR ÜRETİMİ

## ÖZET

Tüm dünyada kauçuk hamur üretimde en çok kullanılan cihazlar açık mil ve banbury'dir. Her iki cihaz da uzun yıllardır kullanılmakla birlikte son yıllarda kauçuk hazırlamada yeni bir yöntem de geliştirilmektedir. Çift vidalı ekstruder ile kauçuk hamur hazırlama yöntemi özellikle banbury üretimine alternatif olarak geliştirilmektedir. Ekstruder ile kauçuk hamur üretiminin avantajları olarak yüksek otomasyon seviyesinde sürekli üretim, yüksek karıştırma verimliliği ve otomatik dozajlama olanağı sayesinde hammadde üretiminde yüksek hassasiyet olarak sıralanabilmektedir.

Silika, karbon karası ile birlikte kauçuk hamurların en önemli dolgularından birisidir. İşlemden geçirilmemiş silika tanecikleri yüksek dolgu-dolgu etkileşimi göstererek topaklanma eğilimi göstermektedirler. Dolgu-dolgu etkileşimine kıyasla polimer-dolgu etkileşimi ise daha küçüktür ve bu yüzden de silikanın takviyelendirici özelliği sınırlıdır. Mekanik özelliklerde iyileşme sağlamak için sisteme uyumlaştırıcı ajan olarak silan katılması gerekmektedir. Silan-silika etkileşimine silanizasyon reaksiyonu denmektedir ve bu reaksiyon sonucunda silikanın yüzeyi kimyasal olarak düzenlenmektedir. Silan-silika arasındaki bu reaksiyona bağlı olarak dolgu-dolgu etkileşimi azalarak silika ve polar olmayan kauçuk polimeri arasındaki etkileşim artmaktadır.

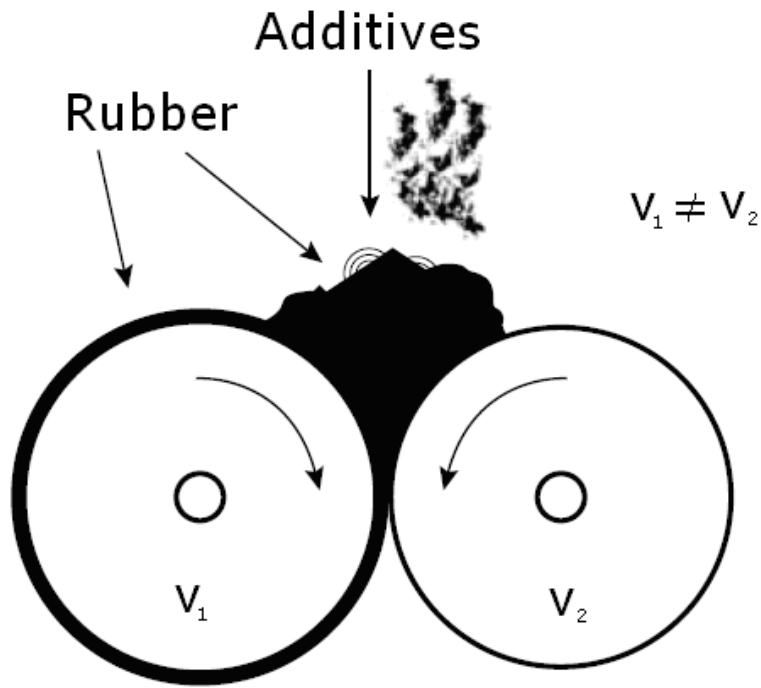
Bu tezin amacı, çift vidalı ekstruderde kauçuk hamur üretimine ait parametrelerin incelenmesi ve sıcaklığın silanizasyon reaksiyonuna olan etkisinin incelenmesidir. Bu amaçla beş farklı hamur formülasyonu açık milde, banbury-açık mil ve çift vidalı ekstruder-açık mil kombinasyonlarında hazırlanmıştır. Hazırlanan bu hamurların vulkanizasyon öncesinde kürlenme karakteristiği ve mooney viskozitelerine bakılmıştır. Daha sonra 180°C'de 6 dakika boyunca preslendikten sonra mekanik ve fiziksel özellikleri test edilmiştir.



## 1. INTRODUCTION

In today's world rubber materials are used in many industry and most of people are familiar with them in their life. This natural material has been used for almost four thousand years. There can be no doubt that the discovery of vulcanization of high polymers with unsaturated carbon backbones (polyolefinic elastomers), such as natural rubber and ethylene propylene diene monomer, change the world as much as, if not more than, any other discovery over the last few hundred years. In non-chemical terms, vulcanization can be described as the process by which the chemical reaction between a polyolefin and sulfur (or peroxide) results in greatly increased elastic properties of the polyolefin and the maintenance of these properties over a comparatively wide temperature range. However heating pure rubber and sulfur will not give a vulcanized product. A fundamental rubber vulcanizing system comprises also activators and accelerators. Addition of these ingredients fillers are used to reinforce the material and reduce the cost. The most common filler is carbon black. But when non-carbon black product is prepared, white fillers such as precipitated silica are used. Silica reinforces the raw gum like carbon black and by its white color, it does not impose a restriction on the color of the vulcanized products. Generally coupling agents such as silanes are used with silica filled compounds. Because silanes give improved processability and provide "crosslinks" between silica particle and rubber molecular chains (Loadman, 2005a).

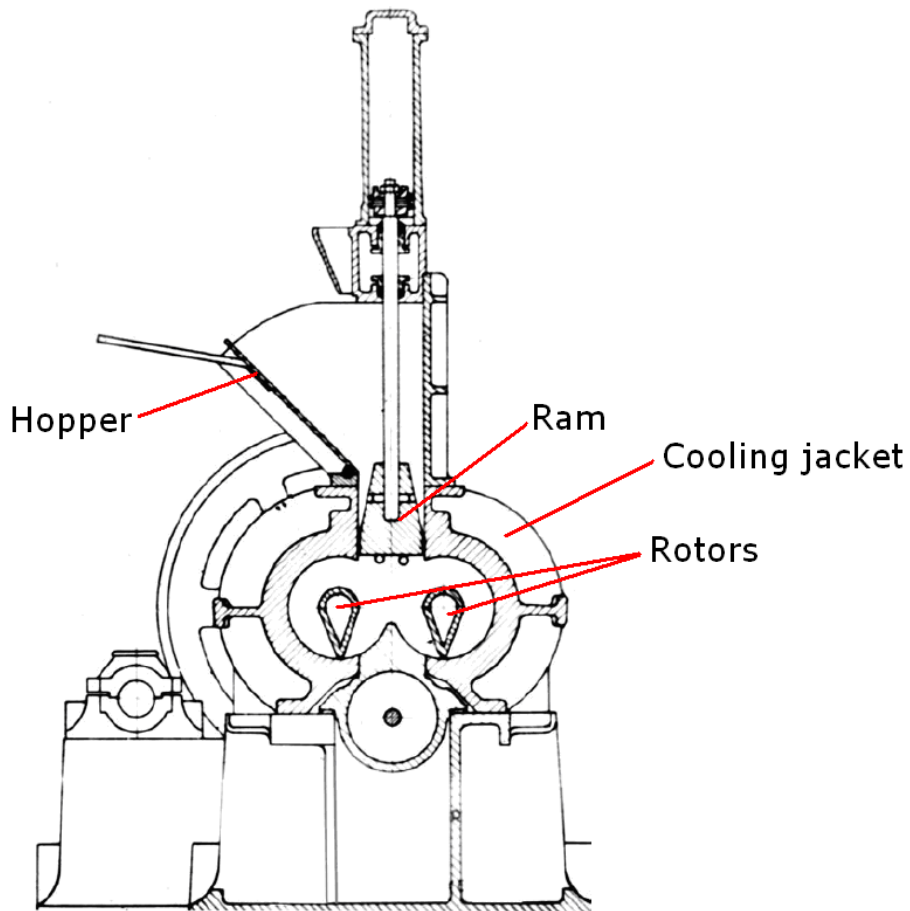
Although natural rubber had known since 17<sup>th</sup> century, the first machinery to process the rubber was developed in 18<sup>th</sup> century. In the 1830s, Chaffee developed the two-roll, two-speed mill, which designed to masticate the rubber. By rotating the horizontally opposed rollers in opposite directions at slightly different speeds, the diagram in Figure 1.1 shows how the rubber bands on the left roller whilst, because here the right one is rotating slower than the left.



**Figure 1.1 :** Diagram of mastication and the addition of additives (Loadman, 2005)

But these mills had one particular disadvantage in that they were open to the atmosphere and the search for new methods of mixing with more compact equipment which was quicker, less power-consuming, and which offered a cleaner working environment than the ‘open’ mill led to various ‘internal mixers’ being developed. Werner Pfleiderer, a company that had begun some thirty years earlier to manufacture machinery for mixing and kneading dough, made the earliest in 1913, while in 1916 Fernley Banbury launched the ‘Banbury’ mixer, which remains probably the most popular mixer for rubber compounding around the world today.

The principle of operation is shown in Figure 1.2. The Banbury used a pair of counter- rotating winged tangential rotors, which can be seen as pear-shaped objects, inside a closed chamber into which the rubber and additives could be dropped via the hopper on the left-hand side and then sealed under pressure by the vertical ram. After mixing, the compound was dropped through the floor of the mixer for subsequent molding and vulcanization.



**Figure 1.2 :** A diagram of banbury (Loadman, 2005)

The compounding of rubber in a twin screw extruder (TSE) represents an interesting alternative to the compounding in an internal mixer due to advantages like the high automation level with respect to dosage and compounding, the flexible configuration of the twin screw extruder, high mixing efficiency, and the continuity of the process (Loadman, 2005b).

In this work, the parameters of compounding rubber in a twin screw extruder was investigated and compared with other rubber production methods which were open mill and banbury-open mill combination. The second part of the work, the effect of the temperature to silanisation reaction was investigated.





## **2. INGREDIENTS OF RUBBER COMPOUNDS**

### **2.1 Elastomers**

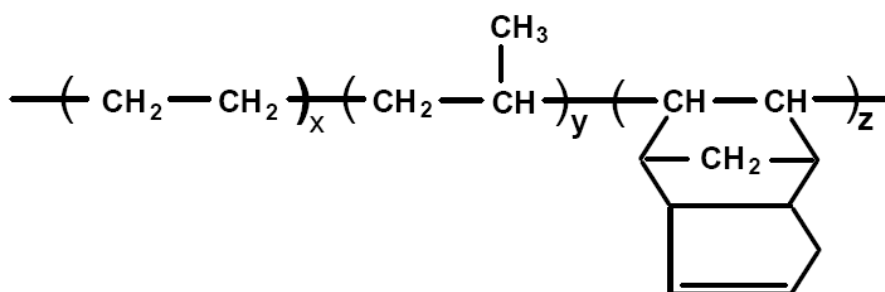
The term elastomer is used to describe vulcanized polymeric materials. They have the ability to be extensively deformed and after release of stress they can return to its original length and their glass transition is sub-ambient. The common characteristics of elastomers are elasticity, flexibility and toughness and each elastomer has its own unique properties, often requiring additives to achieve the appropriate behaviors. Rubber compounding ingredients can be categorized as: rubber, vulcanizing or crosslinking agents, processing aids, fillers, antidegradants, plasticizing and other specialty additives (Karşal, 2008)

#### **2.1.1 Ethylene propylene diene rubber (EPM, EPDM)**

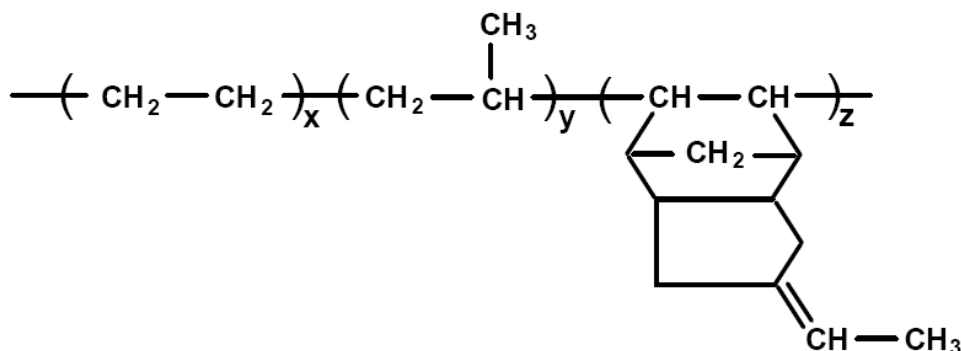
EPDM (Ethylene-Propylene Diene Monomer) contains ethylene, propylene and a third unsaturated monomer for vulcanization purpose. Ethylene content ranging from 40 to 80%wt EPDM is generally used for commercial purposes. As the ethylene content increases, the polymer crystallinity increases. Conversely, as the ethylene content decreases and the propylene content increases, the polymer becomes more amorphous. Therefore, 62 wt% or greater ethylene containing EPDM is classified as semicrystalline while EPDM containing less than 62% ethylene content classified as amorphous. Semicrystalline EPDM shows higher green strength, higher tensile modulus, and higher hardness compared with amorphous EPDM. However, amorphous EPDM is more flexible at low temperatures, lower in hardness and more elastic compared with semicrystalline EPDM. The third unsaturated monomer is typically conjugated diene allowing the use of sulfur vulcanization. As the diene content in EPDM increases, the cure rate increases (İnaler, 2007).

The copolymerization of ethylene and propylene yields useful copolymers, the crystallization of both polymers being prevented if the ethylene content is in the range 45-60%; grades with higher ethylene contents, 70-80%, can partially

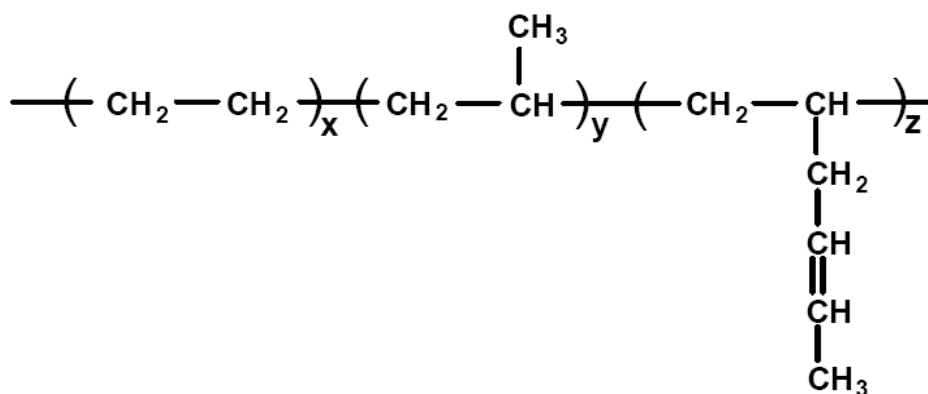
crystallize. The lower ethylene types are generally easier to process, and by increasing the ethylene content green strength and extrudability improves. One disadvantage of the copolymer is that it cannot be crosslinked with sulfur due to the absence of unsaturation in the main chain. To overcome this difficulty a third monomer with unsaturation is introduced, but to maintain the excellent stability of the main chain the unsaturation is made pendant to it. The three types of third monomer used commercially are dicyclopentadiene (Figure 2.1), ethylidene norbornene (Figure 2.2), and 1,4-hexadiene (Figure 2.3). Generally 4-5% of the termonomer will give acceptable cure characteristics, while 10% gives fast cures. Dicyclopentadiene gives the slowest cure rate and ethylidene norbornene the highest.



**Figure 2.1 :** Terpolymer: dicyclopentadiene (Kempermann *et al.*, 1993)



**Figure 2.2 :** Terpolymer: ethylidene norbornene (Kempermann *et al.*, 1993)



**Figure 2.3 :** Terpolymer: 1,4-hexadiene (Kempermann *et al.*, 1993)

Since the main chain of both EPM and EPDM rubbers is saturated, both co- and terpolymers exhibit excellent stability to oxygen, UV light, and are ozone resistant.

EPM and EPDM are not oil resistant, and are swollen by aliphatic and aromatic hydrocarbons, and halogenated solvents. They have excellent electrical properties and stability to radiation. Their densities are the lowest of the synthetics, and they are capable of accepting large quantities of filler and oil. They exhibit poor tack, and even if tackifiers are added, it still is not ideal for building operations. Adhesion to metal, fabrics and other materials, can be difficult to accomplish.

The copolymers can only be cured by peroxides or radiation, while the terpolymers can be cured with peroxides, sulfur systems, resin cures and radiation.

The dicyclopentadiene terpolymer can give higher states of cure with peroxides than the copolymer, although in peroxide curing of both the copolymer and terpolymer it is common practice to add a coagent, to increase the state of cure. Triaryl isocyanurate or sulfur are the most common coagents (Simpson, 2002a).

## **2.2 Fillers**

Fillers are incorporated into rubber matrices mainly to achieve improvement of properties (reinforcing fillers) or to reduce the material cost (diluent fillers). In some applications, special types of fillers are introduced to polymer matrices to achieve specific properties, such as lower degradability and chemical resistance. However, the performance of a filler is related with its characteristics, such as particle size, surface activity, degree of interactions with polymer matrix, chemical composition and degree of irregularity in the shape of fillers. Therefore, depending on the origin, processing conditions and chemical treatments, etc, different grades of fillers (with different properties) from same source are possible. There are a number of widely used commercial fillers, which have different grades with their different characteristics. Carbon black and silica are the classical examples (Siriwardena *et al.*, 2001).

The early nonblack fillers were mainly naturally occurring minerals or by-products of manufacturing such as clay, whiting, barytes. They were added to natural rubber to reduce tack, increase hardness, improve durability and reduce cost. The need for more reinforcing nonblack fillers in many rubber applications led to the introduction

between 1940 and 1960 of calcium carbonates, calcium silicates, hydrated silicas, and fumed silicas. These nonblack fillers are characterized by very small particle size. They are similar to the reinforcing carbon blacks. Today, the principles nonblack fillers are clays, calcium carbonates and silicas. Their consumption in the rubber industry is nearly 600,000 tons per year (Morton, 1987a)

### **2.2.1 Silica**

Silica fillers offered to the rubber industry are of three specific types;

- Ground mineral silica,
- Precipitated silica, and
- Fumed or pyrogenic silica.

#### **Ground Mineral Silica**

Ground silica, generally available below 47 $\mu$ m, is used as a cheap heat resistant filler for a variety of compounds. There is no effect on the rate or state of cure.

#### **Hydrated Precipitated Silica**

Silicon dioxide used as a filler for rubbers is known as silica. Its particle sizes are in the range of 10-40  $\mu$ m. The silica has a chemically bound water content of 25% with an additional level of 4-6% of adsorbed water. The surface of silica is strongly polar and the hydroxyl groups bound to the surface of the silica particles. In a similar way, other chemical groups can be adsorbed onto the filler surface. This adsorption strongly influences silica's behavior within rubber compounds. The groups found on the surface of silicas are principally siloxanes, silanol and reaction products of the various hydrous oxides. It is possible to modify the surface of the silica to improve its compatibility with a variety of rubbers. The reinforcement of the silicas is determined by the ultimate particle size, even though the particle are aggregated to some extent in the rubber (Morton, 1987a).

Silica fillers react with the rubber and this causes an increase in viscosity and dry and unmanageable processing behavior. To overcome these problems filler activators need to be added to silica-reinforced compounds. The usual filler activators used are diethylene glycol, polyethylene glycol (PEG) and amines such as triethanolamine. Some of these activators not only overcome the problems of processing and

accelerator absorption, but depending on the cure system used, will also act as vulcanization activators.

Other additives such as silanes, titanates and zirconates are also used to overcome the processing characteristics of silica fillers. Silanes not only give improved processability of silica-filled compounds, but also provide improved 'crosslinks' between the silica particle surface and the rubber. The use of silane coupling agents at a 2-5% level will improve the reinforcing performance of the silica to that of a similar size carbon black (Simpson, 2002b).

### **2.2.2 Carbon black**

Carbon blacks is second only to rubber as the most critical and widely used raw material of the rubber industry. The recognition of its outstanding ability to strengthen and reinforce to rubber about 1915. Carbon blacks are principally made by incomplete combustion of heavy petroleum products and small amounts from vegetable oils. Two classes predominate: the furnace blacks (95% of black usage) which are active, and thermal blacks (5% of usage) which are inactive. They have very fine particle size for rubber use. The size of the carbon black particle has a profound influence on its dispersion characteristics within a rubber matrix. This dispersion characteristic determines the final vulcanizate properties of the rubber compound. Very fine particle size are difficult to disperse adequately and when dispersion is achieved give a high reinforcement. Although large particle size blacks are easily completely dispersed, they do not give reinforcement. The structure of the black affects the processing properties of the rubber compound, but generally does not have great significance in the reinforcement (Babbitt, 1978).

### **2.2.3 Other fillers**

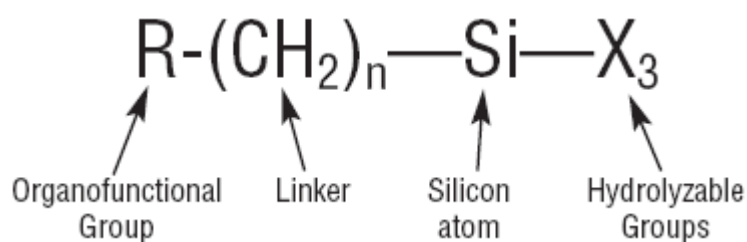
A specialized form of silica, fumed silica, is very highly reinforcing, and it is not easy to disperse in a typical rubber mix. It is used with silicone rubber. The other filler is ground calcium carbonate. The ground material is used as a low cost filler with no reinforcing properties. In its precipitated form it has some reinforcement. Another group of fillers are the clays which are naturally occurring hydrated aluminum silicates. The grades available are lower in cost than silica and reflect a

choice of reinforcement. The soft clays have some reinforcing properties and larger quantities (than hard clay), a few hundred phr (parts per hundred of rubber) can be added to a rubber compound. The hard clays give a distinctly improved level of reinforcement than the softer version. Hard clay can be calcined (heated to remove water) to produce a product with superior electrical (insulating) properties. Organic chemicals added as a surface treatment to the filler and they can improve some properties. Other fillers available are aluminum hydroxide, coal dust, lignin, silicates and talc (Kempermann *et al*, 1993).

## 2.3 Coupling Agents

### 2.3.1 Silane coupling agent

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Between dissimilar materials often involve at least one member which is siliceous or has surface chemistry with siliceous properties such as silicates, aluminates, borates, etc. Interfaces involving such materials have become a dynamic area of chemistry in which surfaces have been modified in order to generate desired heterogeneous environments or to incorporate the bulk properties of different phases into a uniform composite structure (Url-1). General formula of a silane coupling agent is given in Figure 2.4.



**Figure 2.4 :** The general formula for a silane coupling agent (Url-1)

Silane coupling agents improve properties of compounds containing silica and/or silicate fillers by forming chemical bonds across the filler and the rubber interface. They can also give improved properties with other materials, such as carbon blacks. They can be used with clays which do not form strong chemical bonds with the polymer. The improved compound properties result from a better compatibility and

linkage of the rubber and filler. The coupling agent can be added direct to the mixer with the filler, or may be purchased already in place on the intended filler.

The silane coupling agents which are generally used are bis-(3-triethoxysilylpropyl)tetrasulphane and 3-thio-cyanatopropyl triethoxy silane.

The effect of coupling agents on the physical properties of the compound is to:

- ❖ Reduce heat build-up under dynamic conditions,
- ❖ Reduce tan delta,
- ❖ Improve crosslink stability,
- ❖ Improve tear related characteristics,
- ❖ Improve resistance to swelling by water.

The addition of a coupling agent can dramatically improve the abrasion resistance of compounds containing silica reinforcement. The effect is dependent on the surface area of the silica (Ciesielski, 1999).

### **2.3.2 Titanate and zirconate coupling agents**

Organometallic titanate and zirconate coupling agents form monomolecular layers on most materials, such as metals, metal oxides, carbonates, sulphides, sulphates, siliceous materials, carbon black, some synthetic fibers, dispersed dyes and organic pigments. They give the substrate hydrophobic (moisture free), organophilic (rubber compatible and reactive), organofunctional (e.g., phosphato flame retardant functionality to provide controlled intumesence) and catalytically reactive with the polymer phase (Ciesielski, 1999).

## **2.4 Activators**

### **2.4.1 Zinc oxide and stearic acid**

Organic accelerators almost always need activators in order to exert their full effect on sulfur vulcanization. A considerable number of metal oxides are effective as activators. However zinc oxide is the most important representative of the group.

Nearly all recipes for rubber goods contain a percentage of this metal oxide (Keppermann *et al*, 1993)

Zinc oxide (ZnO) plays a multi-functional role in rubber technology. Its main use is as an activator of the sulfur crosslinking reaction. Zinc oxide has been used as a pigmentation ingredient where it is particularly effective in absorbing ultraviolet rays. It can also assist with reduction of mould shrinkage values (Simpson, 2002b).

Stearic acid is important in the rubber vulcanization process. It is believed that the stearic acid reacts with zinc-oxide or other metallic oxides during vulcanization to form a rubber soluble salt or soap. This product reacts with the accelerator and this reaction enables to show full effect of accelerator.

Generally stearic acid and zinc oxide are used together with sulfur and accelerator. Zinc oxide reacts with stearic acid to form zinc stearate and together with the accelerator they speed up the rate at which sulfur vulcanization occurs. With sulfur alone, the curing process might take hours. When zinc oxide and stearic acid are used, it can be reduced to minutes.

The addition of zinc stearate alone as replacement for stearic acid and zinc oxide does not produce the efficiency which the two materials are added separately. Zinc stearate is used by the rubber industry as a dusting agent because of its ability to dissolve into the rubber stock on the application of heat (Simpson, 2002b).

#### **2.4.2 Iron oxide**

Iron oxide is used for compounding silicone rubbers where it is used to improve heat stability. Iron oxide, mainly ferric oxide, also finds application as a pigment (Keppermann *et al*, 1993)

#### **2.4.3 Lead oxide**

Lead monoxide or litharge is mainly used as an accelerator activator, and acid acceptor, and is especially useful in water resistant compounding (Simpson, 2002b).



#### **2.4.4 Magnesium oxide**

Light magnesium oxide is used as an acid acceptor in the vulcanization of halogen containing rubbers; heavy magnesium oxide which has a larger particle size than the light grade, is less active as an acid acceptor (Morton, 1987).

#### **2.5 Process additives**

Rubbers are difficult to process at some stage during their manufacture. Some rubbers are tough materials which are difficult to mix with the compounding ingredients. Other rubbers have a great affinity to the metal of the mixer chamber and rotors and are difficult to remove after being compounded.

A process additive is an ingredient which is added in a small dosage to a rubber compound to influence the performance of the compound in factory processes, or to enhance physical properties by aiding filler dispersion.

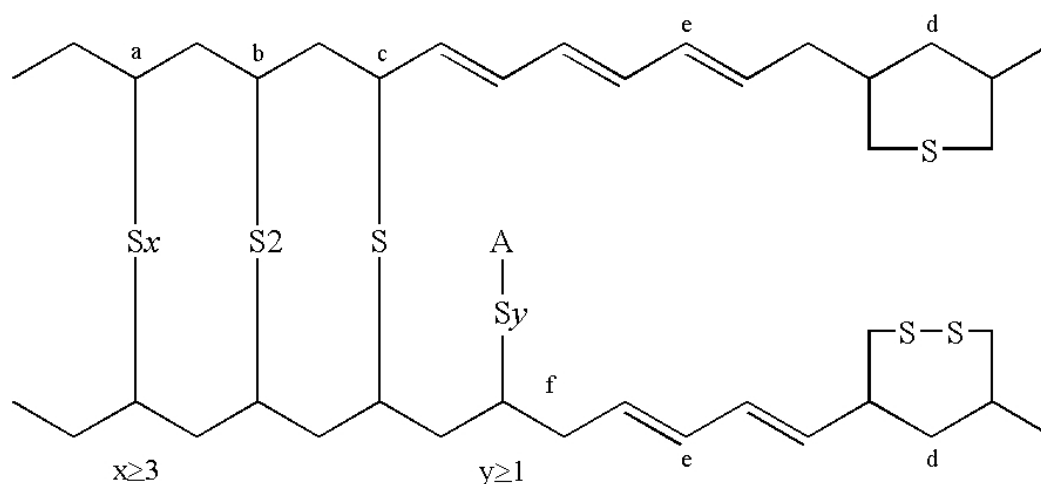
The process additive should ideally:

- ❖ Aid dispersion,
- ❖ Reduce polymer tense,
- ❖ Promote compound flow characteristics,
- ❖ Act at a low dosage level,
- ❖ Not adversely affect the finished product,
- ❖ Reduce power consumption.

#### **2.6 Vulcanizing Agents**

##### **2.6.1 Sulfur**

Sulfur is the most widely used vulcanizing agent in conjunction with activators and organic accelerators. It is a very complex reaction and involves activators for the breakage of the sulfur ring ( $S_8$ ). Sulfur intermediates facilitate sulfur-to-double bond crosslinking as shown in Figure 2.5. Sulfur donors are used to replace part or all of the elemental sulfur to improve thermal and oxidative aging resistance (Morton, 1987 and Karşal, 2008).

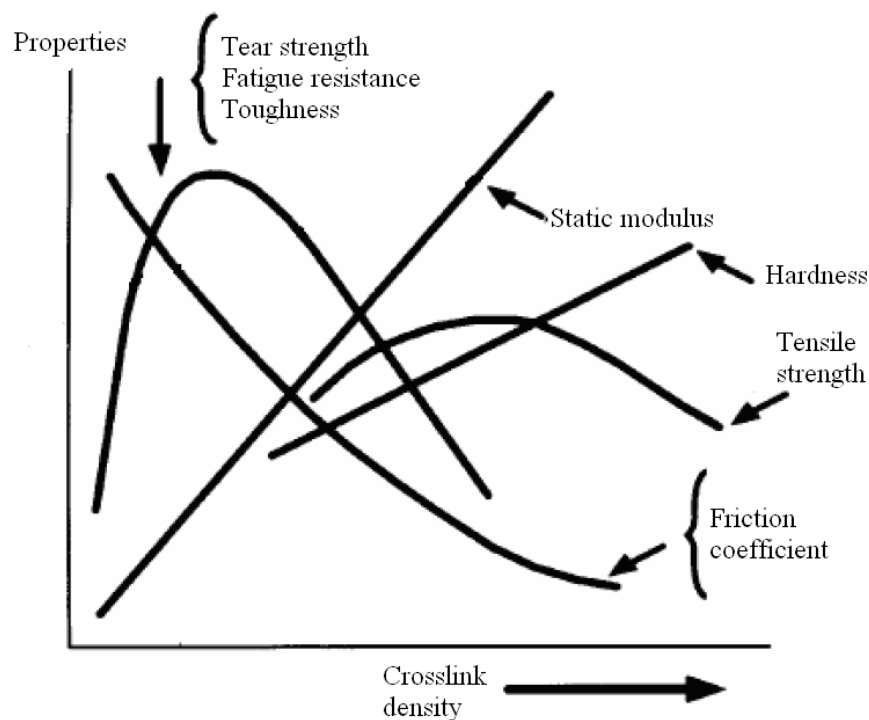


**Figure 2.5 :** Structural features of a vulcanized rubber (Morton, 1987)

There are two basic crystallisation forms for sulfur - monoclinic and rhombic. Rhombic is the most stable form up to 96 °C; the other types revert to this stable form at a rate dependent upon temperature. When sulfur solidifies from the molten state (melting point 114 °C) the crystalline form which occurs is monoclinic. Below 96 °C, the monoclinic form becomes metastable and changes into the rhombic form.

If the level of sulfur in a compound is higher than that necessary for the required degree of crosslinking, bloom problems will be occurred. When the temperature rises during compound mixing, the sulfur becomes soluble within the rubber. Sulfur dissolves into the rubber in excess of its solubility level (i.e., a super saturated solution) at an elevated temperature but it will form an unwanted bloom on the rubber compound surface at ambient temperatures. The rate of crystallization of the excess sulfur from the super saturated solution will depend on the rubber type (Simpson, 2002b).

After vulcanization properties of the rubber compounds change according to crosslink density as shown in Figure 2.6.



**Figure 2.6 :** Properties after vulcanization (Morton, 1987)

### 2.6.2 Peroxide

Only a limited number of peroxides are suitable for crosslinking purposes. The most suitable are those which form radicals through homolytic decomposition. These radicals are so aggressive that they can split hydrogen atoms from the polymer chain. They can produce stable peroxide decomposition products and polymer radicals. These polymer radicals can be recombined, producing stable C-C crosslink bonds.

Crosslinking systems based on peroxides are usually simple. Unlike with sulfur vulcanization systems, the addition of ZnO and stearic acid is not necessary. Thus crosslinking is achieved simply using a crosslinking peroxide (Babbitt, 1978).

### 2.7 Accelerators

The accelerators are usually organic materials, and they speed up the rate of vulcanization. There are many accelerators available and they can be classified into several chemical classes. Some of them have a built in delay time. So when heat is applied to the compound, at the beginning of the curing process no vulcanization takes place for a specified initial period of time. They are appropriately called delayed action accelerators, An example would be the sulfenamides. This delay is

highly beneficial if a compound takes a long time to completely fill a cavity in a heated mold (Simpson, 2002b).

Some accelerators are able to provide sulfur from their own chemical structure. Thus the need for elemental sulfur might be reduced or eliminated in the recipe. They are called sulfur donors (for example tetramethylthiuram disulfide (TMTD)).

The amount of accelerator is determined according to the type of elastomer. For example EPDM which has few double bonds, needs 'faster' curing accelerators to permit a reasonable state of cure.

The table 2.1 is a summary of some typical chemical classes of accelerators available.

**Table 2.1 : Typical accelerators**

<b>Dithiocarbamates</b>	Example: Zinc dibutyl dithiocarbamate (ZDBC).  Very scorchy and very fast curing. Useful in low temperature (down to 100 °C) vulcanization and in elastomers with low levels of unsaturation such as EPDM.
<b>Thiurams</b>	Example: Tetramethylthiuram disulfide (TMTD).  Somewhat less scorchy than dithiocarbamates and fast curing. TMTD is less scorchy in the absence of sulfur.
<b>Thiazoles</b>	Example: Mercaptobenzothiazole (MBT).  Moderate cure rate and scorch giving a low modulus vulcanizate.
<b>Guanidines</b>	Example: Diphenyl guanidine (DPG).  Scorchy and slow curing. Most often used in combination with other accelerators.
<b>Sulfenamides</b>	Example: N-cyclohexyl-2-benzothiazol sulfenamide (CBS).  Long scorch with medium to fast cure.

## **2.8 Other Ingredients**

### **2.8.1 Antioxidants**

The term antioxidants refer only to products that inhibit the effects of oxygen. Antioxidants are used to protect rubbers from the effects of thermal oxidation. Peroxide vulcanizates are usually protected with dihydroquinolines. Other antioxidants react with the peroxide inhibiting the crosslinking reaction (Keppermann *et al.*, 1993).

### **2.8.2 Antiozonants**

Ozone attack on rubbers takes the form of cracking which takes place perpendicular to the direction of the strain. Ozone attack occurs mainly at the olefinic double bond of a diene rubber. If they do not protected against ozone, the result will be loss of physical integrity for thin sectioned articles and surface cracking on larger mass products. Too high a dosage of antiozonant can result in the formation of unsightly blooms on the rubber surface. Too little antiozonant can lead to worse attack than when none is present (Simpson, 2002b).

### **2.8.3 Plasticizers**

Oils and other slippery materials are called plasticizers. ASTM D 1566 defines them as ‘a compounding material used to enhance the deformability of a polymeric material’. Their function at low levels is to aid in the dispersion of fillers. At higher amounts they reduce uncured compound viscosity, lower compound cost, reduce vulcanizate stiffness and in some cases improve low temperature flexibility. They also improve flow in extrusion and molding by making the uncured compound less elastic and reducing viscosity and friction. Petroleum oils are one of the major sources of plasticizers. These oils are divided into three chemical categories, aromatic, naphthenic and paraffinic (Ciesielski, 1999).

### **2.8.4 Pigments**

A relatively small proportion of colored rubber products are produced. When colored products are produced, white fillers are used. These are a good base white

pigmentation as a foundation for the color of the product. Correct color matching is very hard in rubber industry. Matching the color of the unvulcanized compound to a given standard color may not be sufficient. Pigments change color to a minor or major extent when subjected to heat and to protective and vulcanization ingredients in the compound (Morton, 1987).

#### **2.8.5 Antistatic agents**

The production of light colored products with a requirement for low build-up of static electricity requires the addition of an ingredient which is capable of providing the rubber with a low electrical resistance (Simpson, 2002b).

#### **2.8.6 Fire retardants**

The majority of rubbers support combustion. The by-products of the combustion can be lethal. In order to improve the resistance of the rubbers which support combustion, a number of products may be added to the rubber compound. These may be inorganic or organic in nature (Ciesielski, 1999).

#### **2.8.7 Pre vulcanization inhibitors**

Sulfur vulcanization of rubber is catalyzed by the presence of alkali materials. This activation of the vulcanization system can result in unwanted short scorch times. The addition of weak acids to the rubber compound results in retardation of the crosslinking mechanism (Ciesielski, 1999).

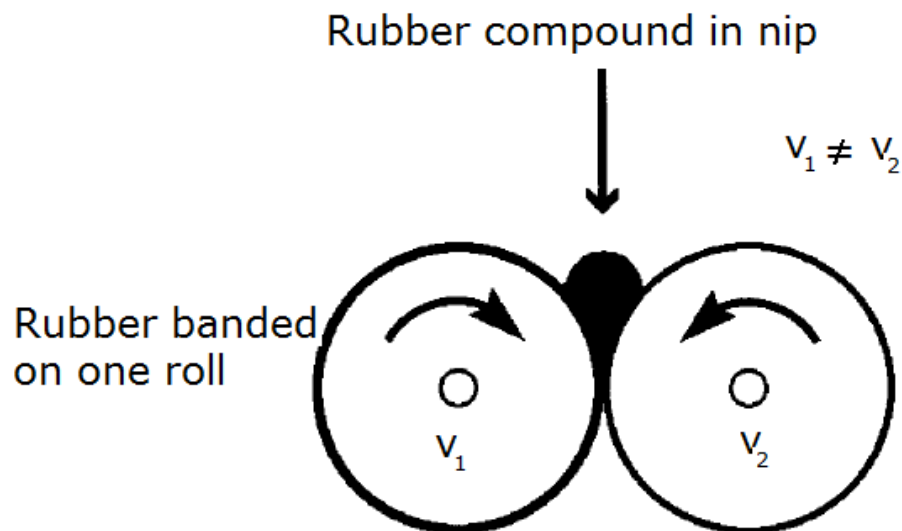
### 3. PRODUCTION METHODS

Ingredients in the rubber recipe are generally bags of powders, drums of liquids and bales or granules of raw gum elastomer. They are weighed out precisely and this should be done for every batch. Some machines such as open mill, internal mixer or extruder are necessary to mix these chemicals and finally solid homogeneous mixture are obtained after blending.

#### 3.1 Open Mill

The open mills have been used since at the beginning of the rubber industry and they are still an essential machinery of rubber processing equipment.

An open mill consists of two horizontally placed hollow metal cylinders rotating towards each other (see Figure 3.1). The distance between the cylinders can be varied, typically between 0.25 to 2.0 cm (Ciesielski, 1999). This gap between the rolls is called a nip.



**Figure 3.1 :** Conceptual view of rubber mill rolls (Ciesielski, 1999)

## ***Operation***

Raw gum elastomer is placed into the gap between the two mill rolls (the mill nip). Then it bands, as a continuous sheet, onto one of the rolls. The speeds of the two rolls are different and generally the back roll rotates faster than the front. The difference in speed between the two rolls is called the friction ratio and allows a shearing action (friction) at the nip to disperse the ingredients and to force the compound to stay on one roll, preferably the front one. A friction ratio of 1.25:1 is common. Powders, liquids, etc., are then added to the nip in a specific way. The process produces friction which creates heat. This excess heat needs to be removed. It can be achieved by spraying or flooding the inside of the roll with cooling water or by passing water through drilled channels in the wall of the roll.

A device is necessary to prevent the rubber from moving past the end of the rollers. This is accomplished by a piece of metal called a guide. It is positioned at each end of the roll and it almost touch the surface. At the beginning of the mixing process, pieces of material tend to fall off the mill rolls. Thus a tray (mill pan) is used to catch them. After this the compound swept up and returns to the rolls. When all the ingredients are completely blended and dispersed, rotating knives can be automatically applied to the rubber covered roll to take off one continuous sheet. Alternatively the operator can use a hand-held mill knife and take off individual sheets.

A knowledge of safety procedures is critical to a mill operator. Older production mills have a wire string or bar above the operator, while other mills have the bar in front of the mill person. When the bar is pushed, or the string pulled, roll rotation quickly stops. Safety standards stipulate the maximum permissible rotation of the roll after the bar or wire is activated. Some mills will throw the rolls into reverse (Barlow, 1993).

## **3.2 Internal Mixing Machines**

Internal mixer's rolls are twisted to produce a corkscrew effect. Moreover a block of steel is placed over the mill nip which is called a ram. When the ram moves up, mixer allows addition of ingredients to the nip. When addition is finished, it moves down to force the compound ingredients into the nip.

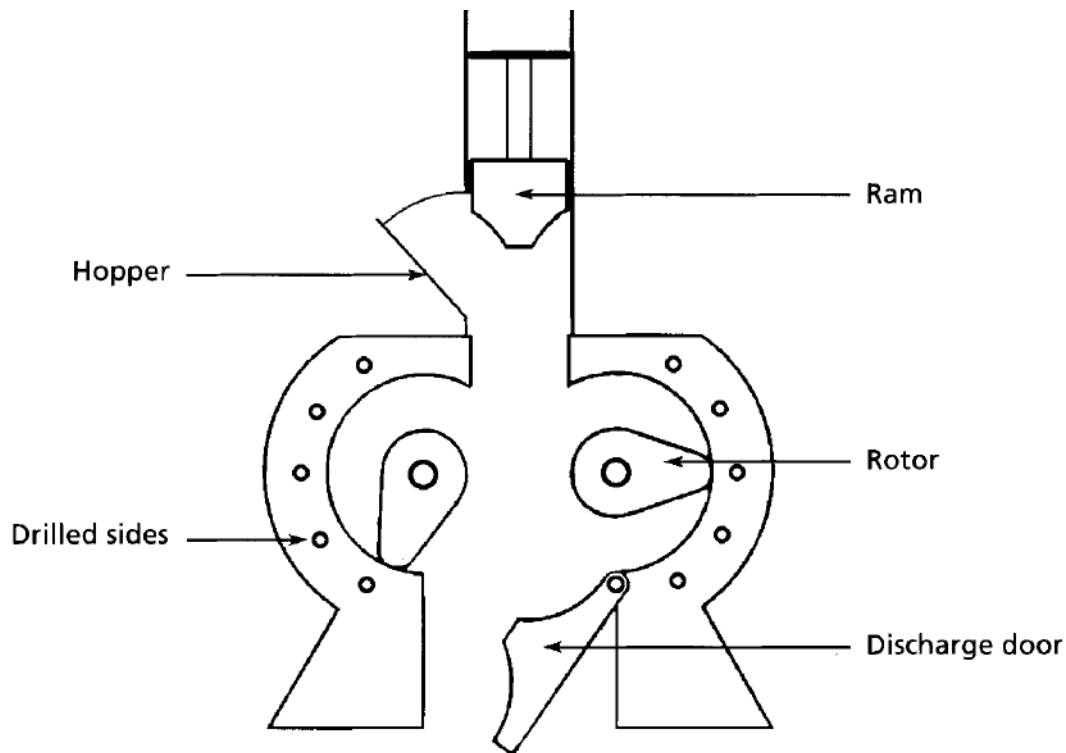


## ***Operation***

In 1916 Mr. Fernley H. Banbury improved on an internal mixing machine. It was built by Werner & Pfleiderer by designing the Banbury mixer. The Banbury mixer had modified rotors and the addition of a floating weight (Figure 3.2). The internal mixer rapidly became an essential part of the rubber industry. Nowadays mixers are available in sizes ranging from those capable of mixing a kg to more than 500 kg per load. The internal mixer is faster, cleaner, (produces less dust from powdery materials such as carbon black, silica and clay), can use less floor space, and is probably less operator sensitive. Thus it has displaced the mill for most compounding operations. However, the variable nip opening on a mill and furthermore immediate visual feedback during mixing, allows mill operator a high degree of control and consequently dispersion.

The internal mixer has a fast mixing capability, from around two to ten minutes, and thus requires an efficient cooling system. This is provided by drilled channels in the walls of the mixing chamber, through which water passes to control the mix temperature. The rotors and discharge door can also be water cooled. The temperature of the compound is measured by a thermocouple in the side of the mixing chamber. Other parameters which can be measured and controlled during the mixing process are electrical power (amperage or watts) and time.

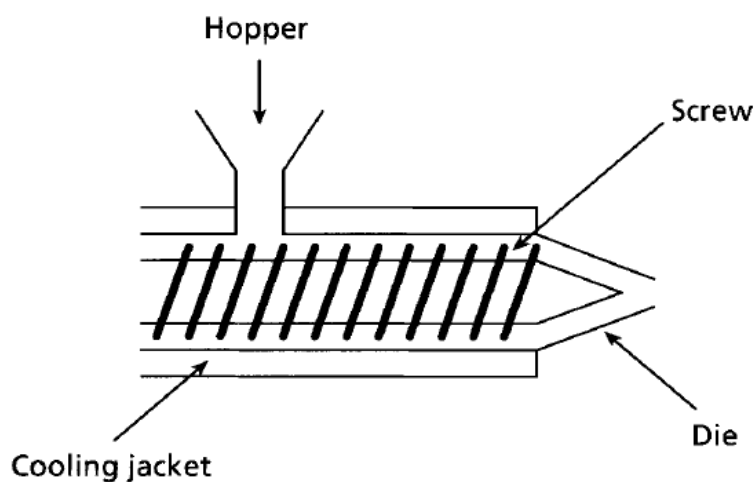
Raw gum elastomer is dropped through the hopper into the mixing chamber where it is mixed by the rotors. The ram which presses on to the rubber mixture, is forced down by a pneumatically or hydraulically controlled cylinder. Oil may be poured in from the hopper, or injected through a valve in the hopper wall just above the mixing chamber. Mixing can occur between the rotors (intermeshing rotors) or between the mixing chamber walls and the rotors (tangential rotors) depending on the machine. To correct mixing gap of rotor to rotor or gap of rotor to wall is very important. Recent modifications are the Banbury ST rotors (synchronous technology) and Pomini's VIC (variable intermeshing clearance) design where the distance between the rotors can be varied. Recently many researchers study new rotor design using finite element analysis techniques. The mixed rubber can be discharged from the machine, either by rotation of the whole mixing chamber or through a discharge door at the bottom of the mixer.



**Figure 3.2 :** Conceptual cross-section through an internal mixing machine, with tangential rotors (Ciesielski, 1999)

### 3.3 Extruders

Extruders (Figure 3.3) can be considered as a pump which consists of a screw to move the material forwards and a barrel around the screw. Screw and barrel help the material to move and provide the temperature control. They have one or more hopper to put rubber into the screw, and the front end has a die through which the rubber extrudes.



**Figure 3.3 :** Conceptual view of a basic extruder (Ciesielski, 1999)

A problem with traditional extruders is the potential for reduced blending of material as it moves along the screw. This causes uneven temperature distribution in the extrudate, which enable to a variable viscosity and therefore a continuously changing die swell. Layers of compound move along without intermingling, i.e., in laminar flow.

In the 1970s a relatively recent idea was introduced. It is to introduce pins protruding from the inside of the barrel towards the screw. This breaks up the layers and enable to mix them, reduce thermal variation and increase homogenization. Such a machine is known as a pin barrel extruder.

An alternative concept is to introduce small bowl shaped cavities into the end section of the screw and the inside of the barrel. This creates turbulent flow in the cavities and therefore increased physical and thermal blending. Such an arrangement would be added onto the end of a standard extruder and is called a cavity transfer mixer (Rodgers, 2004).

Commonly used continuous screw extruders can be classified in two groups: Single screw and twin screw extruders. The former is the most basic form of extruder that simply melts and forms the material. In addition to this, twin screw extruders are more flexible due to their modular design of screw and barrel and they have better feeding, melting, mixing and degassing properties compared to single screw extruders. Twin screw extruders are used extensively in polymer blending and also in many applications such as processing of food, essential oils, paints, and many other highly viscous materials. They provide high shear rate and good mixing of compounding materials at a relatively short residence time (İşlier, 2008).



#### 4. SILICA – SILANE INTERACTION

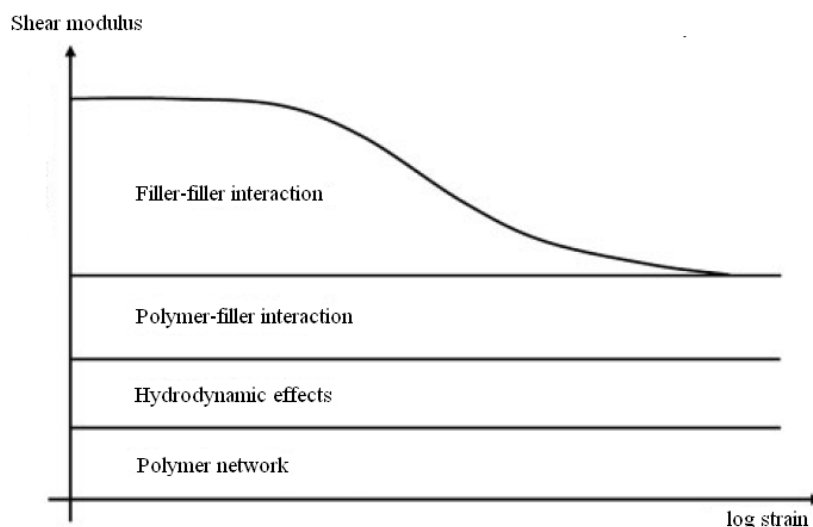
Filled rubbers are used in a wide range of applications especially the most important area is automotive tires industry, where performance characteristics are strongly affected by fillers properties, particle-particle and rubber-filler interactions (Ramier *et al.*, 2006).

Alongside carbon black, silica is one of the most important reinforcing fillers for rubber compounds. Silica as filler in rubber compounds leads to dynamic material properties that cannot be obtained by the use of carbon black. Its application area is in rubber compounds for the tire industry and for technical rubber parts. The improved material properties like a lower rolling resistance and excellent wet grip are of a particular importance for those high-end technical applications. However, the untreated silica particles feature high filler-filler interactions and tend to build agglomerates with strong internal bonding forces. The polymer-filler interaction is small and the reinforcing effect is limited when compared to the filler-filler interaction. The improvement of the dynamic properties can only be achieved through the addition of the coupling agent silane to the rubber compound. The silane bonds to the silica which is called silanisation reaction and chemically modifies the surface of the silica particles. Due to the reaction of the silica and the silane, the filler-filler interaction of the silica particles decreases and the interaction of the silica and a nonpolar rubber polymer increases. A better dispersion of the additives and therefore better material properties can be achieved. The silanisation reaction is a condensation reaction under the formation of ethanol. By extracting the developing ethanol from the compound, the silanisation efficiency and consequently the material properties can be improved. There is no possibility to efficiently remove the condensates from the compound in the internal mixer due to be a closed system. In comparison, the twin screw extruder with its modular set-up and it has vacuum port and degassing can be easily achieved in TSE (Haberstroh and Köppen, 2008).

## 4.1 Silanisation Reaction

Silica alone is building up a strong filler network and shows a limited interaction with the polymer. But if a bifunctional silane is used chemical linkages between silica surface and the polymer are formed. In the case of carbon black linkages between the surface and polymer chains are formed only by physical adsorption. In the past as well as in the present molecular slippages along the carbon black surface as well as adsorption and desorption mechanisms are still under discussion (Fröhlich *et al.*, 2004)).

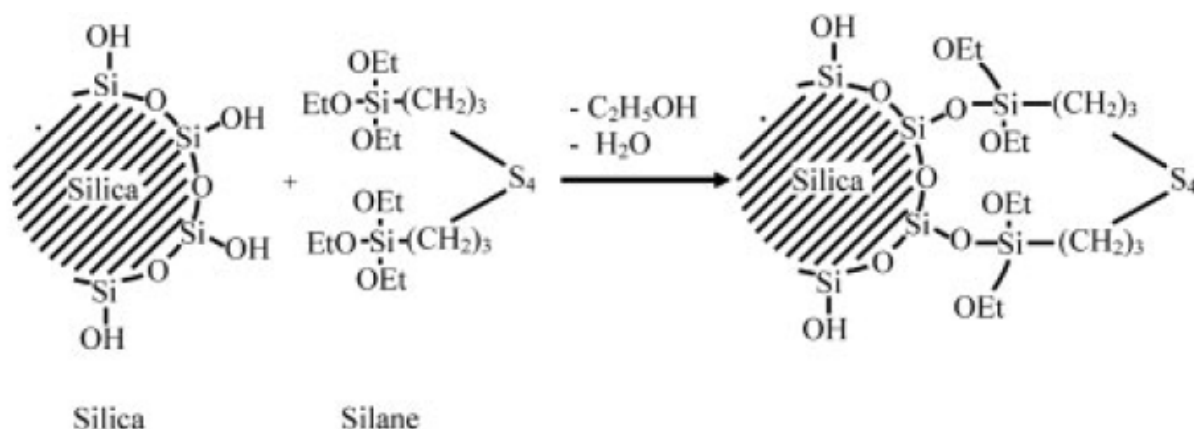
The polymer-filler interaction influences the material properties, e.g. abrasion resistance, tensile strength and tear resistance. In addition, the filler-filler network that is built in the rubber has an impact on the dynamic material properties. It is known that with increasing strain amplitude applied to the filled rubber, the storage modulus decreases. The storage modulus is composed of different strain-dependent and strain-independent contributions as can be seen in Figure 4.1. The strain-independent contributions are the polymer-filler interaction, the polymer-network contribution and hydrodynamic effects. The filler-filler interaction causes the strain-dependent behavior of the storage modulus. With increasing strain, the filler network breaks down and causes the storage modulus to decrease. The phenomenon of the strain-dependence of the storage modulus is called Payne effect. Untreated silica particles have a higher filler-filler interaction and accordingly, they show a higher Payne effect compared to carbon black filled compounds (Haberstroh and Köppen, 2008).



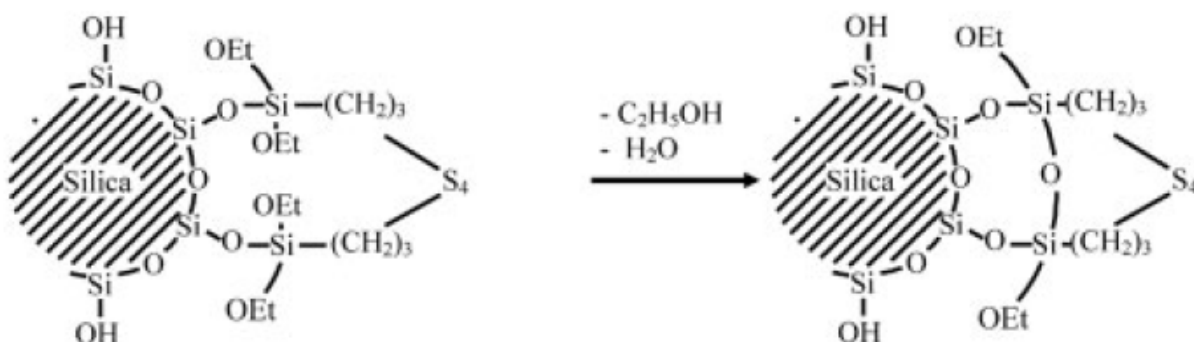
**Figure 4.1 :** Payne effect (Haberstroh and Köppen, 2008)

The dynamic material properties of silica filled rubber compounds can be improved by decreasing the filler-filler interaction. Untreated silica with its high filler-filler and low polymer-filler interaction needs the coupling agent silane to reach this requirement. In the silanisation reaction, the silane reacts with the silica, forms a hydrophobic shell around the silica particles and decreases the filler-filler interaction.

A two step-reaction model suggested for the silanisation reaction. In the primary step, the alkoxy groups of the silane react with the silanol groups of the silica particle (Figure 4.2). In the secondary step, the adjacent alkoxy groups of the silane react with each other (Figure 4.3). Both steps take place under the formation of ethanol and water. The reinforcing effect of the silica particles is further improved by the use of bifunctional silanes with sulfur groups that can react with unsaturated polymers during the vulcanization of the compound (Hunsche *et al.*, 1997).



**Figure 4.2 :** Silanisation reaction – primary reaction (Hunsche *et al.*, 1997)



**Figure 4.3 :** Silanisation reaction – secondary reaction (Hunsche *et al.*, 1997)

Because the filler-filler interaction is decreased during the silanisation reaction, the analysis of the Payne effect is a means to evaluate the silanisation efficiency of the

process. With increasing silanisation grades, the Payne effect decreases due to the decreasing filler-filler interaction of the silica (Haberstroh and Köppen, 2008).

#### **4.1.1 Discontinuous compounding in an internal mixer**

The internal mixer is the conventionally used compounding system for the production of rubber compounds. On the one hand, high temperatures of the compound have to be realized to conduct the silanisation reaction with an acceptable reaction rate. On the other hand, the curing system has to be added at lower temperatures to prevent scorch. Therefore, complex mixing procedures with up to three mixing stages are applied to produce silica filled rubber compounds. In the first stage, the rubber, silica, silane and the chemicals are added to the internal mixer. Those ingredients are then mixed at high temperatures. A precise temperature control has to be realized in this mixing stage. Low temperatures result in low silanisation rates and thus in long mixing times. However, high temperatures result in scorch due to the reaction of the sulfur groups of the silane with the rubber. During the mixing process, the temperature of the compound increases steadily. To prevent scorch, the mixing process has to be interrupted. A second mixing stage has to be applied to obtain high silanisation grades.

In this second stage, the compound is mixed again at high temperatures. This leads to a higher silanisation rate and homogenization of the material. In the third mixing stage, the curing system is added to the internal mixer. The compound is then mixed at low temperatures to prevent scorch. The removal of the ethanol that is formed during the silanisation reaction is challenging for rubber compounded in the internal mixer. The mixing with an open ram allows the degassing of the condensates. Lower fill factors than those used for mixing procedures with a closed ram result in the highest silanisation grades. However, the throughput is decreased due to those lower fill factors. Another possibility to degas the compound is the air injection into the internal mixer. A current of air is blown through the mixing chamber and drags the ethanol out of the internal mixer.

A further technical improvement is the tandem mixer, consisting of an upper mixer with a ram and a lower mixer without a ram. In the upper mixer, the compound filled with silica is produced under conventional conditions at high temperatures. In the lower mixer, which is directly connected to the upper mixer by a duct, the curing



agents are added to the compound at low temperatures (Haberstroh and Köppen, 2008).

#### **4.1.2 Continuous compounding in a twin screw extruder**

The continuous compounding in a twin screw extruder is used to compound thermoplastics. The standard system for the compounding of thermoplastics is the co-rotating twin screw extruder because of its open duct in axial direction, the high mixing efficiency and a high shear deformation of the melt. Different screw elements e.g. kneading blocks, mixing and conveying elements, define the dispersive and distributive mixing of the thermoplastics. Both, the barrel and the screws of the twin screw extruder have a modular configuration. The dosage of the material to the twin screw extruder is continuous and fully automated.

In a twin screw extruder, the barrel temperature, the screw speed can be easily varied. Furthermore, the configuration of the screw, the set-up of the barrel and the position of the feeding influence the resulting compound properties. The mass temperature is mainly influenced by the shear deformation of the melt depending on the screw configuration, but also by the barrel temperature. Temperature controlling is very important point for the silanisation reaction. To achieve silanisation reaction the temperature should be between 130-160°C. Below 130°C require inadequately long mixing cycles and above 160°C sulfur may split off and react with the rubber, causing a prescorch. In the internal mixer temperature controlling is very difficult and dropped compound's temperature fluctuates. However in an extruder temperature controlling is superior than internal mixer and temperatures for the silanisation reaction are set easily (Rodgers, 2004).

#### **4.1.3 Continuous compounding of silica/silane compounds**

The condensates produced during the silanisation reaction can easily be degassed because the twin screw extruder has a vacuum port. The material dosage and the extruder configuration are usually tailored to the specific compounding task also entails a major disadvantage. The change of compound recipes, which normally includes the alteration of the dosage system, the barrel and the screw configuration, is time consuming. Therefore, the continuous compounding in a twin screw extruder

is only suitable for the production of large compound quantities, e.g. in the tire industry.

Because of the specified advantages and above all because of its high degassing efficiency, the presented research project focuses on the twin screw extruder as an alternative compounding system to produce silica filled rubber. The high degassing efficiency of the twin screw extruder promises higher silanisation grades and therefore better material properties (Haberstroh and Köppen, 2008).

## **5. EXPERIMENTAL WORK**

### **5.1 Materials**

In this work ethylene propylene diene rubber (EPDM) was used as base elastomer matrix, grade Dutral Ter 4436. EPDM had ethylene content of 66.5%, propylene content of 28%, oil content of 40%, and ENB content of 5.5%. It was supplied from Polimeri Europa, Italy.

Silica which was used as a filler, grade is Egesil BM30, specific surface area  $175\text{m}^2/\text{g}$ . Zinc oxide (ZnO) and stearic acid (St. acid) were used as activators. They were supplied from Ege Kimya, Turkey.

Bis[3-(triethoxysilyl) propyl] tetrasulfide was used a coupling agent and it was trade name of Si69. Polyethylene glycol 4000 (PEG 4000) was used as a process aid. Sulfur was used a vulcanizing agent, MBT (mercaptobenzotiazol), TMTD (tetramethyl thiuram disulfide), ZDBC (Zinc dibutyl dithiocarbamate) were used as accelerators. They were supplied from RDC Chemical, Italy.

### **5.2 Compounding Recipes**

Nine different recipes were prepared to investigate the effect of silane coupling agent, the effect of polyethylene glycol, and the synergistic action of silane and polyethylene glycol. The recipes were given in Table 5.1.

**Table 5.1 : Recipes of experimental works**

	<i>SP00</i> (phr)	<i>SP10</i> (phr)	<i>SP80</i> (phr)	<i>SP140</i> (phr)	<i>SP02</i> (phr)	<i>SP04</i> (phr)	<i>SP06</i> (phr)	<i>SP14</i> (phr)	<i>SP84</i> (phr)	<i>Unr.*</i> (phr)
EPDM***	170**	170	170	170	170	170	170	170	170	170
Silica	50	50	50	50	50	50	50	50	50	0
ZnO	5	5	5	5	5	5	5	5	5	5
St. acid	1	1	1	1	1	1	1	1	1	1
Silane	0	1	8	14	0	0	0	1	8	0
PEG	0	0	0	0	2	4	6	4	4	0
MBT	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZDBC	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
TMTD	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
S	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

\* Unreinforced recipe

\*\* phr: parts per hundred of rubber

\*\*\* Dutral Ter 4436 is a oil extended grade (100 phr EPDM + 70 phr oil = 170 phr).

In addition to nine recipes with silica one unreinforced recipe was prepared in the open mill for the comparison with other results.

### 5.3 Manufacturing Process

In this thesis, nine different recipes were prepared with open mill operation, banbury-open mill sequentially operation (named as banbury operation) and twin screw extruder-open mill sequentially operation (named as extruder operation).

#### 5.3.1 Open mill operation

The open mill was Met-Gür MG/H-300 (see Figure 5.1), with 300 mm rotor diameter and 800 mm rotor length. The front rotor of the mill was rotating with 12,8 rpm and the back rotor of the mill was rotating with 14,7 rpm (Friction ratio is 1.15).



**Figure 5.1 :** Met-Gür MG/H-300 open mill

In this work, all nine recipes were prepared by open mill. Open mill was also used after banbury and twin screw extruder process to add PEG, zinc oxide, stearic acid, accelerators and sulfur.

##### 5.3.1.1 Compounding of the rubber by open mill

All ingredients were introduced in the open mill. The maximum temperature of the compounds was between 55 to 60 °C. Mixing cycles of open mill operation is given in Table 5.2.

**Table 5.2 : Mixing cycles of open mill operation**

Mixing Steps	Time (min)
Added EPDM and band on the front roll. Cut and folded it back on itself three times.	4
Added silica. Cut from each side and folded it back on itself three times.	5
Added silane. Cut from each side and folded it back on itself three times.	2
Added PEG. Cut from each side and folded it back on itself three times.	2
Added ZnO and stearic acid. Cut from each side and folded it back on itself three times.	2
Added sulfur and accelerator. Cut from each side and folded it back on itself three times.	2
Total time	17

Unreinforced recipe was also prepared with open mill. Mixing cycle is given in Table 5.3.

**Table 5.3 : Mixing cycles of unreinforced recipe**

Mixing Steps	Time (min)
Added EPDM and band on the front roll. Cut and folded it back on itself three times.	4
Added ZnO and stearic acid. Cut from each side and folded it back on itself three times.	2
Added sulfur and accelerator. Cut from each side and folded it back on itself three times.	2
Total time	8

### 5.3.2 Banbury

The banbury was Met-Gür MG-15 (see Figure 5.2), with 15 L. The fill factor was selected 0.85 and it was constant for every recipes.



**Figure 5.2 :** Met-Gür MG-15 banbury

#### 5.3.2.1 Compounding of the rubber by banbury

In the first stage of the banbury operation EPDM, silica and silane were mixed in banbury. The dump temperature was between 100 to 110 °C. After this, the other ingredients were introduced in the open mill. The maximum temperature which was reached in the open mill, was 55-60°C Mixing cycles of banbury operation is given in Table 5.4.

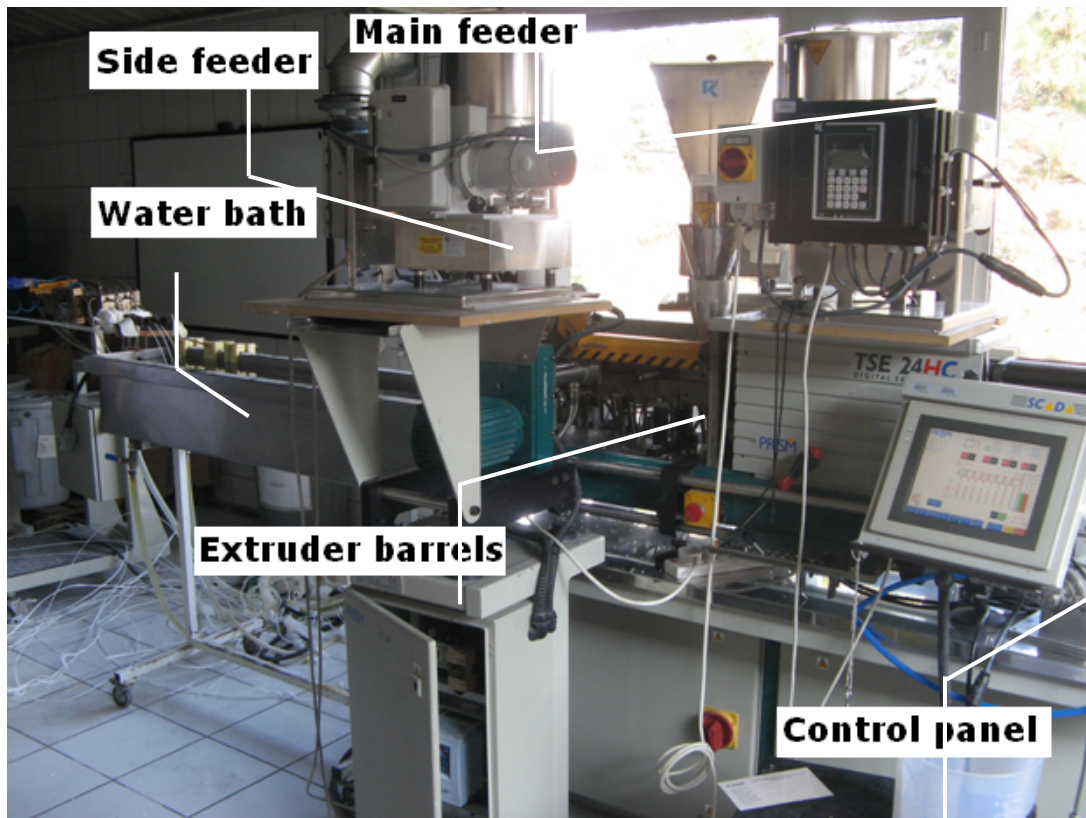
**Table 5.4 : Mixing cycles of banbury operation**

Mixing Steps	Time (min)
Added EPDM into banbury	3
Added silica and silane into banbury	3,5
Dump	-
Added into open mill	0,5
Added PEG. Cut from each side and folded it back on itself three times	2
Added ZnO and stearic acid. Cut from each side and folded it back on itself three times	2
Added sulfur and accelerator. Cut from each side and folded it back on itself three times	2
Total time	13

### 5.3.3 Twin screw extruder

In this work, an intermeshing co-rotating twin screw extruder was used to prepare rubber. The modular twin screw extruder used was PRISM TSE 24 HC (see Figure 5.3), with 24 mm screw diameter (D) and 28:1 L/D ratio (shaft length over screw diameter). Some useful properties according to product specifications were given in Table 5.5.





**Figure 5.3 : Prism TSE 24 HC 28:1 extruder**

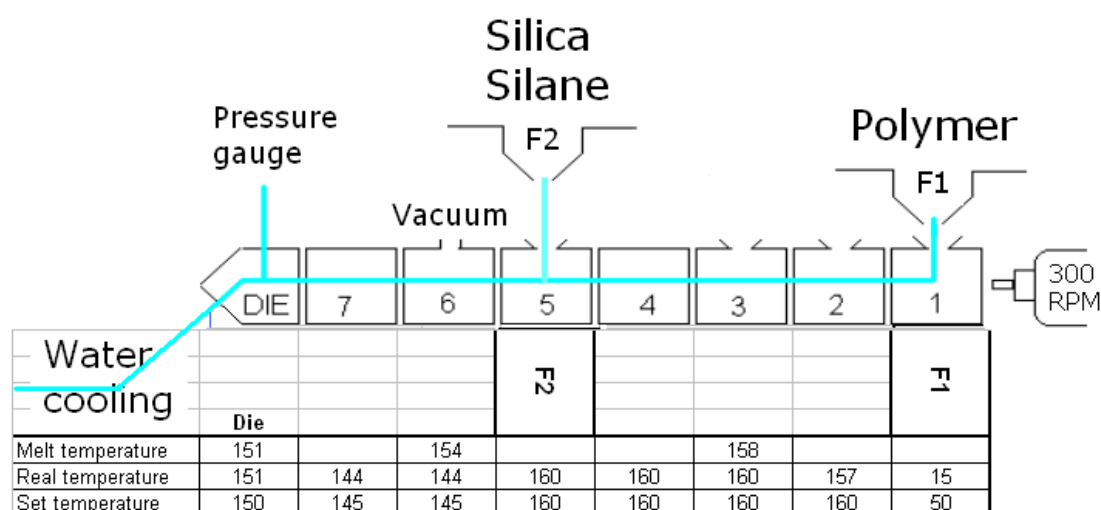
**Table 5.5 : Technical specifications of Prism TSE 24 HC 28:1 extruder**

<b>PRISM TSE 24 HC 28:1</b>	<b>Units</b>	<b>Values</b>
Barrel bore diameter	mm	24
Screw diameter	mm	23.6
Channel depth	mm	5.15
Max. screw speed	rpm	1000
Power at max. screw speed	kW	9.0
Max. torque/shaft	Nm	43
Barrel zones	Qty.	7
Extruder dimensions (L x W x H)	cm	165 x 60 x 135

Prism TSE 24 HC extruder had 7 modular barrel segments, each were heat controlled and had a length of 4D. Barrel profiles were illustrated in Figure 5.4. Set temperatures were controlled by electrical resistances and water cooling channels, the 3rd, 5th, and 7th barrels had thermocouples mounted to measure the melt temperature of the mixture inside the barrels.

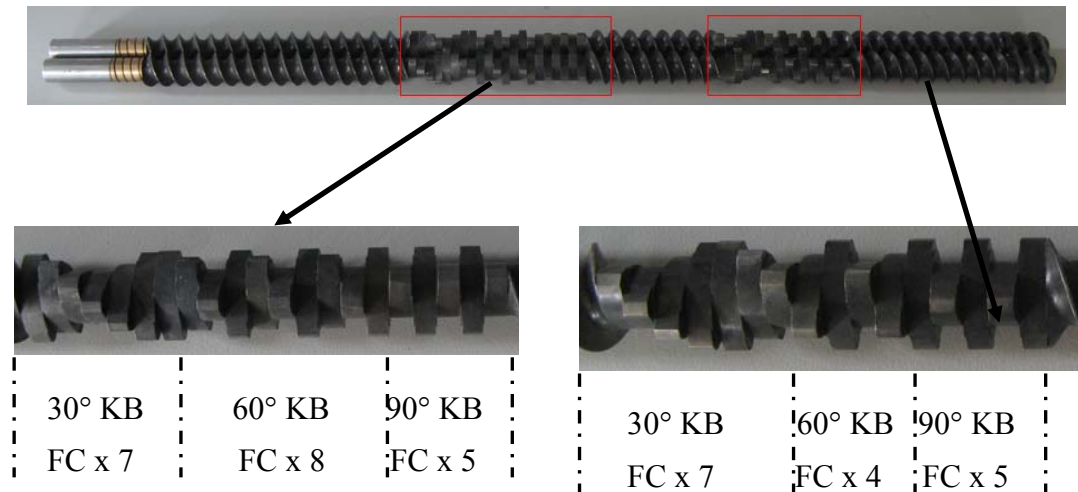
The first barrel was called inlet zone, polymeric materials were fed from here and conveyed through the barrels by the effect of torque applied by the extruder screws. At the 6th barrel, there was a degassing unit connected. Generated gases during the process were removed from here by a vacuum pump.

The extruder was equipped with two feeder which were K-Tron gravimetric feeder and they were controlled with their own software program.



**Figure 5.4 : Barrel profile**

In the production the screw speed of extruder was constant at 300 rpm. The screw design was shown in Figure 5.5. Feed screws were at the beginning of the screw and they had a length D (D=24 mm). Forward conveying (FC) screw elements each had a length D. Forward conveying kneading blocks (KB) were 30°, 60°, and 90° mixing elements and they each had length D/4.



**Figure 5.5 :** Screw configuration (KB: Kneading block, FC: Forward conveying)

### 5.3.3.1 Compounding of the rubber by twin screw extruder

In this part of the work EPDM, silica and silane were mixed properly in twin screw extruder. EPDM was fed into the main feeder and silica and silane were fed into the side feeder. This mixture could be called masterbatch. The masterbatch's temperature was 150°C. The maximum temperature which was reached in the open mill, was 55-60°C. Mixing cycles of TSE operation is given in Table 5.6.

**Table 5.6 :** Mixing cycles of extruder operation

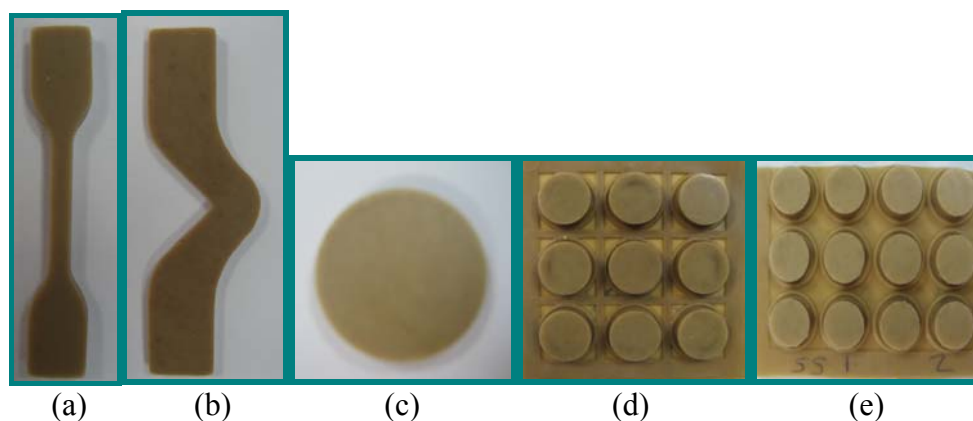
Mixing Steps	Time (min)
Masterbatch added into open mill	0,5
Added PEG. Cut from each side and folded it back on itself three times.	2
Added ZnO and stearic acid. Cut from each side and folded it back on itself three times.	2
Added sulfur and accelerator. Cut from each side and folded it back on itself three times.	2
Total time	6,5

### 5.3.4 Compression molding

In this work, a laboratory compression press which was supplied from Gibitre (Figure 5.6), was used to vulcanize the compounds. It had hydraulic press with 20 tons clamping force and 250x250 mm electrically heated plates. To complete the vulcanization the compounds were pressed 6 minutes at 180°C at 225 bar.. With compression molding 200x200x2 mm flat test plates necessary for mechanical test, 39 mm diameter and 6 mm thickness hardness specimens, 16.60 mm diameter and 6 mm thickness abrasion resistance test specimens and 12 mm diameter and 6 mm thickness compression set specimens were produced (Figure 5.7).



**Figure 5.6 :** Laboratory compression press



**Figure 5.7 :** Test specimens (a: tensile strength; b: tear strength; c: hardness; d: abrasion resistance; e: compression test specimen)

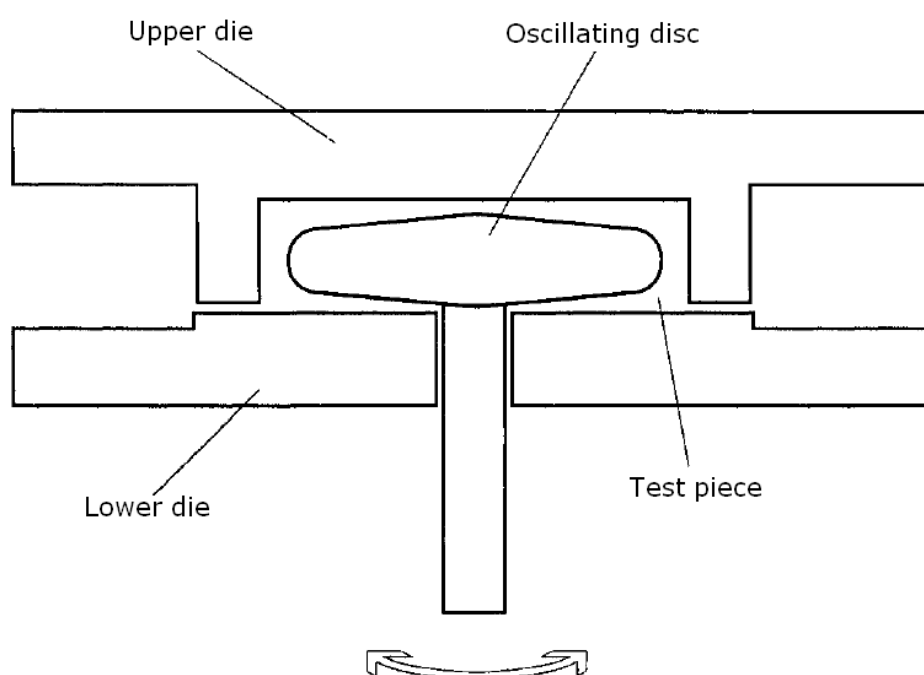
## 5.4 Testing and Characterization of Compounds

### 5.4.1 Rheological properties (Test on unvulcanized rubbers)

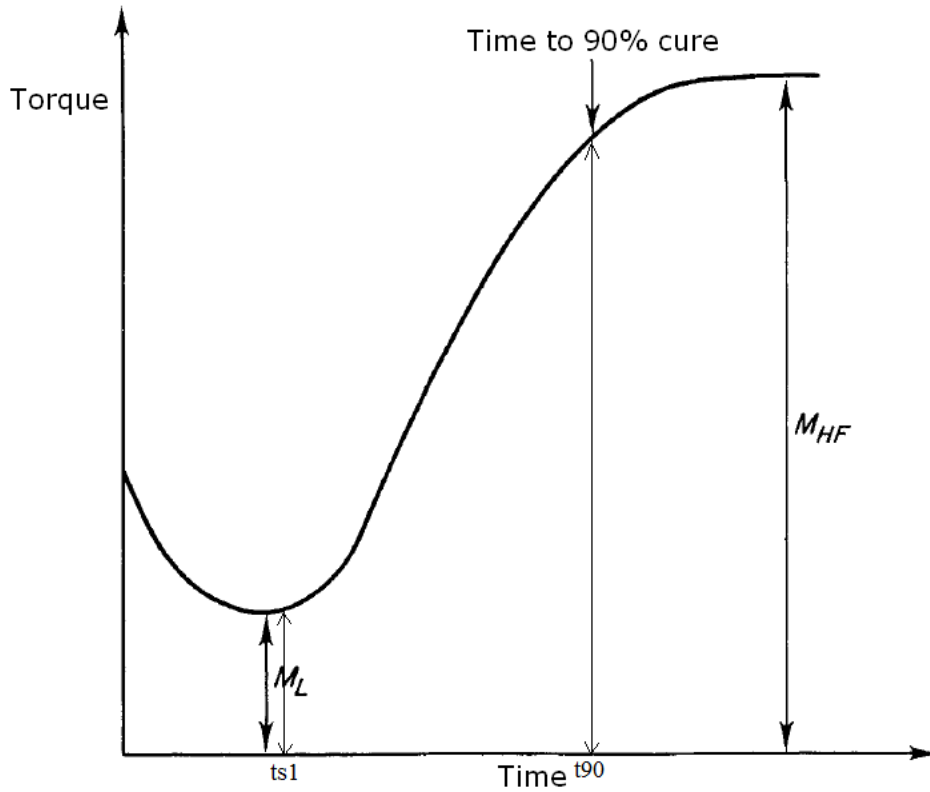
Rheological properties were measured with uncured rubbers. In this work, oscillating disc rheometer (ODR) and Mooney viscometer were used to determine vulcanization characteristics.

#### 5.4.1.1 Oscillating Disc Rheometer

The oscillating disc rheometer was introduced in 1963 and is considered a great improvement over the Mooney Viscometer because the ODR measures not only scorch, but also cure rate and state and cure. Even though thousands of ODRs have been used worldwide, the ODR itself has a design flaw which involves the use of ODR itself. The most problems by ODR were greatly reduced with the introduction of new rotorless curometers, i.e. moving die rheometer (MDR) in 1985 (Rosca and Vergnaud, 2003 and Çavdar, 2007). In ODR type, a bi-conical disc was embedded in the rubber in a closed cavity (Figure 5.8). The disc is oscillated through constant angular displacement and the torque required monitored. An example ODR curve is given in Figure 5.9.



**Figure 5.8 :** Principles of oscillating disc rheometers (Morton, 1987)



**Figure 5.9 :** Oscillating disc rheometer trace (Morton, 1987)

The basic principles of curemetering are covered and typical vulcanization curves illustrated together with the parameters that can be derived from them. By way of illustration the curve for a plateau type cure on an oscillating disc curemeter is shown in Figure 5.9. Minimum torque, maximum torque or the slope of the curve (cure rate) can be taken but perhaps the most useful single figure is the time to achieve a given degree of cure which is the time for the torque to increase to:

$$M_L + 0.01y(M_{HF} - M_L) \quad (5.1)$$

where  $y$  is the percentage cure required, (usually 90% for a 'practical' cure,  $M_{HF}$  is the plateau torque and  $M_L$  is the minimum torque.  $t_{s1}$  value is showed that the time until one torque unit rise above the minimum is achieved and  $t_{90}$  value is showed that the time is the time for the sample to reach 90 percent of the final torque observed during the test).

In this work, oscillating disc rheometer was supplied from Gibitre (Figure 5.10). Torque of the instruments was 49.40 dNxm. Test temperature was 180°C and test duration was 4 minutes. Experimental work of this study was carried out by repeating the tests at least 4 times in oscillating disc rheometer.

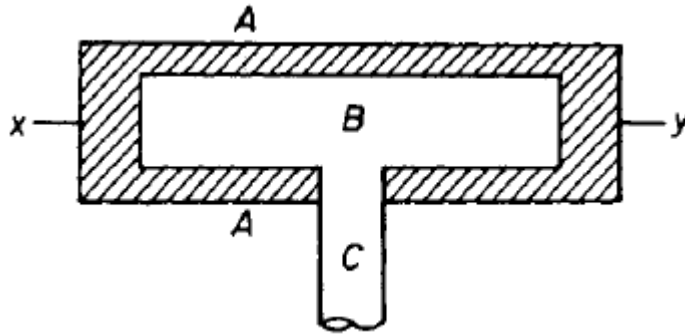


**Figure 5.10 :** Oscillating disc rheometer

#### **5.4.1.2 Mooney Viscometer**

The Mooney Viscometer which was developed by Melvin Mooney of U.S. Rubber Co. It was the first instrument used to measure scorch safety of a mixed stock. The principle of the mooney is that the rotor turns at a constant rate inside a closed cavity containing the test piece so that a shearing action takes place between the flat surfaces of the rotor and the walls of the chamber (Figure 5.11). The torque required to rotate the rotor is monitored by a suitable transducer.





**Figure 5.11 :** Mooney geometry. A is usually the stator and B the rotor, C is the rotating shaft, (Morton, 1987)

In this work, Gibitre Mooney Viscometer was used as mooney viscometer (Figure 5.12). Test temperature was 125°C and test duration was 1+4 minutes. The first 1 minutes allowed for heating the rubber before starting the motor. The test piece was formed by two discs of rubber about 50 mm in diameter and thickness about 6 mm sufficient to completely fill the die cavity. Experimental work of this study was carried out by repeating the tests at least 3 times in mooney viscometer.



**Figure 5.12 :** Mooney viscometer



### 5.4.2 Mechanical properties (Test on vulcanized rubbers)

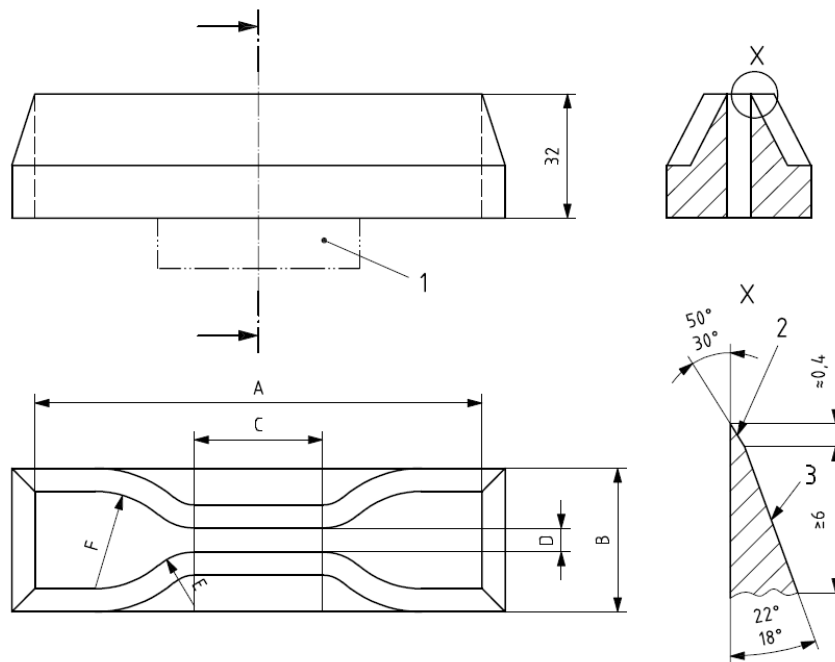
Compression molded test specimens were brought to an air conditioned room and they were left here for at least 48 hours. Room temperature was fixed at  $23 \pm 2$  °C and the relative humidity was 50%. The mechanical tests were also performed at these conditions except compression set tests.

Tensile test and tear resistance test were measured and were reported below. Experimental work of this study was carried out by repeating the tests at least 6 times for tensile strength tests and 5 times for tear strength tests. The results obtained were tabulated and compared with each other.

#### 5.4.2.1 Tensile test

Tensile strength and elongation at break of the materials were measured by a Zwick Universal Tensile Testing Machine Z020 according to ISO 37. Load indicator equipment was a 2.5 kN load cell and extension indicator was a mechanical long stroke extensometer.

Test specimens (Figure 5.13) were cut from the 2 mm vulcanized flat test plate (according to ISO 23529) and they were left at the air conditioned room ( $23 \pm 2$  °C and 50% relative humidity) for at least 48 hours, and then measured in thickness and width before testing to obtain the cross section area of the sample.



**Figure 5.13 :** Tensile test specimen (ISO 37, 2005)

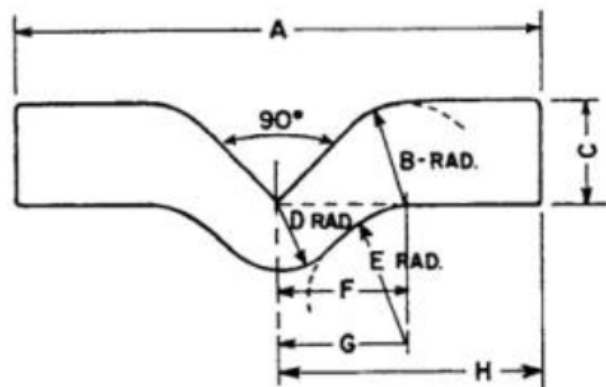
**Table 5.7 :** Dimension of test specimens (ISO 37, 2005)

Dimension	Type 2 (ISO 37)
A Overall length (mm)	75
B Width of ends (mm)	12.5±1
C Length of narrow portion (mm)	25±1
D Width of narrow portion (mm)	4±1
E Transition radius outside (mm)	8±1
F Transition radius inside (mm)	12.5±1

#### 5.4.2.2 Tear strength test

Tear strength test of the materials was measured by a Zwick Universal Tensile Testing Machine Z020 according to ASTM D624. Load indicator equipment was a 2.5 kN load cell.

Test specimens (Figure 5.14) were cut from the 2 mm vulcanized flat test plate (according to ASTM D624) and they were left at the air conditioned room ( $23 \pm 2$  °C and 50% relative humidity) for at least 48 hours, and then measured in thickness and width before testing to obtain the cross section area of the sample.



**Figure 5.14 :** Tear strength test specimen (ASTM D624, 2007)

**Table 5.8 :** Dimension of test specimens (ASTM D624, 2007)

Dimension	Die C (ASTM D624)
A (mm)	102±0.5
B (mm)	19±0.05
C (mm)	19±0.05
D (mm)	12.7±0.05
E (mm)	25±0.05
F (mm)	27±0.05
G (mm)	28±0.05
H (mm)	51±0.25

#### **5.4.3 Physical properties (Test on vulcanized rubbers)**

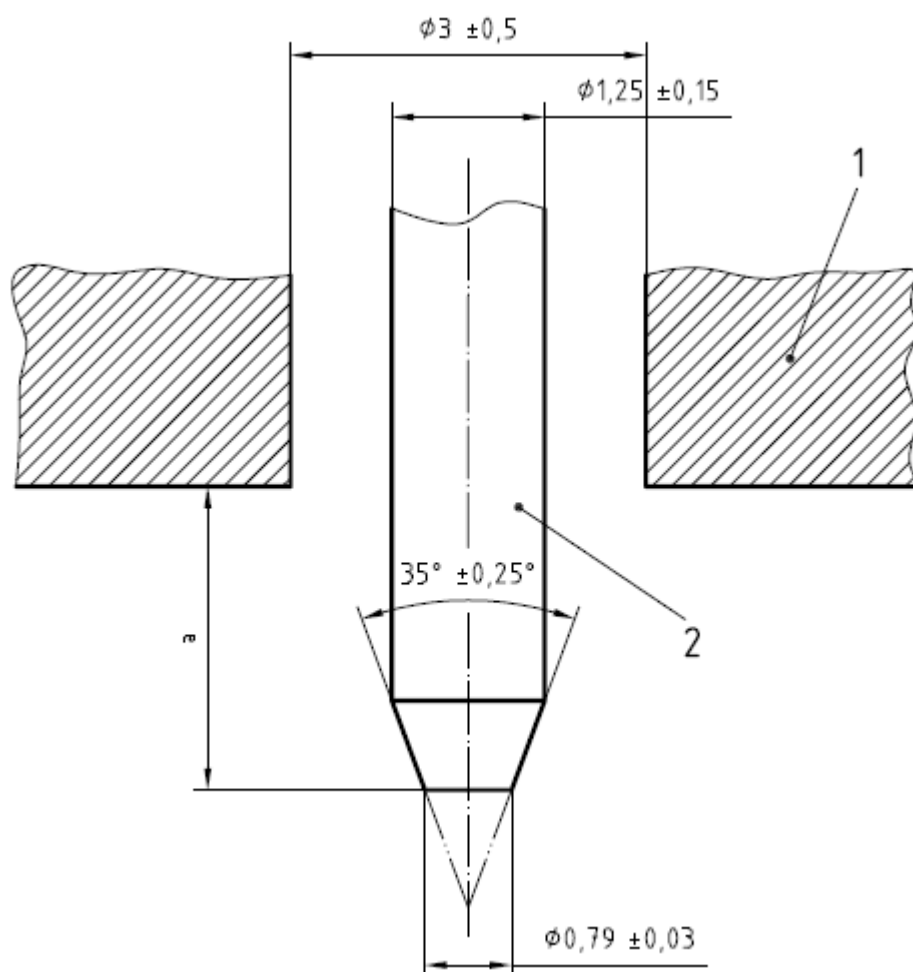
Compression molded test specimens were brought to an air conditioned room and they were left here for at least 48 hours. Room temperature was fixed at 23±2 °C and the relative humidity was 50%. The physical tests were also performed at these conditions except compression set tests.

Hardness, abrasion resistance and compression set test were measured and were reported below. Experimental work of this study was carried out by repeating the tests at least 6 times for hardness measurement, 5 times for abrasion resistance, and 6 times for compression set. The results obtained were tabulated and compared with each other. In addition to these test density measurements and determination of ash content were performed.

##### **5.4.3.1 Hardness**

Hardness of the materials was measure by a Frank Analog Shore A Durometer according to ISO 868. Indenter formed from a hardened steel rod of diameter

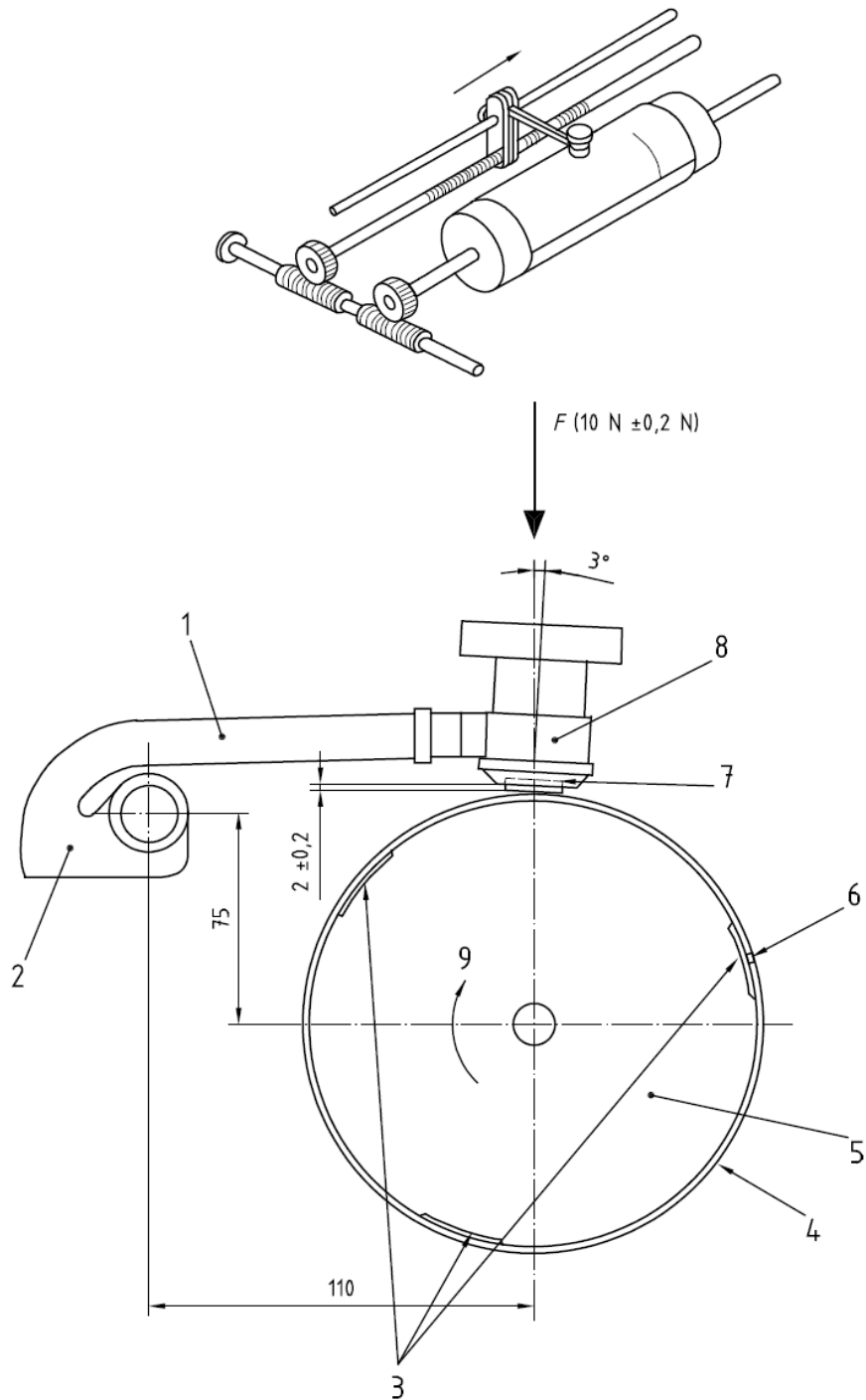
1.25±0.15 mm to the shape and dimensions shown in Figure 5.15. Hardness test specimens had 6 mm thickness and 78 mm diameter.



**Figure 5.15 :** Indenter for type Shore A durometer (1: presser foot; 2: indenter) (ISO 868, 2003)

#### 5.4.3.2 Abrasion resistance test

Abrasion resistance of the materials was measure by a Coesfeld Abrasion Tester according to ISO 4649-A. The cylindrical rubber test pieces were made to slide over an abrasive sheet of specified abrasive grade at a specified contact pressure over 21 m. Abrasion took place over one of the end surfaces of the cylindrical test piece (Figure 5.16). The loss in mass of the test pieces was determined and the volume loss was calculated from density of the material used for the test pieces. The volume loss of the test pieces were compared to that of a reference compound tested under the same conditions.



**Figure 5.16 :** Schematic illustration of apparatus (ISO 4649-A, 2002)

(1: Swivel arm; 2: Sledge; 3: Double sided adhesive tape; 4: Abrasive sheet; 5: Cylinder; 6: Gap < 2; 7: Test piece; 8: Test piece holder; 9: Rotational speed  $40 \pm 1$  rpm)

The swivel arm and test piece holder was free from vibration during operation and so disposed that the test piece was pressed against the drum with a vertical force of  $10 \pm 0.2$  N obtained by adding weights to the top of the test piece holder. Test pieces

were removed after an abrasion run of  $20 \pm 0.1$  m (equivalent to 42 revolutions) and test was ended automatically. The relative volume loss was given, in  $\text{mm}^3$ , by the equation

$$\Delta V_{\text{rel}} = (\Delta m_t \times \Delta m_{\text{const}}) / (\rho_t \times \Delta m_r) \quad (5.2)$$

where

$\Delta m_t$  is the mass loss, in mg, of the test rubber test piece

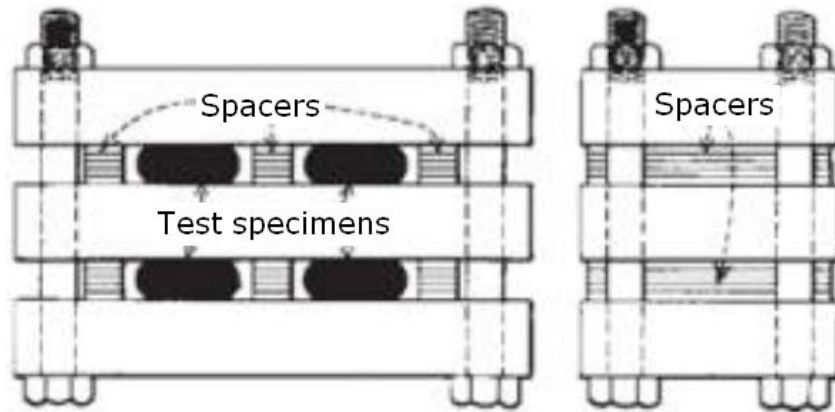
$\Delta m_{\text{const}}$  is the defined value of the mass loss, in mg, of the reference compound test piece

$\rho_t$  is the density, in  $\text{mg}/\text{mm}^3$ , of the test rubber

$\Delta m_r$  is the mass loss, in mg, of the reference compound test piece

#### 5.4.3.3 Compression set test

Compression set of the materials were measure by a compression set device and an oven according to ISO 815. Compression set device consisted two flat steel plates between the parallel faces of which the specimens were compressed as shown in Figure 5.17.



**Figure 5.17 :** Device for compression set under constant deflection (ISO 815, 2008)

Before starting to test specimens thickness were measured. The amount of compression employed was approximately 30%. The gap between the spacers was set 30% of thickness of specimens with a dial indicator. After steel spacers were placed on each side of the rubber specimens while compressed. These devices waited for 72 hours in 100 °C oven. While cooling, allowed the specimens to rest on a poor

thermally conducting surface, such as wood for 30 minutes before making the measurement of the final thickness. The compression set as a percentage of the original thickness was calculated:

$$C_A = [(t_0 - t_1) / (t_0 - t_n)] \times 100 \quad (5.3)$$

where:

$C_A$  = Compression set as a percentage of the original thickness

$t_0$  = original thickness of specimen

$t_1$  = final thickness of specimen

$t_n$  = thickness of the spacer bar used

#### **5.4.3.4 Density**

Density of the materials were measure by a Mettler AT201 Electronic Analytical SemiMicro Balance according to ISO 2781. Firstly the specimen was weighted in air and then same specimen was weighted in water. Water's density was assumed to be 1 g/cm<sup>3</sup>. So density of specimen was found with mass in air per mass in water.

#### **5.4.3.5 Determination of ash content**

Ash contents of the materials were determined by a Heraeus Thermicon P Muffle Furnace according to ISO 247. Firstly a clean a empty crucible heated about 30 minutes in the muffle furnace at 550°C and after then allowed to cool to ambient temperature in a desiccators and weighted. Test portion of about 1-5 g of rubber compound weighted and placed in the crucible. The crucible heated about 1 hour in the muffle furnace at 950°C and after then allowed to cool to ambient temperature in a desiccators and weighted. The ash content was given, as a percentage by mass, by the formula

$$(m_2 - m_1) / m_0 \times 100 \quad (5.4)$$

where

$m_0$  is the mass, in grams, of the test portion;

$m_1$  is the mass, in grams, of the empty crucible;

$m_2$  is the mass, in grams, of the crucible and ash.





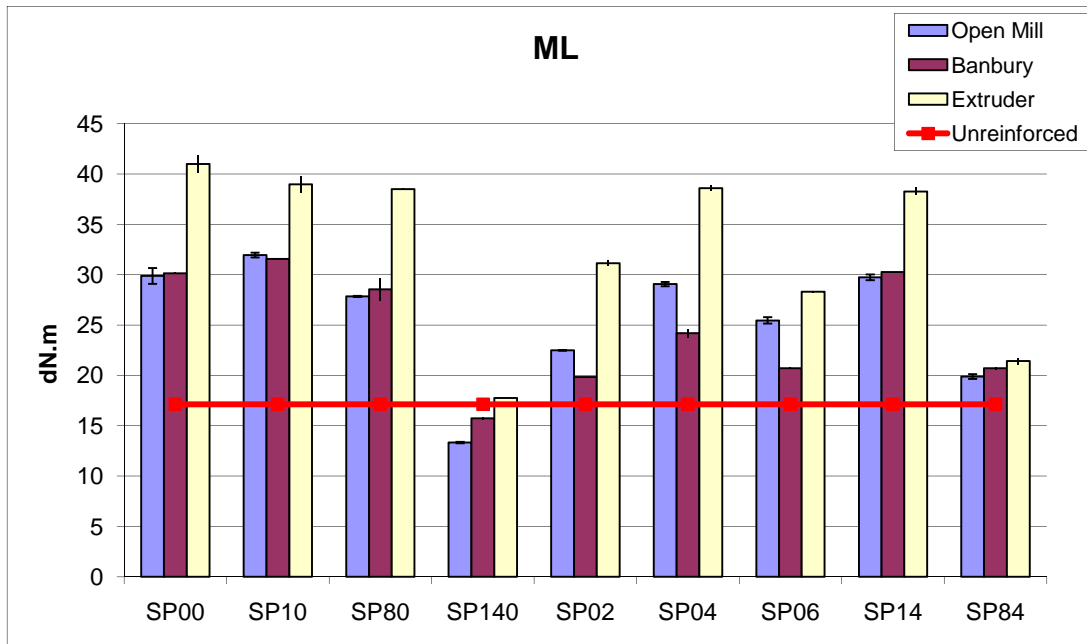
## 6. RESULTS AND DISCUSSION

### 6.1 Rheological Properties

Curing characteristics were measured according to the explanations in section 5.4.1.1.  $M_L$  results are shown in Table 6.1 and Figure 6.1.

**Table 6.1 :  $M_L$  results**

<i>Recipes</i>	<i><math>M_L</math> (dNxm)</i>		
	Open mill	Banbury	Extruder
SP00	29.88	30.14	41.01
SP10	31.95	31.57	38.97
SP80	27.85	28.55	38.49
SP140	13.32	15.73	17.77
SP02	22.49	19.83	31.15
SP04	29.07	24.18	38.59
SP06	25.46	20.72	28.30
SP14	29.73	30.27	38.27
SP84	19.88	20.71	21.43
Unreinforced	17.13		

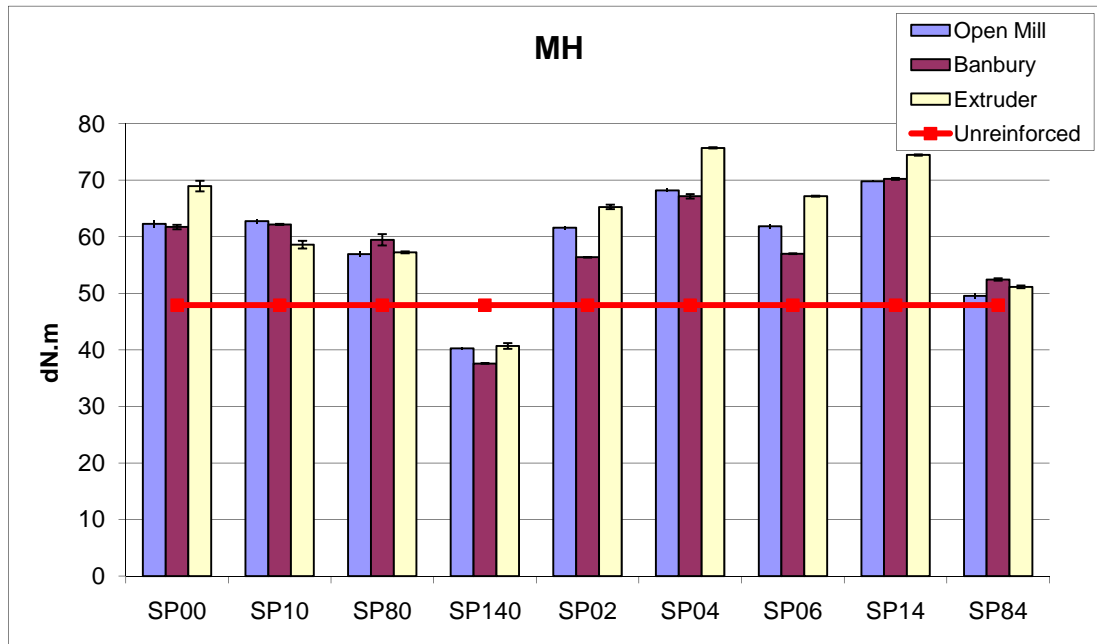


**Figure 6.1 :  $M_L$  results**

$M_H$  results are shown in Table 6.2 and Figure 6.2.

**Table 6.2 :  $M_H$  results**

<i>Recipes</i>	<i><math>M_H</math> (dNxm)</i>		
	Open mill	Banbury	Extruder
SP00	62.27	61.72	68.96
SP10	62.74	62.18	58.58
SP80	56.95	59.46	57.24
SP140	40.24	37.59	40.67
SP02	61.59	56.37	65.27
SP04	68.20	67.17	75.72
SP06	61.87	56.99	67.18
SP14	69.81	70.23	74.76
SP84	49.55	52.43	51.14
Unreinforced	47.90		



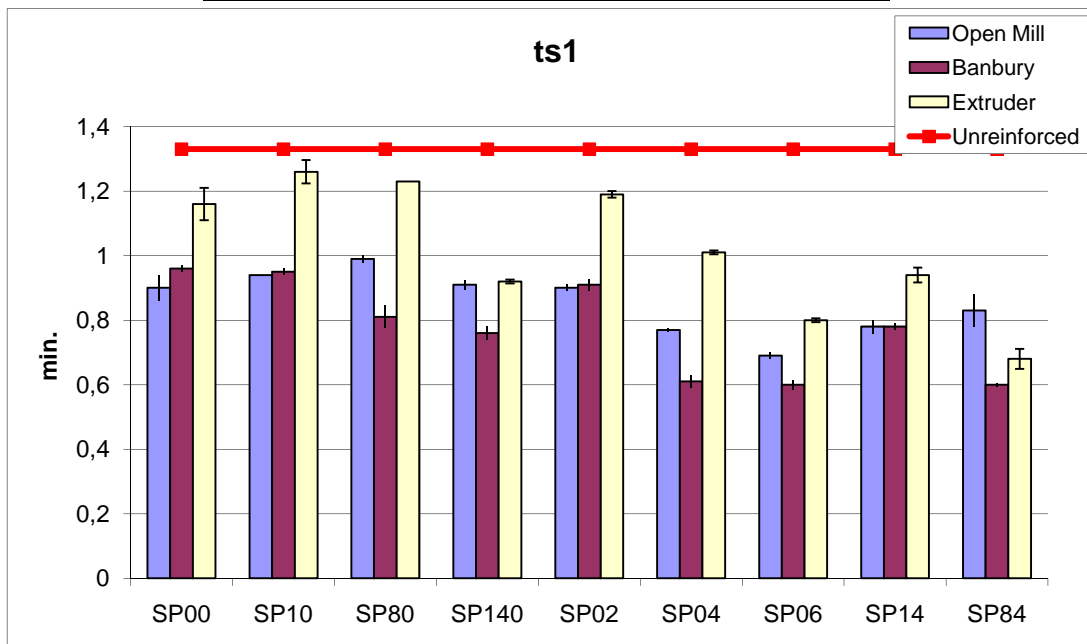
**Figure 6.2 :  $M_H$  results**

The highest  $M_L$  values were obtained with TSE operation. It was considered that silica particles were agglomerated in the polymer matrix. These agglomerated structures might be broken down and well distributed with twin screw extruder. When silane was added the recipes,  $M_H$  value was decreased (SP10, SP80 and SP140). However when PEG was added,  $M_H$  was increased dramatically (SP04). It was observed that when silane and PEG were used in together (SP14), it seemed that PEG was the determinative and  $M_H$  value was closed to SP04.

$t_{s1}$  results are shown in Table 6.3 and Figure 6.3.

**Table 6.3 :  $t_{s1}$  results**

<i>Recipes</i>	<i><math>t_{s1}</math> (min)</i>		
	Open mill	Banbury	Extruder
SP00	0.90	0.96	1.16
SP10	0.94	0.95	1.26
SP80	0.99	0.81	1.23
SP140	0.91	0.76	0.92
SP02	0.90	0.91	1.19
SP04	0.77	0.61	1.01
SP06	0.69	0.60	0.80
SP14	0.78	0.78	0.94
SP84	0.83	0.60	0.68
Unreinforced	1.33		

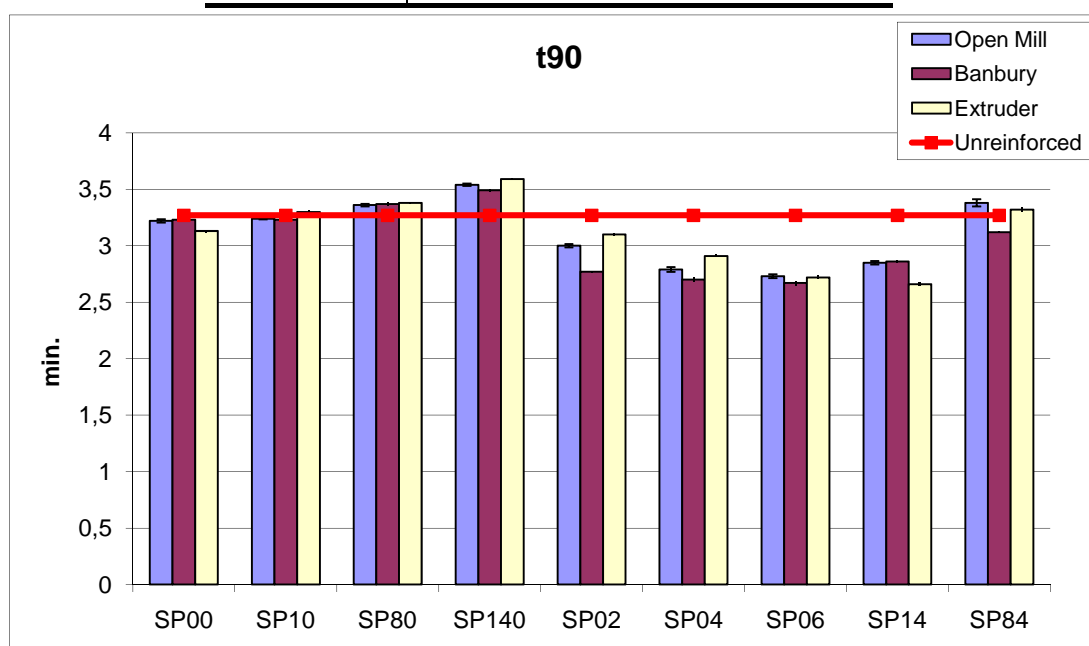
**Figure 6.3 :  $t_{s1}$  results**

When the samples were prepared with open mill operation and banbury operation,  $t_{s1}$  values were similar to the each other. However when TSE operation were used,  $t_{s1}$  value was increased and the maximum values of every recipes were obtained by TSE operation. When silane was added the recipe in TSE operation (SP10),  $t_{s1}$  reached the highest value. But it was not affected by the increasing of silane ratio in the recipes (SP80 and SP140). If open mill operation and banbury operation were used in the production, the effect of the addition of silane was not observed.

$t_{90}$  results are shown in Table 6.4 and Figure 6.4.

**Table 6.4 :  $t_{90}$  results**

<i>Recipes</i>	<i><math>t_{90}</math> (min)</i>		
	Open mill	Banbury	Extruder
SP00	3.22	3.23	3.13
SP10	3.24	3.23	3.30
SP80	3.36	3.37	3.38
SP140	3.54	3.49	3.59
SP02	3	2.77	3.10
SP04	2.79	2.70	2.91
SP06	2.73	2.67	2.72
SP14	2.85	2.86	2.66
SP84	3.38	3.12	3.32
Unreinforced	3.27		



**Figure 6.4 :  $t_{90}$  results**

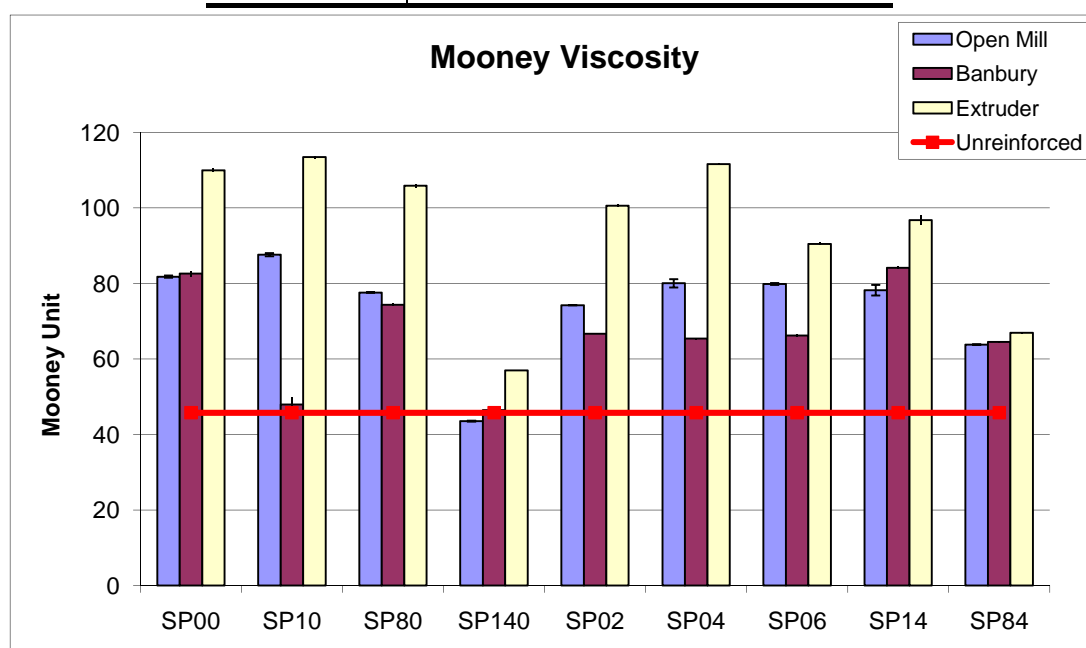
$t_{90}$  values of samples SP00 were similar to each of them regardless of the production method. When silane was added into the recipe (SP10),  $t_{90}$  value was not affected remarkably. By the increasing of silane ratio in the recipes (SP80 and SP140), it was increased slightly. It was also observed that PEG had a strong effect on  $t_{90}$  values. Curing time was decreased with addition of PEG remarkably in neither silane exists or not in the recipe. This could be explained that silica particles had highly reactive

hydroxyl groups on the surface that would react with accelerators to slow the cure rate. PEG might coat the surface of the silica by replacement of hydroxyl group on the surface of the silica. This coating could cause to decrease curing time (De and White, 2001).

Mooney viscosity were measured according to the explanations in section 5.4.1.2. Mooney viscosity results are given in the Table 6.5 and Figure 6.5.

**Table 6.5 : Mooney viscosity results**

<i>Recipes</i>	<i>Mooney viscosity (Mooney unit)</i>		
	Open mill	Banbury	Extruder
SP00	81.80	82.58	110.00
SP10	87.63	47.92	113.45
SP80	77.61	74.32	105.89
SP140	43.55	46.46	56.92
SP02	74.24	66.66	100.55
SP04	80.04	65.38	111.65
SP06	79.87	66.24	90.50
SP14	78.23	84.14	96.79
SP84	63.79	64.48	66.89
Unreinforced	45.76		



**Figure 6.5 : Mooney viscosity results**

It was clearly observed that mooney viscosity of the samples which were prepared by TSE operation were higher than the open mill operation and banbury operation. It might be the consequence of high mixing efficiency of TSE. It could be also related with reducing the mobility of the macromolecular rubber chains because of well dispersion in the TSE. The mooney viscosity of samples which were prepared by open mill operation and banbury operation were closed each other.

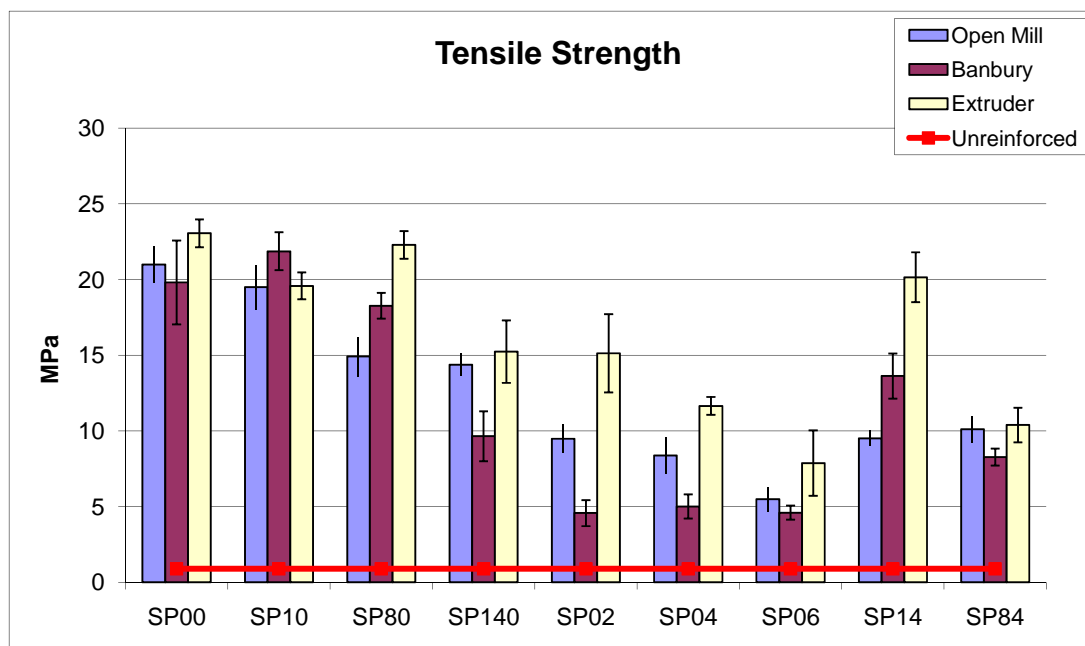
## 6.2 Mechanical Properties

### 6.2.1 Tensile strength test

Tensile strength test were done according to the procedure explained in section 5.4.2.1. Tensile strength test results are given in Table 6.6 and Figure 6.6.

**Table 6.6 : Tensile strength results**

<i>Recipes</i>	<i>Tensile strength (MPa)</i>		
	Open mill	Banbury	Extruder
SP00	20.99	19.81	23.06
SP10	19.5	21.87	19.58
SP80	14.92	18.27	22.29
SP140	14.37	9.65	15.24
SP02	9.49	4.57	15.13
SP04	8.38	5.01	11.6
SP06	5.49	4.6	7.87
SP14	9.51	13.63	20.15
SP84	10.12	8.27	10.39
Unreinforced	0.89		



**Figure 6.6 :** Tensile strength results

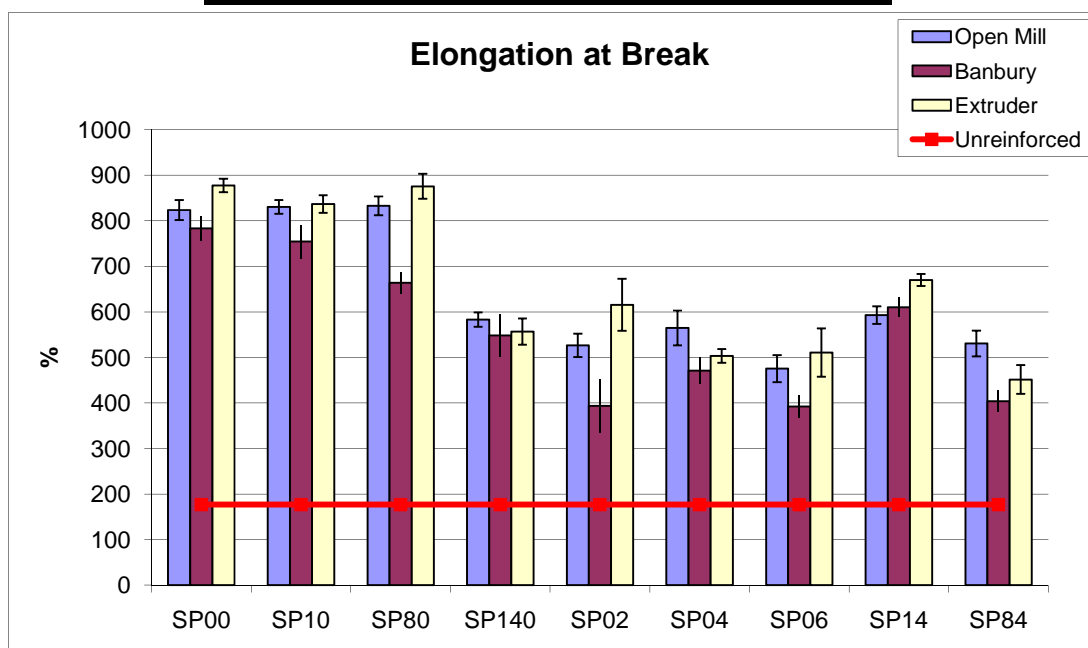
It was observed that process had no effect on tensile strength (SP00). It was also found that any relation was not observed between tensile strength and addition of silane (SP10, SP80 and SP140). But when silane ratio was increased and the recipe was prepared by open mill operation, tensile strength was decreased (SP80 and SP140). The highest tensile strength was obtained without silane and PEG by using the twin screw extruder (SP00). This seemed to be due to silica tends to agglomerate and so that high shear was desirable when the compound was being mixed to break down these agglomerates. This was necessary for good reinforcement (Ciesielski, 1999). Addition of PEG reduced the tensile strength remarkably (SP02, SP04 and SP06). When silane and PEG were added together, tensile strength was increased regarding to addition of PEG only (SP14). When tensile strength results were investigated carefully, it could be considered that if PEG was in the recipe, silane might be added in the recipe too in TSE operation

Elongation at break results are given in Table 6.7 and Figure 6.7.



**Table 6.7 : Elongation at break results**

<i>Recipes</i>	<i>Elongation at break (%)</i>		
	Open mill	Banbury	Extruder
SP00	823.78	783.26	877.40
SP10	830.15	754.26	836.71
SP80	832.77	663.46	875.69
SP140	582.98	548.58	556.77
SP02	526.51	393.56	615.50
SP04	564.69	470.77	503.19
SP06	475.35	392.33	510.70
SP14	592.98	610.25	670.10
SP84	530.54	403.50	451.70
Unreinforced	177.03		

**Figure 6.7 : Elongation at break results**

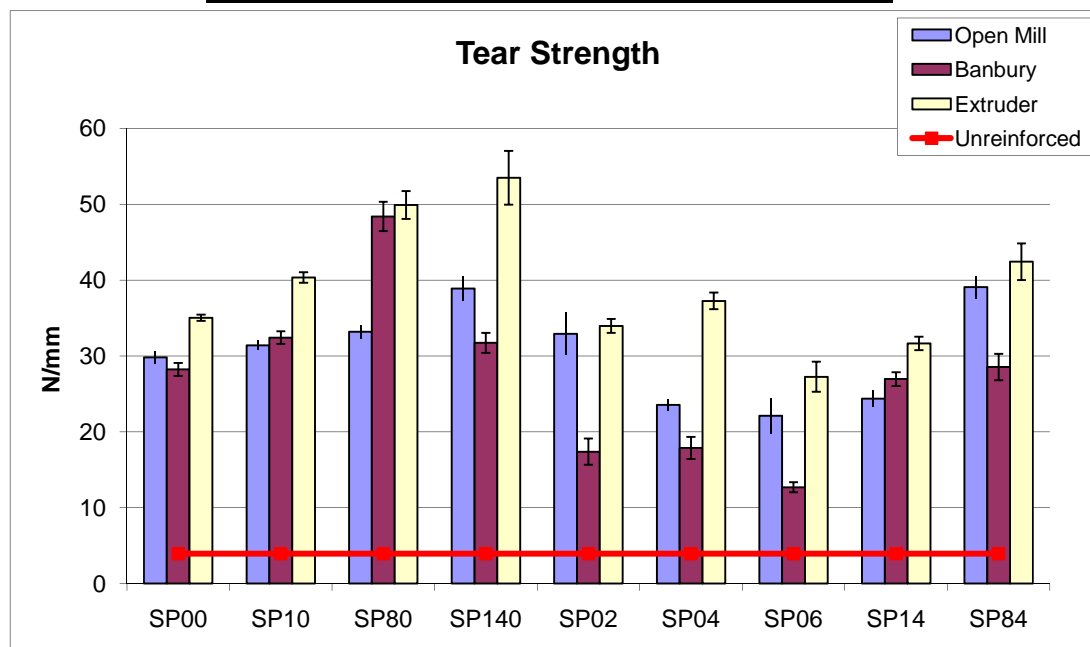
It was noted that elongation at break properties of the samples which were prepared by banbury were lower than the samples which were prepared by open mill and TSE. It might be a consequence of agglomeration of silica in the banbury (Siriwardena *et al.*, 2001). Due to polar characteristics of silica particles, they were easily agglomerated and hard to disperse in the rubber matrix (Kim and VanderKooi, 2004). Elongation at break values were changed independent from the production method. It was decreased with addition of PEG

## 6.2.2 Tear strength test

Tear strength test were done according to the explanations in section 5.4.2.2. Tear strength test results are given in Table 6.8 and Figure 6.8.

**Table 6.8 : Tear strength results**

<i>Recipes</i>	<i>Tear strength (N/mm)</i>		
	Open mill	Banbury	Extruder
SP00	29.80	28.22	35.04
SP10	31.41	32.42	40.35
SP80	33.21	48.39	49.91
SP140	38.9	31.73	53.49
SP02	32.92	17.39	33.96
SP04	23.56	17.88	37.26
SP06	22.11	12.69	27.26
SP14	24.36	26.96	31.65
SP84	39.08	28.54	42.43
Unreinforced	3.93		



**Figure 6.8 : Tear strength results**

It was observed that tear strength of the samples prepared by twin screw extruder were better than other ones because of better dispersion of silica in TSE (SP00). When the silane was added the recipes (SP10), tear strength was increasing

according to silica-silane interaction. This effect was observed clearly especially compound prepared by TSE operation. Increasing the amount of silane resulted in much higher tear strength (SP80 and SP140).

With addition of PEG into the recipes (SP02, SP04 and SP06), tear strength was decreased when samples were prepared by the open mill and banbury. However the recipe was prepared by TSE, tear strength was increased compared to SP00. It was also found that the highest tear strength values were observed with high ratio silane and without PEG (SP80).

### 6.3.1 Hardness

Hardness measurements were done according to the explanations in section 5.4.3.1. Hardness results are given in Table 6.9 and Figure 6.9.

**Table 6.9 : Hardness results**

<i><b>Recipes</b></i>	<i><b>Hardness (Shore A)</b></i>		
	Open mill	Banbury	Extruder
SP00	55.42	55.50	54.50
SP10	56.17	56.75	57.67
SP80	59.5	63.63	65.25
SP140	60.17	55.33	63.83
SP02	56.92	51.83	59.25
SP04	55.83	56.50	59.00
SP06	54.00	52.67	57.17
SP14	56.38	57.88	55.00
SP84	59.17	57.67	61.17
Unreinforced	41.50		



**Figure 6.9 : Hardness results**

When the recipe did not contain silane (SP00), hardness values were not affected by the production method. However it was found that when silane was added the recipes, production method affected the hardness values slightly (SP10). Especially hardness value increased by using the twin screw extruder. By the increasing of silane ratio in the recipes (SP80 and SP140), hardness differences between production methods were observed much clearly. It was also found that the hardness was increased with addition of silane in the open mill. We assumed that although the adequate temperature for silanisation reaction was not reached in the open mill operation, some silanisation reaction might be occurred in the hot press.

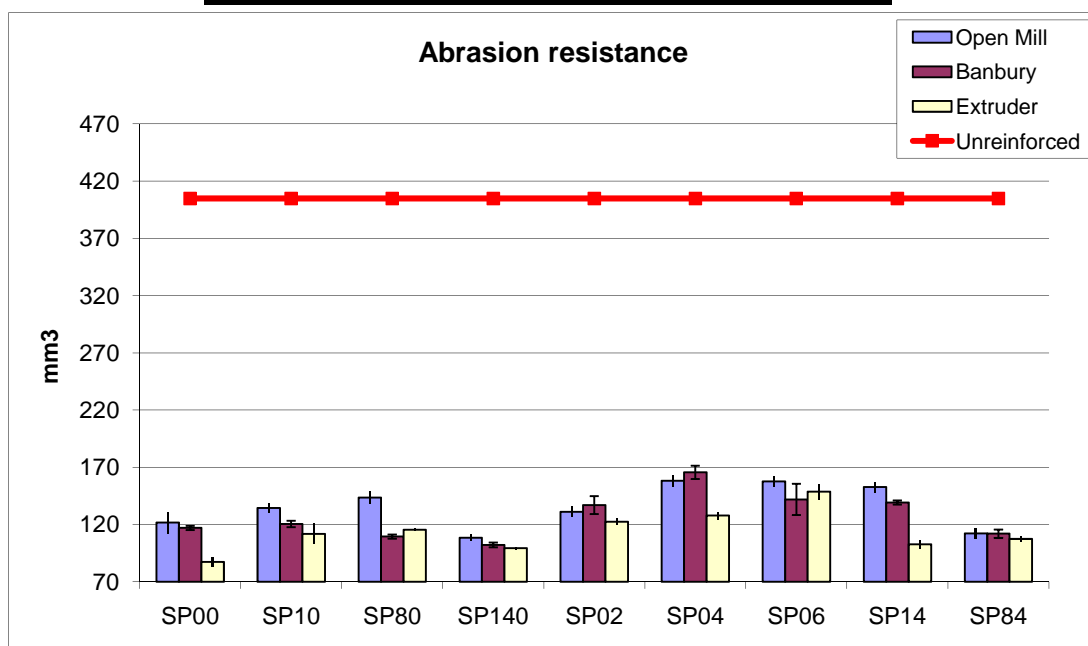
When PEG was used in the recipe, hardness was increased especially when the twin screw extruder was used. This increasing might be consequence of during hot mixing, some of the adsorbed water was removed and left a very reactive filler surface. However if PEG was present in the recipe (SP02, SP04 and SP06), it might be replaced the volatilized water and reduced the reactivity of the silica surface.

### 6.3.2 Abrasion resistance

Abrasion resistance test applied according to the procedure explained in section 5.4.3.2. Abrasion resistance results are given in Table 6.10 and Figure 6.10.

**Table 6.10 : Abrasion resistance results**

<i>Recipes</i>	<i>Abrasion resistance (mm<sup>3</sup>)</i>		
	Open mill	Banbury	Extruder
SP00	121.62	116.96	87.27
SP10	134.44	120.47	111.80
SP80	143.36	109.39	115.45
SP140	108.37	102.00	99.36
SP02	130.94	136.89	122.27
SP04	158.21	165.52	127.79
SP06	157.57	141.85	148.82
SP14	152.75	139.19	102.77
SP84	112.31	111.91	107.38
Unreinforced	404.90		

**Figure 6.10 : Abrasion resistance results**

When silane and PEG were not added into the recipe (SP00), much better abrasion resistance was obtained because of better dispersion of silica. Although when TSE was used preparation of recipes, abrasion resistance values were better compare to the other production method. It was observed abrasion resistance was decreased with addition of silane (SP10) and increasing in content of silane results in further decrease in especially in open mill operation due to inadequate silanisation temperature (SP80 and SP140). It was observed that abrasion resistance were not affected by addition of much more amount of silane in banbury and TSE. Silica

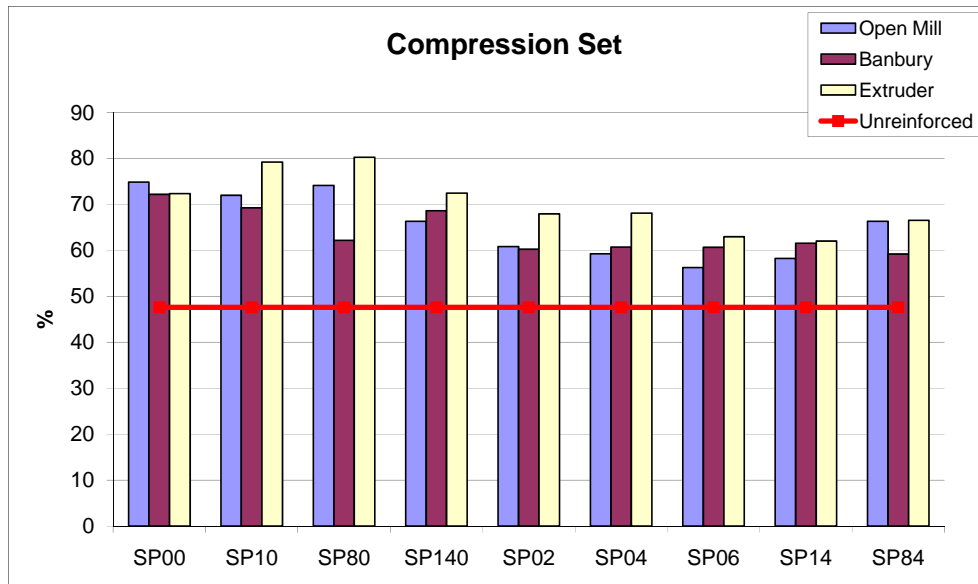
particles were coated with silane and chemical linkage formed between EPDM matrix and surface of silica (Dick, 2001). When the abrasive touched the surface of cured compound surface, it stated to remove material from surface. If the silane was used, the EPDM coated silica particles probably removed from the surface by crack formation around the particle. However if silane was not existed in the recipe, the abrasive might removed the material from the surface of the compound by grinding the silica particles into smaller one. Moreover when PEG was added the recipes (SP04), it coated the surface of silica without forming chemical linkage between EPDM matrix and filler surface. So abrasive could pull out the particles from EPDM much easier. However when silane and PEG were used together (SP14 and SP84), silane made better chemical linkage leading better abrasion resistance.

### 6.3.3 Compression set

Compression set tests were done according to the explanation in section 5.4.3.3. Compression set results are given in Table 6.11 and Figure 6.11.

**Table 6.11 : Compression set results**

<i><b>Recipes</b></i>	<i><b>Compression set (%)</b></i>		
	Open mill	Banbury	Extruder
SP00	74.80	72.16	72.30
SP10	71.93	69.19	79.17
SP80	74.06	62.16	80.21
SP140	66.30	68.59	72.4
SP02	60.80	60.21	67.9
SP04	59.24	60.70	68.08
SP06	56.22	60.65	62.93
SP14	58.20	61.52	61.97
SP84	66.27	59.15	66.50
Unreinforced	47.59		



**Figure 6.11 : Compression set results**

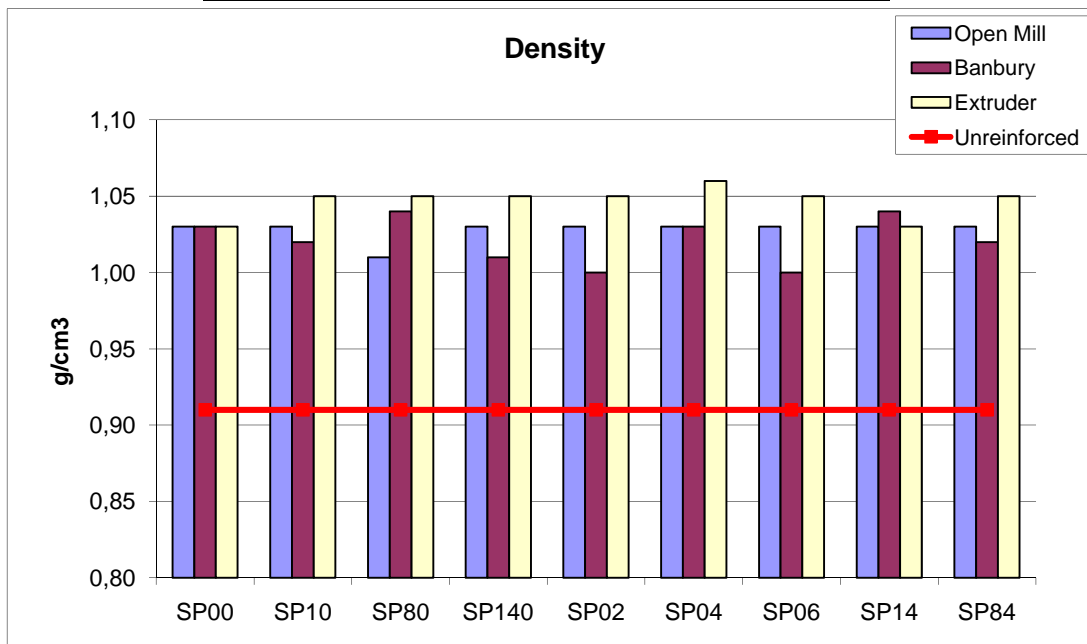
As shown in Figure 6.11 compression set values were not affected by production method if the recipes were prepared without silane (SP00). When 1 phr silane was added the recipe (SP10) and they were prepared by the open mill operation and banbury operation, change in compression set were not observed clearly. When 8 phr silane was added the recipe (SP80) and it was prepared by the open mill, compression set value was increased compared to SP10 because of lack of degassing. This could be explained as follows; while silanisation reaction was occurring, alcohol was formed. But silanisation reaction could not be completed when the open mill was used due to low temperature at open mill operation. Although this reaction might be occurred in the press, alcohol was not degassed. Furthermore, it might be relevant with after compression of the elastomer to a fixed deformation, breakdown of the network of long-chain polymer molecules occurred and this was to some extent measured by stress relaxation. However, crosslinks might be formed in the strained state and formed a “second network”. These crosslinks had no effect on stress relaxation, but could dominate the value of compression set (Gent, 2001).

#### 6.3.4 Density measurement

Density measurements were done as explained in section 5.4.3.4. Density measurement results are given in Table 6.12 and Figure 6.12.

**Table 6.12 : Density measurement results**

<i>Recipes</i>	<i>Density (g/cm<sup>3</sup>)</i>		
	Open mill	Banbury	Extruder
SP00	1.03	1.03	1.03
SP10	1.03	1.02	1.05
SP80	1.01	1.04	1.05
SP140	1.03	1.01	1.05
SP02	1.03	1.00	1.05
SP04	1.03	1.03	1.06
SP06	1.03	1.00	1.05
SP14	1.03	1.04	1.03
SP84	1.03	1.02	1.05
Unreinforced	0.91		

**Figure 6.12 : Density measurement results**

Density values were approximately similar because of same filler content ratio. However some samples which were prepared by TSE, density values were higher than the other values. It might be the consequence of overloading of silica.

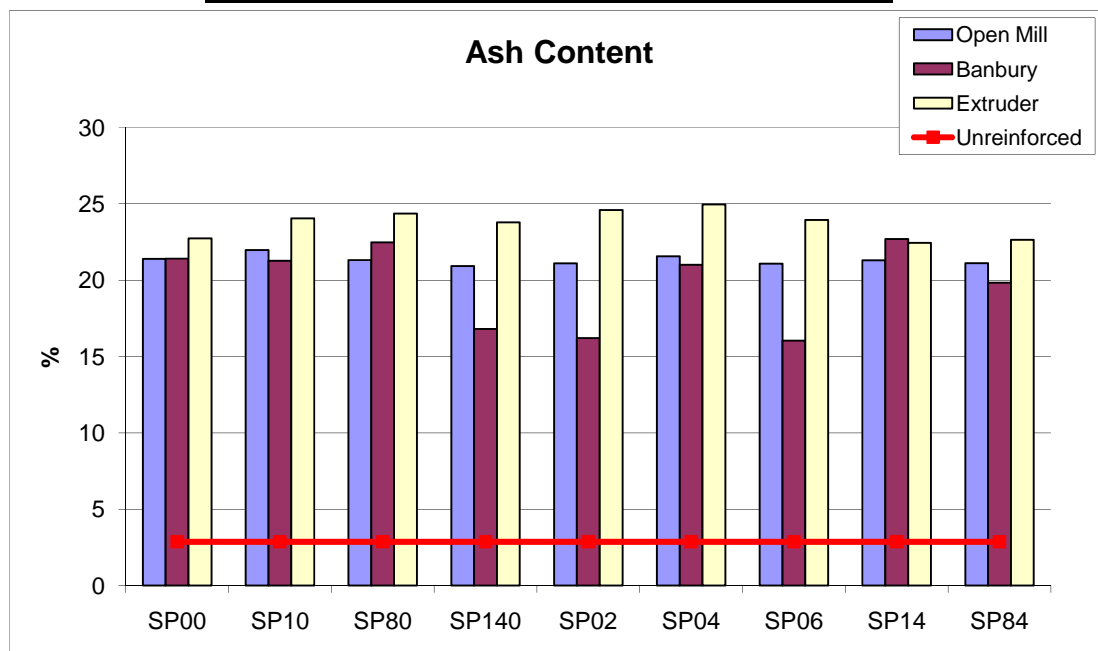
### 6.3.5 Ash content

Determination of ash content method was explained in section 5.4.3.5. Ash content results are given in Table 6.13 and Figure 6.13.



**Table 6.13 : Ash content results**

<i>Recipes</i>	<i>Ash content (%)</i>		
	Open mill	Banbury	Extruder
SP00	21.40	21.42	22.74
SP10	21.98	21.28	24.06
SP80	21.32	22.47	24.37
SP140	20.93	16.81	23.79
SP02	21.10	16.22	24.60
SP04	21.57	21.01	24.96
SP06	21.08	16.04	23.95
SP14	21.30	22.70	22.45
SP84	21.12	19.84	22.65
Unreinforced	2.87		

**Figure 6.13 : Ash content results**

Similar to the density results, some samples had higher ash content value because of overloading of filler.



## 7. CONCLUSION

The aim of this study was to investigate the parameters of continuous compounding of silica loaded rubber in a twin screw extruder and compare the results with other compounding methods. The effect of silanisation reaction within twin screw extruder was also investigated according to different ratios of silane. Effect of PEG was also investigated while special attention was paid into combine used of silane and PEG together. At first, a unreinforced recipe was prepared which did not contain any filler, silane and PEG. Apart from this, nine different formulations in which the ratio of silane and PEG were changed, were prepared. In the first stage, EPDM was fed from the main feeder and silica and silane were fed from the side feeder. After compounding in twin screw extruder, PEG, activators, accelerators and sulfur were added in the open mill in the second stage. The same formulations were also prepared by open mill operation and banbury operation.

It was observed that twin screw extruder operation was better than banbury operation considering tensile strength, elongation at break, abrasion resistance and compression set. When the recipes were prepared by open mill operation, the results were much worse than banbury operation and extruder operation. This might be the consequence of the inadequate temperature to silanisation reaction and inadequate mixing efficiency.

When silane was added into the recipes, better tensile strength, elongation at break and tear resistance were obtained by twin screw extruder operation comparing to banbury operation. Although abrasion resistance results were similar between banbury operation and TSE operation, hardness values of the samples were produced by banbury operation were better than TSE operation. When silane was added in the open mill, the results were much worse than other production method. Because temperature which was necessary to silanisation reaction, was not obtained in the open mill.

It was observed that mechanical and physical properties were get worse with addition of PEG in open mill operation and banbury operation except of compression set.

However when PEG was in TSE operation, tensile strength, tear resistance and abrasion resistance were improved remarkably. When the recipe had both silane and PEG, better abrasion resistance and very good compression set values were obtained. Besides that tensile strength and tear resistance were obtained acceptable results.

As a conclusion, better results considering all mechanical and physical tests were obtained by twin screw extruder operation due to better distributive and dispersive mixing efficiency, and controlled temperature for silanisation reaction comparing to the other conventional process. In addition to this, continue process could be achieved by TSE operation. When silane and PEG were used together and the recipe was prepared by TSE operation, optimum values were obtained when it was desired to accomplish fast curing time, better mechanical properties such as tensile strength, elongation at break and tear resistance, better compression set and abrasion resistance.

## REFERENCES

- ASTM D624**, 2007: Standard test method for tear strength of conventional vulcanized rubber and thermoplastic elastomers, *American Society for Testing and Materials*
- Babbitt, R.O.**, 1978: the Vanderbilt rubber Handbook, R.T. Vanderbilt Company, USA, 408-409
- Barlow, F.W.**, 1993: Rubber Compounding: Principles, materials, and techniques, CRC Press, USA, 211-221
- Ciesielski, A.**, 1999: An introduction to rubber technology, Rapra Technology LTD., United Kingdom, 31-41
- Çavdar, S.**, 2007: Effect of different compositions on rheological and mechanical properties of EPDM rubber, *M.Sc. Thesis*, METU, Ankara
- De, S.K., White, J.R.**, 2001: Rubber Technologist's Handbook, Rapra Technology LTD., United Kingdom, 439
- Dick, J.S.**, 2001: Rubber technology: Compounding and testing for performance, HanserGardner Publications, USA,
- Fröhlich, J., Niedermeier, W., Luginsland, H.D.**, 2004: The effect of filler-filler and filler-elastomer interaction on rubber reinforcement, *Composites Part A: Applied Science and Manufacturing*, **36**, 449-460
- Gent, A.N.**, 2001: Engineering with rubber: How to design rubber components 2<sup>nd</sup> edition, HanserGardner Publications, USA, 184
- Haberstroh, E., Köppen, H.**, 2008: Continuous compounding of silica filled rubber in a twin extruder, Machinery and equipments of Aachen University, 20-25
- Hunsche, A., Görl, U., Müller, A., Knaack, M., Göbel T.**, 1997: Investigation concerning the reaction silica/organosilane and organosilane/polymer, *International Rubber Conference IRC'97*, Nuremberg, Germany, 30<sup>th</sup> June 1997
- ISO 37**, 2005: Rubber, vulcanized or thermoplastic – Determination of tensile stress-strain properties, *International Organization for Standardization*
- ISO 247**, 2006: Rubber – Determination of ash, *International Organization for Standardization*
- ISO 815**, 2008: Rubber, vulcanized or thermoplastic – Determination of compression set – Part 1: At ambient or elevated temperature, *International Organization for Standardization*
- ISO 868**, 2003: Plastics and ebonite – Determination of indentation hardness by means of a durometer (Shore hardness), *International Organization for Standardization*

- ISO 2781**, 2008: Rubber, vulcanized or thermoplastic – Determination of density, *International Organization for Standardization*
- ISO 4649**, 2002: Rubber, vulcanized or thermoplastic – Determination of abrasion resistance using a rotating cylindrical drum device, *International Organization for Standardization*
- ISO 23529**, 2004: Rubber – General procedures for preparing and conditioning test pieces for physical test methods, *International Organization for Standardization*
- İnaler, E.**, 2007: Accelerated aging of elastomers in aqueous media, *M.Sc. Thesis*, METU, Ankara
- İşlier, M.B.**, 2008: Effects of compatibilizer type and processing parameters on mechanical properties of polypropylene-clay nanocomposites prepared by melt mixing, *M.Sc. Thesis*, Boğaziçi University, İstanbul
- Karşal, Ç.**, 2008: Preparation and physical characterization of clay/EPDM nanocomposites, *M.Sc. Thesis*, İzmir Institute of Technology, İzmir
- Kempermann, T., Koch, S., Summer, J.**, 1993: Manuel for rubber industry, Bayer AG, Germany, 237
- Kim, K., VanderKooi, J.**, 2004: Temperature effects of silane coupling on moisture treated silica surface, *Journal of applied polymer science*, **95**, 623-633
- Loadman, J.**, 2005a: Tears of the tree: The story of rubber – A modern marvel – Oxford University Press, United Kingdom, xxv
- Loadman, J.**, 2005b: Tears of the tree: The story of rubber – A modern marvel – Oxford University Press, United Kingdom, 188-206
- Moribe, T.**, 2008: Advanced mixing technologies of intermeshing mixer for silica-filled compound, *Rubber World Magazine*, 29-32
- Morton, M.**, 1987a: Rubber technology (third edition), Van Nostrand Reinhold, USA, 86-94
- Öztürk, E.**, 2008: Farklı kauçuk karışımlarının vulkanizasyonuna hızlandırıcıların etkisi, *M.Sc. Thesis*, Sakarya University, Sakarya
- Ramier, J., Gauthier, C., Chazeau, L., Stelandre, L., Guy, L.**, 2006: Payne Effect in Silica-Filled Styrene-Butadiene Rubber: Influence of Surface Treatment, *Journal of Polymer Science Part B*, **45**, 286-298
- Rodgers, B.**, 2004: Rubber compounding: Chemistry and applications, Marcel Dekker Inc., USA, Chapter 8
- Rosca, I.D., Vergnaud, J.M.**, 2003: Rheometers with square root of time-temperature programming for the cure of rubbers, *Polymer*, **44**, 4067-4074
- Simpson, R.B.**, 2002a: Rubber basics, Rapra Technology LTD., United Kingdom, 89-90
- Simpson, R.B.**, 2002b: Rubber basics, Rapra Technology LTD., United Kingdom, 121-153

**Siriwardena, S., Ismail, H., Ishiaku, U.S.,** 2001: A comparison of white rice husk ash and silica as fillers in ethylene-propylene-diene terpolymer vulcanizates, *Polymer International*, **50**, 707-713

**Url-1** <<http://www.pcimag.com>>, accessed at 30.04.2010





## **CURRICULUM VITA**

**Candidate's full name :** Eren DALGAKIRAN

**Place and date of birth :** İstanbul, 17.12.1984

**Permanent Address :** Şehit Mücahit Sokak Maltepe/İstanbul

**Universities and  
Colleges attended :** Yıldız Technical University / Chemical Engineer