REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE EFFECT OF Sb_2O_3/DBDPE RATIO ON THE FLAME RETARDANCY AND PHYSICO-MECHANICAL PROPERTIES OF EPDM ELASTOMER

ŞİRİN ÇAVUŞOĞLU

MSc. THESIS
DEPARTMENT OF CHEMICAL ENGINEERING
PROGRAMME OF CHEMICAL ENGINEERING

ADVISER
ASSIST. PROF. DR. EMEL AKYOL

ISTANBUL, 2014

T.C.
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE EFFECT OF Sb_2O_3/DBDPE RATIO ON THE FLAME RETARDANCY AND PHYSICO-MECHANICAL PROPERTIES OF EPDM ELASTOMER

prepared by Şirin ÇAVUŞOĞLU was accepted for the degree of **Master of Science in Chemical Engineering Department, Yıldız Technical University** by the jury below in 02.01.2014.

Thesis Advisor
Assist. Prof. Dr. Emel Akyol
Yıldız Technical University

Co-Advisor
Prof. Dr. Mualla Öner
Yıldız Technical University

Jury Members
Assoc. Prof. Dr. Emel Akyol
Yıldız Technical University

Prof. Dr. Mualla Öner
Yıldız Technical University

Prof. Dr. Ayfer Saraç
Yıldız Technical University

Prof. Dr. Zuhal Turgut
Yıldız Technical University

Assoc. Prof. Dr. Seyfullah Keyf
Yıldız Technical University

This work was supported by Yıldız Technical University Research Projects Coordination, Project Number 2012-07-01-YL06.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis advisor Assist. Prof. Dr. Emel Akyol for her guidance, understanding, kind support, encouraging advices, criticism, and valuable discussions throughout my thesis.

I appreciate to my co-advisor Prof. Dr. Mualla Öner for her kind supports during my master education.

I express my special thanks to my chief Hasan Esen and Aktaş Holding laboratory employees and my colleague Merve Kolay to get the study materials and for all her help during my experiments.

I would also like to thank to Assoc. Prof. Dr. Mehmet Doğan from Erciyes University Textile Engineering Department for conducting UL-94 and LOI test apparatus and for all his help during my experiments.

I would also like to thank to TÜBİTAK-BUTAL textile laboratory employees for their helps.

I would sincerely thank to Sibel Çalışkan and Neşe Aslan for their endless friendship, support and help in all parts of my life.

Last but not the least; I wish to express my sincere thanks to my family for supporting, encouraging, and loving me all through my life.

January, 2014

Şirin ÇAVUŞOĞLU

TABLE OF CONTENTS

Page

LIST OF SYMBOLS……viii

LIST OF ABBREVIATIONS……ix

LIST OF FIGURES……x

LIST OF TABLES……xii

ABSTRACT……xiii

ÖZET……xv

CHAPTER 1

INTRODUCTION……1

1.1 Literature Review……1
1.2 The Objective of The Thesis……2
1.3 Original Contribution……2

CHAPTER 2

ELASTOMER……3

2.1 Ethylene-Propylene Rubbers & Elastomers……4
2.1.1 EPDM-Filler Composites……4
2.1.2 Properties and Applications……5
2.1.3 Producers……7
2.1.4 Chemistry and Manufacturing Processes……7
2.1.5 Vulcanization of EPDM……9
2.1.6 Vulcanization Accelerators……10
2.1.7 Vulcanization Activators……10
2.2 Fire and Polymers……11
2.2.1 The Definition of Flame Retardant Polymeric Materials ……11
2.2.2 The Need For Flame Retardant Polymeric Materials……12
2.2.3 General Concepts of Polymer Combustion……12
2.2.4 General Approaches To Obtain Flame Retardancy in Polymers……15

2.3 What It Means To Be Fire Retardant 16
2.4 Fire Retardant Chemistry 19
2.4.1 Mechanism of Flame Retardancy 21
2.4.1.1 Condensed-Phase Mechanism 21
2.4.1.2 Vapor-Phase Mechanism 21
2.5 Flame Retardant Additives 22
2.5.1 Bromine Compounds in Elastomers 24
2.5.2 General Mechanism of Flame Retardant Additives 25
2.5.3 Synergistic and Catalytic Effects in Flame Retardancy of Polymeric Materials 27
2.5.3.1 Halogen Antimony Synergism 29
2.5.3.2 Antimony Trioxide Synergistic 30
2.5.4 Decabromodiphenylethane 32
2.6 Flame Retardancy and Mechanical Retardancy 33
2.7 Compounding Basics 33
2.7.1 Compound 34
2.7.2 The Formula 35
2.7.3 Formula Mixing 36
2.8 Rubber Processing Techniques 36
2.8.1 Mixing 36
2.8.2 Vulcanization Techniques 37
2.8.2.1 Press Vulcanization 38
2.9 Characterization Techniques 38
2.9.1 UL-94 39
2.9.2 Limiting Oxygen Index (LOI) 40
2.9.3 Rheological Measurements 41
2.9.4 Thermogravimetric Analysis (TGA) 46
2.9.5 Differential Scanning Calorimeter (DSC) 47
2.9.6 Tensile Test of Elastomers 48
2.9.7 Hardness Test 50
2.9.8 Density Test 50

CHAPTER 3

EXPERIMENTAL 51

3.1 Production of Flame Retardant EPDM Blends 51
3.2 Materials 52
3.2.1 Ethylene Propylene Diene Monomer 52
3.2.2 Fillers 52
3.2.2.1 Carbon Black 52
3.2.2.2 Inactive Filler 52
3.2.3 Curing Activators 53
3.2.3.1 Zinc Oxide and Stearic Acid 53
3.2.4 Process Oil 53
3.2.5 Decabromodphenylethane 53
3.2.6 Antimony Trioxide 55
3.2.7 Accelerator 55
3.2.8 Sulphur 55

3.3 Preparation of Flame Retardant EPDM Blends 55
3.4 Characterization Techniques For Polymer Blends 60
3.4.1 UL-94 60
3.4.2 Limiting Oxygen Index (LOI) 60
3.4.3 Rheological Measurements 61
3.4.4 Thermogravimetric Analysis (TGA) 61
3.4.5 Diffrential Scanning Calorimeter (DSC) 61
3.4.6 Tensile Test of Elastomers 61
3.4.7 Hardness Test 62
3.4.8 Density Test 62

CHAPTER 4

RESULTS 63

4.1 Rheological Results 63
4.2 Flammability Properties 68
4.2.1 LOI Results 68
4.2.2 UL-94 Results 70
4.3 Thermal Properties 71
4.3.1 Thermogravimetric Analysis Results 71
4.3.2 Differential Scanning Calorimeter Results 73
4.4 Mechanical Properties 74
4.4.1 Tensile Test Results 74
4.4.2 Hardness Test Results 77
4.4.3 Density Test Results 77

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS 79

REFERENCES 81

APPENDIX-A

RHEOLOGICAL TEST REPORTS 89

APPENDIX-B

TGA-DTA, DSC RESULTS 95

APPENDIX-C

MECHANICAL TEST REPORTS 99

CIRRICULUM VITAE 105

LIST OF SYMBOLS

ML	Minimum torque
MH	Maximum torque
t90	Optimum cure time
ts2	Scorch time
V-0	Specimens must not burn with flaming combustion for more than 10 seconds after either test flame application
V-1	Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application
V-2	Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application, specimens can drip flaming particles that ignite the cotton
UL-94	The standard for safety of flammability of plastic materials for parts in devices and appliances testing
T_g	Glass transition temperature
T_c	Crystallization temperature
T_m	Melting temperature
T_D	Decomposition temperature
L	Stretched length
L_o	Original length

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATO	Antimony Trioxide
DBDPE	Deca Bromo Diphenyl Ethane
DBDPO	Deca Bromo Diphenyl Oxide
DSC	Differential Scanning Calorimetry
EEF	Flame Retardant Effectiviy
EPDM	Ethylene Propylene Diene Terpolymer
EPM	Ethylene Propylene Polymers
FR	Flame Retardant
LOI	Limiting Oxygen Index
MDR	Moving Die Rheometer
NBR	Nitrile Rubber
ODR	Oscillating Disc Rheometer
OI	Oxygen Index
Phr	Parts Per Hundred Rubber
PBDD	Polybrominated Dibenzo-p-dioxine
PBDE	Polybrominated Diphenyl Ethers
PBDF	Polybrominated Dibenzofuranes
PE	Polyethylene
PP	Polypropylene
PVC	Poly Vinyl Chloride
SBR	Styrene Butadiene Rubber
TGA	Thermo Gravimetric Analysis

LIST OF FIGURES

Page

Figure 2. 1 (a) Structure of EPM (b) Structure of EPDM 9
Figure 2. 2 Four individual stages involved polymer flammability 13
Figure 2. 3 Combustion process 14
Figure 2. 4 Combustion cycle 14
Figure 2. 5 Stages of a fire 17
Figure 2. 6 The fire cycle 18
Figure 2. 7 General mechanisms of flame retardant additives 26
Figure 2. 8 Molecular structure of Sb_2O_3 31
Figure 2. 9 Molecular structure of decabromodiphenylethane 32
Figure 2. 10 The effect of processing on heat history 33
Figure 2. 11 Schematic view of an internal mixer 37
Figure 2. 12 The schematic view of the UL-94 test 39
Figure 2. 13 The schematic representation of LOI test 41
Figure 2. 14 Typical oscillating disc curemeter curve 43
Figure 2. 15 Normal ODR curve 43
Figure 2. 16 Detailed oscillating curve 44
Figure 2. 17 Shows a TA thermogram of an elastomer compound 47
Figure 2. 18 A typical DSC curve showing the transitions in a system 48
Figure 2. 19 Rubber “dumbell” tensile test sample 49
Figure 3. 1 TGA curve of decabromodiphenylethane 54
Figure 3. 2 YI-TZUNG laboratory intensive mixer 56
Figure 3. 3 YI-TZUNG MT2-2 Basic model laboratory mill 57
Figure 3. 4 Alpha technologies MDR 2000 moving die rheometer 58
Figure 3. 5 Compression type laboratory-press 59
Figure 3. 6 Zwick Z10 tensometer 59
Figure 3. 7 FTT fire testing technology,elevated temperature oxygen index apparatus 60
Figure 3. 8 The schematic drawing of LOI 61
Figure 3. 9 Tensile test specimen 62
Figure 3. 10 Durometer 62
Figure 3. 11 Pcynometer 62
Figure 4. 1 Rheometer curve of ALFT 398 sample 64
Figure 4. 2 Rheometer curve of ALFT 399 sample 65
Figure 4. 3 Rheometer curve of ALFT 400 sample 65
Figure 4. 4 Rheometer curve of ALFT 401 sample 65
Figure 4. 5 Rheometer curve of ALFT 402 sample 66

Figure 4. 6 Comparison of rheometer curve 66
Figure 4. 7 Cross-linked complex 67
Figure 4. 8 LOI values of EPDM Blends 70
Figure 4. 9 TGA curves of EPDM Blends 71
Figure 4. 10 DSC curves of polymer blends 74
Figure 4. 11 Tensile strength of EPDM/DBDPE and Sb_2O_3 blends at break 76
Figure 4. 12 Elongation at break values of EPDM/DBDPE and Sb_2O_3 blends 76
Figure 4. 13 Hardness of EPDM/DBDPE and Sb_2O_3 blends 77
Figure 4. 14 Density values of EPDM/DBDPE and Sb_2O_3 blends 78

LIST OF TABLES

		Page
Table 2. 1	Properties of ethylene-propylene elastomers	7
Table 2. 2	Formula components and associated properties	35
Table 2. 3	Criteria for UL-94 classifications	40
Table 2. 4	Tensile test parameters	49
Table 3. 1	Typical properties of decabromodiphenylethane	54
Table 3. 2	Typical properties of antimony trioxide	55
Table 3. 3	Mixing formulas of untreated and treated EPDM	56
Table 3. 4	Rheological parameters of rubber	58
Table 4. 1	Rheometer test results of flame-retardant EPDM formulations	64
Table 4. 2	The ΔLOI value of EPDM containing DBDPE and Sb_2O_3	69
Table 4. 3	UL-94 and LOI values of untreated and treated EPDM	70
Table 4. 4	Typical TGA thermograms of EPDM blends	72
Table 4. 5	Melting points of EPDM blends	73
Table 4. 6	Mechanical properties of untreated and treated EPDM samples	75

ABSTRACT

THE EFFECT OF Sb_2O_3/DBDPE RATIO ON THE FLAME RETARDANCY AND PHYSICO-MECHANICAL PROPERTIES OF EPDM ELASTOMER

Şirin ÇAVUŞOĞLU

Department of Chemical Engineering

MSc. Thesis

Adviser: Assist. Prof. Dr. Emel AKYOL

Co-Adviser: Prof. Dr. Mualla ÖNER

The flammability of ethylene-propylene-diene terpolymer (EPDM) filled with decabromodiphenylethane (DBDPE) and antimony trioxide (Sb_2O_3) is investigated. The effects of DBDPE and Sb_2O_3 on flammability and physico-mechanical properties of EPDM mixture is examined.

In order to determine the optimum DBDPE/Sb_2O_3 ratios in EPDM mixture, the amount of DBDPE and Sb_2O_3 has been changed while all the other parameters were kept constant. EPDM blends that contains with different amounts of flame retardants mixed in laboratory-mixer and vulcanized in compression type laboratory-press. While rheometer tests were done in semi product step, density, hardness, tensile strength, elongation at break tests have been done to the final product for each formulation.

To compare the results limiting oxygen index (LOI) and UL-94 flammability tests, thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used. The best result for flame retardant properties was found for the blend contains 20 phr DBDPE and 10 phr Sb_2O and the LOI's of this mixture was found as 25.6. The results showed that flame retardancy is inadequate when DBDPE and Sb_2O_3 were used alone but combination of DBDPE and Sb_2O_3 is increased flame retardancy of EPDM. The results showed that increasing content of Sb_2O_3 in DBDPE/ Sb_2O_3 improved the flame retardant property and thermal stability of EPDM.

While the addition of DBDPE and Sb_2O_3 flame retardants improved the flame retardation of EPDM, it caused deterioration of tensile strength and elongation at break of EPDM.

Keywords: EPDM, flame retardation, antimony trioxide, decabromodiphenylethane, synergism

ÖZET

Sb_2O_3/DBDPE ORANININ EPDM ELASTOMERİNİN ALEV GECİKTİRİCİLİK VE FİZİKO-MEKANİKSEL ÖZELLİKLERİ ÜZERİNE ETKİSİ

Şirin ÇAVUŞOĞLU

Kimya Mühendisliği Anabilim Dalı

Yüksek Lisans Tezi

Tez Danışmanı: Yrd. Doç. Dr. Emel AKYOL

Eş Danışman: Prof. Dr. Mualla ÖNER

Dekabromodifeniletan (DBDPE) ve antimon trioksit (Sb_2O_3) alev geciktiricileri ile desteklenmiş etilen-propilen dien terpolimerinin alevlenmesi incelenmiştir.

Tüm diğer parametreler sabit tutularak EPDM (etilen propilen dien terpolymer) karışımı içinde optimum DBDPE/Sb_2O_3 oranlarını tespit etmek amacıyla, farklı DBDPE ve Sb_2O_3 miktarlarında çalışılmıştır. Farklı miktarlarda alev geciktirici içeren EPDM karışımları laboratuvar mikserinde karıştırılmış ve laboratuvar presinde vulkanize edilmiştir. Farklı her bileşim için yarı mamul aşamasında reometre testleri, mamul aşamasında ise yoğunluk, sertlik, kopma mukavemeti ve kopma uzaması testleri yapılmıştır.

Ayrıca mamulün sınırlayıcı oksijen indeksi (LOI) ve UL-94 alev testleri, termo-gravimetrik analizi (TGA), diferansiyel taramalı kalorimetre (DSC) analizi gerçekleştirilmiştir. Alev geciktirme özellik için en iyi sonuç 20 phr DBDPE ve 10 phr Sb_2O_3 içeren EPDM karışımında elde edilmiş, bu karışımın LOI değeri 25,6 bulunmuştur. Sonuçlar, DBDPE ve Sb_2O_3'nin tek başına kullanıldığında alev geciktiriciliğin yetersiz olduğunu, ancak DBDPE ve Sb_2O_3' in birlikte kullanımıyla halojen-antimon sinerjisi ile EPDM'in alev geciktiriciliğinin arttığını gösterdi. Karışım içindeki Sb_2O_3 miktarı arttıkça, EPDM'in alev geciktiricilik özelliği ve termal kararlılığını arttı.

DBDPE ve Sb_2O_3 alev geciktiricilerinin ilavesinin EPDM'in alev geciktirme özelliğini artırdığı, çekme dayanımı ve kopma uzamasını olumsuz etkilediği belirlendi.

Anahtar Kelimeler: EPDM, alev geciktirme, antimon trioksit, dekabromodifeniletan, sinerji

CHAPTER 1

INTRODUCTION

1.1 Literature Review

The polyolefins are a major class of plastic (or elastomer) used in wire and cable, other electrical and electronic applications, automotive parts, roofing, and seating. They present challenges in applications requiring flame retardancy due to high heat of combustion and low char-forming tendency. Furthermore polyolefins usually accept high loadings of flame retardant additives without losing useful properties. Rubbery copolymers as EP (ethylene propylene), EPDM (ethylene propylene diene monomer), other olefin copolymers, and diene elastomers generally accept loadings of flame retardant additives as retaining useful properties [1].

Polymers have been used in many fields of industrial applications due to their spesific mechanical, thermal and electrical properties. The flame retardation behavior that one of the important properties for polymers, can be improved by using flame-retardants such as decabromodiphenylethane and antimony trioxide. But in some cases these flame retardant systems have some disadvantages such as a more additive amount of filler which may cause to the low flexibility and poor mechanical properties of end products, difficulties in processing. So halogenated compounds should be used in the optimal levels as flame retardants [2, 3].

Antimony trioxide (Sb_2O_3) has long been known as a synergistic agent with halogen, which is widely used as a flame retardant in plastics, rubber, textile, and coatings [4].

A usual mode of use of halogenated flame retardants is to combine them with antimony oxide, a strong synergist which works through the formation of flame-

quenching antimony trichloride or tribromide, i.e. a vapor-phase mechanism of action [1].

1.2 The Objective of The Thesis

Ethylene propylene diene terpolymer (EPDM), as one of the most useful synthetic rubbers composed of ethylene, propylene and unsaturated diene, is resistant to heat, light, ozone, and UV radiation and has been widely used in electrical applications for a long time [5, 6]. However, special precautions must be taken when it is applied in electrical engineering due to its flammability hazard. Therefore, enhancement of its flame resistance and thermal stability becomes a very important requirement. The aim of this study is to improve flame retardation of EPDM without deterioration of mechanical properties.

1.3 Original Contribution

Flame retardation is a technology by which the normal degradation or combustion of polymers is altered by addition of certain chemicals. Some polymers are inherently, to a relative degree, fire retardant or smoke retardant and their fire performance is acceptable for certain applications. However, for many polymers, it is necessary to improve their fire performance by incorporating commercially available flame retardant [7]. Traditionally, the halogenated organic compounds were well known flame retardant additives for the host polymers. They were generally used in incorporation with antimony trioxide compounds to enhance their flame retardant efficiency [8]. On the whole, flame retardant systems based on halogenated organic compounds frequently had a negative effect on mechanical properties of the polymers. The presence of antimony trioxide acting in synergy with the halogenated organic compounds created interfaces with the host polymers, which may lead to a deterioration of tensile strength and elongation at break [9].

Decabromodiphenylethane (DBDPE) and Sb_2O_3 had little flame retardation effect on EPDM when they were used alone. DBDPE/Sb_2O_3 combination had very good flame retardation and could display synergism in EPDM. In this study DBDPE and Sb_2O_3 were used together in order to get the best result for flame retardation of EPDM.

CHAPTER 2

ELASTOMER

Elastomers have been played vital role in the human life since the beginning of life. The applications spectrum of elastomers has already far exceeded that of any other class of materials available to human. Current applications of elastomers have extended from adhesives, domestic appliances, coatings, foams, packaging materials, textile and sporting goods to transportations, building infrastructures, space explorations and electronic, medical and optical devices.

All elastomeric materials are composed of macromolecules of long-chains with low physico-mechanical properties. Various ingredients such as reinforcement fillers, crosslinking agents, anti-oxidants, process aids, tackifiers, and colorants are added to elastomers for imparting desired properties [10]. After vulcanization (cross linking) these materials become rubber with improved properties. The base elastomer for a particular application is selected on the basis of final required properties. The selected base elastomer limits the choice of reinforced fillers. Both elastomer and fillers then further define the selection of other necessary ingredients such as curing package, process aids, plasticizer etc and processing methods e.g. mixing and curing etc.

The main shortcoming of temperature vulnerability of the elastomers has been removed by vulcanization. Goodyear was the first to discover accidentally the fact that rubber could be transformed to hard vulcanized material by the application of sulfur in year 1839 [11]. Goodyear's novelty inspired the development of the rubber industry as vulcanized rubbers were much more durable than un-vulcanized. However, the major draw back of low mechanical properties was still remained unsolved problem despite

Goodyear's discovery. Mathews and coworkers, in 1904 found that carbon black when blended with natural rubber significantly increased mechanical properties of the rubber [12, 13]. The discovery of the reinforcing effect of carbon black had a profound effect on the production of rubbers and manufacturers started to use various types of fillers to enhance the mechanical properties of the rubbers. The purpose was not only to improve the mechanical properties but also to increase the processability and lower the cost of the elastomers composites.

In present study an effort has been made to quantify the effects of flame retardants types of fillers loadings on above mentioned properties of ethylene–propylene–diene terpolymers (EPDM). Decabromodiphenylethane and antimony trioxide have been used as flame retardant additives. Since therefore, it is aimed that to bring in non-combustibility properties to EPDM rubber which has many application areas.

2.1 Ethylene-Propylene Rubber & Elastomers

EPDM rubber (ethylene propylene diene terpolymer a type of synthetic rubber, is an elastomer which is characterized by a wide range of applications. The E refers to ethylene, P to propylene, D to diene. EPDM rubber is closely related to ethylene propylene rubber (ethylene propylene rubber is a copolymer of ethylene and propylene whereas EPDM rubber is a terpolymer of ethylene, propylene and a diene-component) [14].

2.1.1 EPDM-Filler Composites

EPDM is the fastest growing elastomer on industrial level as it is more stable than other conventional elastomers, such as silicon rubber, butadiene rubber, butyl rubber, acryl nitrite rubber, natural rubber and isoprene rubbers. In EPDM terpolymers, ethylene and propylene monomers provide a saturated backbone and non-conjugated diene monomers provide un-saturations [15]. The prominent characteristics of EPDM are excellent resistance to ozone and oxidation without the use of anti-degradants, low temperature flexibility, color stability and thermal aging resistance [16]. EPDM are amorphous elastomers and exhibit weak physico-mechanical properties [17, 18]. Reinforced fillers and other additives are generally added to enhance the physicomechanical properties of EPDM [19]. One of the most important characteristic

of EPDM is it ability to accommodate large quantities of fillers and other additives without affecting processability and without creating unnecessary instability in the composites structure [20, 21]. So various purpose based EPDM-filler composites can easily be prepared by compounding various types and amount of fillers to EPDM without the use of process oil which degrades composites properties in melts as well as in solid state. One of the most important application of EPDM-fillers composite is to be used as fire-retardant product for automobile tyres, rubber footwear, hoses, tapes, insulating layer and sheath, damping materials and other general rubber products.
Polymers are known for their relatively high flammability. In many aspects, the combustion of polymers is similar to the combustion of many other solid materials.

However, the tendency of polymers to spread flame away from a fire source is critical because many polymers melt and tend to produce flammable drips or flows. Therefore, testing the combustibility of polymeric products under conditions close to those of the final application or even when assembled with other materials is always important [22].

The use of EPDM blends has been continuously growing in various industrial domains for several decades. In some cases, however, these materials exhibit poor thermal resistance. Nonetheless, thermal resistance can be reinforced conveniently by a number of approaches, including the addition of fillers, such as flame retardants. [23, 24]. Obviously, flame retardants are an important part of polymer formulation for applications, in which polymers have a significant chance of being exposed to an ignition source (electrical and electronic goods), where polymers are easily ignited (upholstered furniture) or where a fire spreads quickly and causes serious problems (associated with building materials and transportation) when evacuating people.

2.1.2 Properties and Applications

Ethylene-propylene rubbers & elastomers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and general-purpose applications. Sales have grown to 870 metric tons (or 1.9 billion pounds) in 2000 since commercial introduction in the early 1960's. Polymerization and catalyst technologies in use today provide the ability to design

polymers to meet specific and demanding application and processing needs. Versatility in polymer design and performance has resulted in broad usage in automotive weather-stripping and seals, glass-run channel, radiator, garden and appliance hose, tubing, belts, electrical insulation, roofing membrane, rubber mechanical goods, plastic impact modification, thermoplastic vulcanizates and motor oil additive applications.

Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather aging due to their stable, saturated polymer backbone structure. Properly pigmented black and non-black compounds are color stable. As non-polar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies, phosphate esters and many ketones and alcohols. Amorphous or low crystalline grades have excellent low temperature flexibility with glass transition points of about minus 60°C.

Heat aging resistance up to 130°C can be obtained with properly selected sulfur acceleration systems and heat resistance at 160°C can be obtained with peroxide cured compounds. Compression set resistance is good, particularly at high temperatures, if sulfur donor or peroxide cure systems are used.

These polymers respond well to high filler and plasticizer loading, providing economical compounds. They can develop high tensile and tear properties, excellent abrasion resistance, as well as improved oil swell resistance and flame retardance. A general summary of properties is shown in Table 2. 1 below.

Table 2. 1 Properties of ethylene-propylene elastomers [25, 26, 27]

Polymer Properties	
Mooney Viscosity, ML 1+4 @ 125°C	5-200+
Ethylene Content, wt. %	45 to 80 wt. %
Diene Content, wt. %	0 to 15 wt. %
Specific Gravity, gm/ml	0.855-0.88 (depending on polymer composition)
Vulcanizate Properties*	
Hardness, Shore A Durometer	30 A to 95 A
Tensile Strength, MPa	7 to 21
Elongation, %	100 to 600
Compression Set B, %	20 to 60
Useful Temperature Range, °C	-50° to +160°
Tear Resistance	Fair to Good
Abrasion Resistance	Good to Excellent
Resilience	Fair to Good (stable over wide temp. ranges)
Electrical Properties	Excellent

* Range can be extended by proper compounding. Not all of these properties can be obtained in one compound.

2.1.3 Producers

Major producers and suppliers of EPDM and EPM are Bayer Polymers, Crompton Corp., Exxon-Mobil Chemical Co., DSM Elastomers, Dupont Dow Elastomers, Herdillia, JSR, Kumho Polychem, Mitsui Chemicals, Polimeri Europa, and Sumitomo Chemical Co. Wide ranges of grades are available worldwide to provide solutions to many product requirements.

2.1.4 Chemistry and Manufacturing Processes

Ethylene-propylene rubbers use the same chemical building blocks or monomers as polyethylene (PE) and polypropylene (PP) thermoplastic polymers. These ethylene (C_2) and propylene (C_3) monomers are combined in a random manner to produce rubbery and stable polymers. A wide family of ethylene-propylene elastomers can be produced ranging from amorphous, non-crystalline to semi-crystalline structures depending on

polymer composition and how the monomers are combined. These polymers are also produced in an exceptionally wide range of Mooney viscosities (or molecular weights). The ethylene and propylene monomers combine to form a chemically saturated, stable polymer backbone providing excellent heat, oxidation, ozone and weather aging. A third, non-conjugated diene monomer can be terpolymerized in a controlled manner to maintain a saturated backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification chemistry [25, 26, 27].

EPDM was first made by Professor K. Ziegler by the polymerization of ethylene and propylene in the presence of Ziegler-Natta catalyst [28]. Polyethylene is a crystalline plastomer at room temperature and can pass through an elastomeric phase on heating. If propylene is incorporated in the polyethylene chain during its crystallization, saturated elastomer material, ethylene-propylene-monomer (EPM) produces. But the addition of a third monomer, diene during the copolymerization of ethylene and propylene results an unsaturated rubber, EPDM [29-30]. In ASTM standard D-1418 for EPDM, 'E' stands for ethylene 'P' for propylene 'M' for polymethylene and 'D' for diene [31]. The third monomer is usually non-conjugated diene, such as 2-ethylidene-5-norbornene, 1, 4-hexadiene or dicyclopetadiene. The structures of EPM and EPDM are shown in Figure 2. 1 [32]. It is clear from Figure 2. 1 that in EPDM, ethylene and propylene monomers provide a saturated backbone and nonconjugated diene provides un-saturation in side chains. The unsaturated bonds located on the side chain of EPDM make the vulcanization process easily while preventing the instability of the main chain [17].

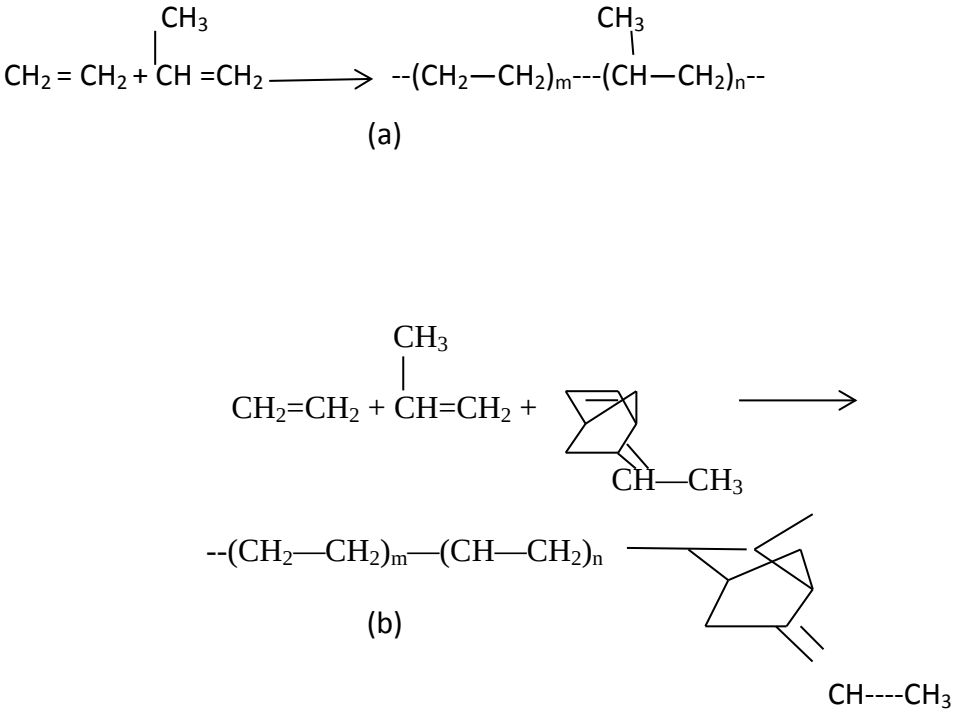


Figure 2. 1 (a) Structure of EPM (b) Structure of EPDM [17]

2.1.5 Vulcanization of EPDM

All elastomers are high molecular weight viscous liquid consisting of long chains of one or more types of molecules. The chains of uncured elastomer may readily slide past one another, take up variety of configurations and can disentangle under applied forces. Vulcanization produce chemical links between the loosely polymeric chains to form a network, thereby transforming the material from a viscous liquid to a tough elastic solid of permanent shape with no plastic deformation zone [33]. Sulfur is the first and most widely used vulcanizing agent for rubber containing dienes in their structure since its discovery by Goodyear in 1839 and subsequently by John Hancock in 1843 [34]. These dienes containing elastomers are vulcanized by sulfur in the presence of the organic activators and accelerators with the application of heat [34].

The following two types of vulcanizations systems are available for the rubber cross linking;

1. Sulfur vulcanization.

2. Peroxide vulcanization

The choice of particular type of the system is depended on the main structure of the rubber. Polymers having un-saturations in their structure can be cross linked by sulfur as well as by peroxides. However, polymers containing no un-saturations in their structure can not be cross linked by sulfur. However, majority of rubber are modified for sulfur cross-linking because of simplicity and ability to form cross link chains of various length and distributions [35].

2.1.6 Vulcanization of Accelerators

Cross-linkings with sulfur alone is quite inefficient and time consuming. Much of the sulfur is not involved in cross-linkings between chains and the networks are unstable and have poor aging resistance. The poor aging and slow cure rate by sulfur alone was

identified by Goodyear and others in the early age of sulfur vulcanization development [36, 37]. Moreover, bloomings occur when sulfur in high concentration is used for fast curing. Onsenlenlgar, in 1906 discovered aniline as accelerator for sulfur vulcanization. Now a days accelerators in sulfur vulcanization are not only used to increase the rate and efficiency of curing but also increased resistance to heat and aging [17, 37]. The selection of the accelerators depends on the nature of the base polymer, the designing product service life and the designing parameters. The most widely used accelerators are guanidines, thiazoles, dithiocarbamates, xanthates, and thiurams. Of these, the guanidinetype accelerators, such as diphenyl guanidine (DPG) have relatively slow onset of vulcanization which is desirable to prevent pre-mature vulcanization or scorching.

The vulcanization of the EPDM by sulfur is very slow as the EPDM contains relatively low and un-reactive dienes than the available rubbers such as Natural rubber, SBR, NBR etc. Therefore high dose of accelerator to sulfur curing is required.

2.1.7 Vulcanization Activators

Most of the vulcanization accelerators require activators for best performance as activators extract the full potential from the accelerators. Zinc oxide (ZnO) is the most widely used inorganic activator for accelerators. Nowaday's most of the rubber manufacturers utilize the combination of the inorganic activator, ZnO and organic

activators such as stearic acid. Stearic acid acts as plasticizer to reduce the viscosity and solubalize ZnO to form zinc stearate [38]. Zinc stearate provides means for the formation of the zinc-accelerator complex resulting delay in scorch and enhances vulcanization efficiency. Paris et al showed the synergetic effect of ZnO on the sulfur vulcanization [39]. Zinc stearate also lowers the viscosity of the elastomers and thus enables a rubber compound to be fabricated with less energy and good mixing.

2.2 Fire and Polymers

Fire is an ever present hazard. American homes suffer an unwanted fire every ten seconds. Every 60 seconds there is a fire serious enough to call the fire department. In our lifetime we each have a 40 percent chance of having a fire large enough to cause a fire department to arrive at our door. Every two hours someone in the United States is killed In a home fire, about 4,000 people per year. Some 19,300 people are injured in home fires in a typical year. Over the period 1985-1994 the United States had an average of 2.2 million fires reported each year, causing an average 5,300 civilian deaths, 29,000 injuries, and a $9.4 billion property loss. While the fire problem in the United States is less severe now than it was a decade ago, because the populafion has grown faster than fire casualties, the U. S. fire death rate is still higher than that in most developed nations. Of western industrialized nations the United States ranked behind only Hungary as having the highest per capita fire death rate, with an average of 26.5 deaths per million population. The rate in the United States is more than five times that of Switzerland (5.2 deaths per million population), which had the lowest rate of countries considered. The higher rate of fire in the United States has its origins in several factors including the commitment of fewer resources to fire prevention activities than other nations, a greater tolerance for "accidental" fires, the practice of riskier and more careless behavior, less use of compartmentation and fire resistance in home construction, and the presence of more "stuff' (higher fire load) and a higher use of energy (more ignition sources) than in other countries [40].

2.2.1 The Definition of Flame Retardant Polymeric Materials

The terms flame resistant, flame retardant, fire retardant and fire resistant are all similar terms and can be used interchangeably. The terms “flammable” and

“nonflammable” are rarely used by fire researchers as regards to polymer based compounds. A polymeric material that is flame or fire resistant does not continue to burn or glow once the source of ignition has been removed, although there are some changes in the physical and chemical characteristics. An ideal flame retardant polymeric material must have some special characteristics; high resistance to ignition and flame propagation, a low rate of combustion and smoke generation, low combustibility and toxicity of combustion gases, acceptability in appearance and properties for specific uses and little or no economic penalty [41-43].

2.2.2 The Need for Flame Retardant Polymeric Materials

The need for flame retardant polymeric materials increases in the last years due to the increase of the usage of plastic materials in our daily life, not only in bulk parts but also as films, fibers, coatings and foams. The regulations made by developed countries, especially by European countries, also increased the need for flame retardant polymeric materials in new areas [41, 42].

2.2.3 General Concepts of Polymer Combustion

Polymers are the long-chain molecules that constitute most of our environment, both natural and synthetic. The combustion of polymeric materials, like the combustion of any other fuel material, is a combination of complex physical and chemical processes, which include the transformation of initial products. This whole conversion process may be divided into stages, with specific physical and chemical processes occurring in each of these stages [44]. There are four individual stages involving polymer flammability; heating of flammable substrate (pre-heating), degradation and decomposition, the ignition of flammable gases evolved and combustion and propagation. Four individual stages involved in polymer flammability are shown in Figure 2.2.

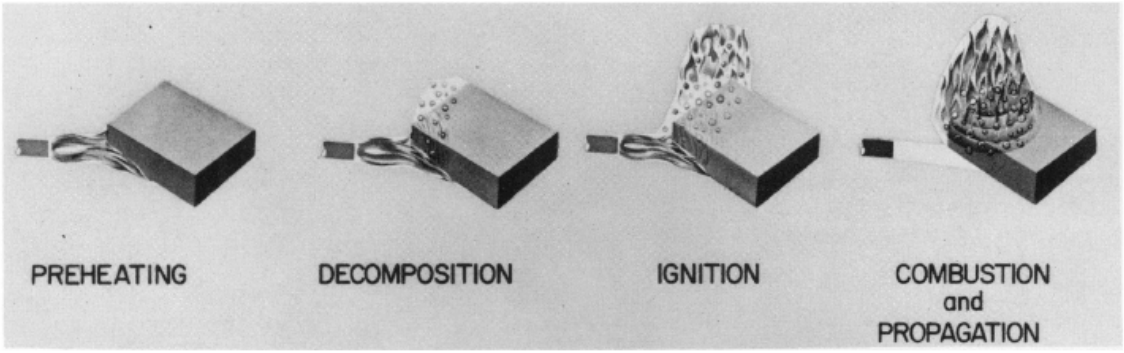


Figure 2. 1 Four individual stages involved polymer flammability [44]

Preheating involves heating of the material by means of an external source which raises the temperature of the material at a rate dependent upon the thermal intensity of the ignition source, thermal conductivity of the material, specific heat of the material and latent heat of fusion and vaporization of the material. When sufficiently heated, the material begins to degrade and it loses its original properties as the weakest bonds begin to break. Gaseous combustion products may be formed that depend on such factors as intensity of external heat, temperature required for decomposition and rate of decomposition. By the effect of ignition source (heat, flame and etc.), the gaseous products can be ignited and combustion starts. Ignitability depends on how quickly the surface can be raised to the ignition temperature. If the heat evolved is larger than the heat consumed during combustion, combustion propagates when the heat source is removed [45, 46].

Contrary to conventional wisdom, solid materials do not burn directly. To burn, solid materials must first be decomposed by heat into shorter chain molecules that eventually vaporize as flammable gases. These flammable gases combine with oxygen in the air to produce visible flames. The presence of H^+ and OH^- free radicals are key to sustaining a fire. These free radical species break down molecules and liberate carbon, which then reacts with oxygen in the air to “burn” [47].

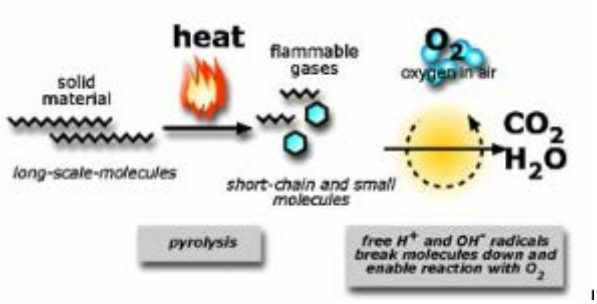


Figure 2. 3 Combustion process [European flame retardants association]

When solid materials do not break down into gases, they will typically smolder and produce a char layer. The char layer acts as a barrier to further flame propagation and can lead the material to self extinguish [47].

The presence of heat, fuel and air in a fire can act in concert to propagate combustion until one or more is removed. Heat causes the thermal degradation of fuel into combustible gases and heats the air, making it more reactive. Flammable gases combine with air to generate a fire. The fire in turn releases heat, which continues the cycle [47].

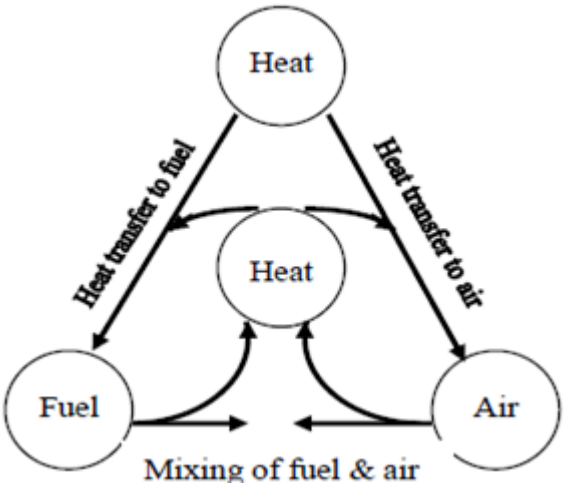


Figure 2. 4 Combustion cycle [European flame retardants association]

In the flames, self-propagation combustion reactions are present. The principal reactions in the flames are free-radical reactions. The flames of the polymers are generally hydrocarbon flames due to the structures of the polymers. In the hydrocarbon flames, H•, O• and OH• radicals are the most important radicals whereas small amount of HO_2•, HCO• and CH_3• radicals are also present. Chainbranching reactions during combustion accelerate the burning process since

more radicals are formed as a result of these reactions [48]. The chain propagating reaction and chain branching reactions can be seen in Equations below [49].

$$CH_4 + O_2 \longrightarrow CH_3\bullet + H\bullet + O_2 \quad (2.1)$$

$$H\bullet + O_2 \longrightarrow OH\bullet + O\bullet \quad (2.2)$$

$$CH_4 + OH\bullet \longrightarrow CH_3\bullet + H_2O \quad (2.3)$$

$$CH_3\bullet + O\bullet \longrightarrow CH_2O\bullet + H\bullet \quad (2.4)$$

$$CH_2O\bullet + OH\bullet \longrightarrow HCO\bullet + H_2O \quad (2.5)$$

$$HCO\bullet + O_2 \longrightarrow H\bullet + CO + O_2 \quad (2.6)$$

$$CO + OH\bullet \longrightarrow CO_2 + H\bullet \quad (2.7)$$

2.2.4 General Approaches to Obtain Flame Retardancy in Polymers

A flame retardant polymeric article can be obtained during polymerization by using flame retardant co-monomers. This is called reactive approach. Flame retardant additive can be added into the polymer. This is called additive approach. Flame retardant polymeric articles can also be obtained by surface modification by grafting flame retardant substances. This is called surface approach. Reactive, additive and surface approaches can be applied both to polymers [50].

Flame retardation is to decrease the flammability of a polymer by altering or retarding the degradation or combustion processes of the polymer with the addition of certain chemicals [51]. These chemicals act through a chemical or physical mechanism and interrupt the combustion cycle in heating, thermal decomposition, ignition or combustion steps [52]. In flame retardancy in polymers, the main aim is to decrease the flammability of a polymer by decreasing the amount and rate of combustible gaseous decomposition product formation [48]. In addition, flame retardancy in polymers aim to decrease the 20 ease of ignition, the flame spread, the fire endurance meaning the speed of fire penetrating through a wall or barrier, the rate of heat release, the smoke evolution and to increase the ease of extinction [48].

There are two types of flame retardant approaches in polymer flame retardancy [48, 52]: (1) reactive type flame retardants and (2) additive type flame retardants. In the

reactive type flame retardation, flame retardant unit containing heteroatoms is chemically incorporated into the polymer either in the chain or as a pendant group. This approach involves designing of a new polymer or modification of the existing polymer. Reactive flame retardation approach is the most effective way since it provides efficient flame retardancy without destroying the original physical and mechanical properties of the polymer. However additive type flame retardants are more common due to economical reasons. In the additive type flame retardants, the flame retardant is mixed with the polymer physically. This approach is widely used since it is very economical and it provides an easy method for the flame retardancy of commercial polymers. However there are some limitations in the additive type flame retardants such as poor compatibility, reduction in mechanical properties and increase in the smoke and CO production [48, 52].

2.3 What It Means to Be Fire Retardant

The term is "fire retardant" or "flame retardant" are not absolute. Combustibility can depend as much on fire conditions as on polymer composition. Whether a material is fire retardant is in the context of the application. And whether a material is fire retardant is very much in the context of tests, tests specifically relevant to the intended application. Fire retardancy is not a single property but a sequence of properties, some more important to a given application than others. The behavior of materials in a fire can be described as follows [53, 54]:

(1) Ease of Ignition - how readily a material ignites.

(2) Flame Spread - how rapidly fire spreads across a surface

(3) Fire Endurance - how rapidly fire penetrates a wall or barrier.

(4) Rate of Heat Release - how much heat is released and how quickly.

(5) Ease of Extinction - how rapidly or how easily the flame chemistry leads to extinction.

(6) Smoke Evolution - amount, evolution rate, and composition of smoke released during stages of a fire.

(7) Toxic Gas Evolution - amount, evolution rate, and composition of gases released during stages of a fire.

A multitude of flammability tests measuring one or more of these properties have been developed over the years. There are more than 100 tests used in the United States. Other countries use different tests and rating systems, often making comparisons difficult. A material acceptable in one country for an application may be rejected in another. A polymer may be more ignition resistant than the parent polymer or another polymer and thus be "ignition resistant" or "flame retardant" but still have insufficient fire performance in the context of tests appropriate for the application. One unifying approach which is increasingly successful is the use of bench scale tests which measure fundamental properties, then using those properties in mathematical models to calculate the impact of candidate materials on the fire performance of the system. Figure 2.5 [55] shows fire as a series of stages [56]. Fire starts with an Ignition source and a first item to be ignited. For an electrical appliance one wants a material which will resist a small electrical arc or a small, short duration flame. One does not want the appliance to be the source of fire. One does not expect an appliance, however, to survive a house fire. Thus ignition resistance is what is required.

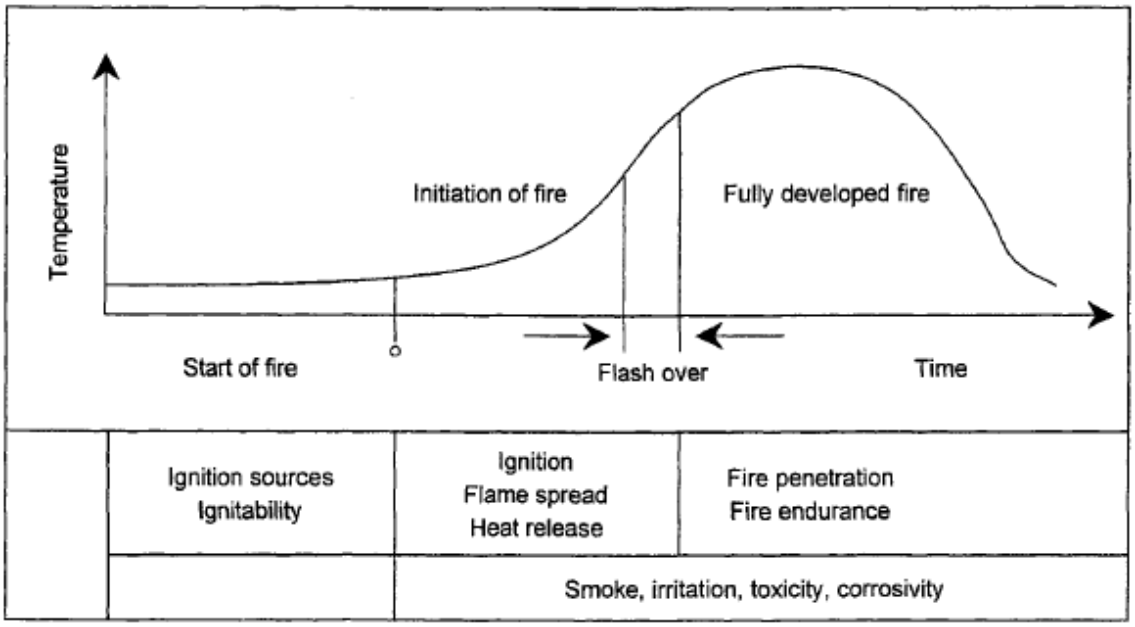


Figure 2. 5 Stages of a fire [55]

Following ignition there is a period of reaction of materials to fire. Once fire fills a compartment, the ability of the compartment to contain fire is at issue. Throughout, smoke and toxic and corrosive gases are emitted.

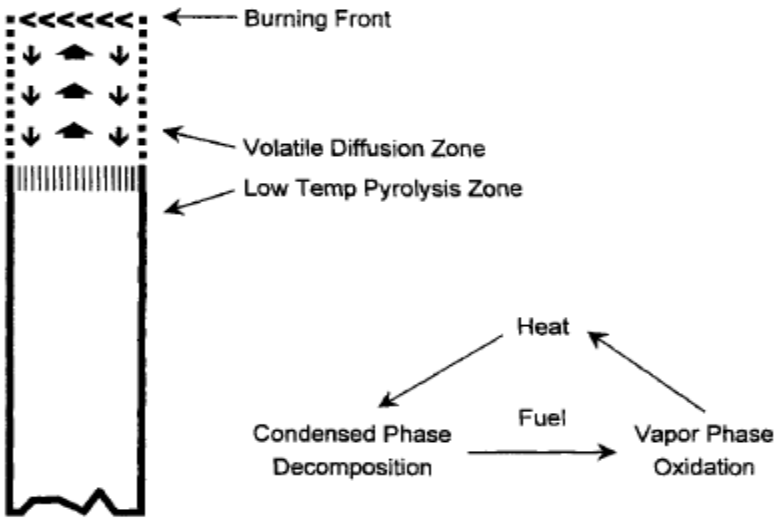


Figure 2. 6 The fire cycle [53-57]

Fire involves the thermal decomposition of materials to give volatile fuel, which oxidizes in the vapor phase to give heat, which continues the cycle.

Given ignition of an initial item, fire begins to spread and heat is released. For a wall covering, for example, flame spread should not be rapid. Indeed, wall coverings and other interior finish are regulated by rate of flame spread. As fire spreads from item to item, more heat is released, and combustible gases rise. A point is reached when fire engulfs the upper part of the room or compartment (flashover). The upper part of the room exceeds 600°C. If a door is open, fire moves down from the ceiling and begins to exit the room. The fire is fully developed. Given a fully developed fire the issue then is the ability of barriers to contain the fire. Can the assembly of materials resist penetration (fire endurance), to allow evacuation and to protect adjacent property? Walls and floors/ceilings are rated for their fire endurance against standard time temperature curves. The answer as to whether a material is fire retardant clearly depends upon its use. A material suitable as an appliance enclosure because of its ignition resistance, would be totally unsuitable as a seal in a wall or floor where the

expectation might be resistance to a room burnout on the other side of the wall or floor for several hours duration [53-57].

2.4 Fire Retardant Chemistry

Polymer combustion occurs in a continuous cycle in Figure 2.6.

Heat generated in the flame is transferred back to the polymer surface producing volatile polymer fragments, or fuel. These fragments diffuse into the flame zone where they react with oxygen by free radical processes. This in turn produces more heat and continues the cycle. Flame retardancy is achieved by interrupting the cycle by one of two methods [53-57].

In the first method, vapor phase inhibition, one introduces changes in the flame chemistry. Reactive species are built into the polymer which are transformed into volatile free-radical inhibitors during burning. These species diffuse into the flame and inhibit radical reactions, particularly the branching radical reaction. As a result, increased energy is required to maintain the flame and the cycle is interrupted.

In the second method, solid phase inhibition, one introduces changes in the polymer substrate. Systems that promote extensive polymer crosslinking at the surface, form a carbonaceous char upon heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning. Other systems evolve water during heating, cooling the surface and increasing the amount of energy needed to maintain the flame [53-57].

Many polymers are intrinsically fire retardant; examples include high temperature aromatic polymers and polyvinyl chloride. Some high temperature materials are stable for a few minutes at extreme temperatures, 600-1000°C, while others can perform at 200-300°C for long periods of time. There are three general types of aromatic structures: linear single-strand polymers such as aromatic polyamides and polyamides based on benzenoid systems, ladder polymers consisting of an uninterrupted sequence of cyclic aromatic or heterocyclic structures, and spiro polymers in which one carbon is common to two rings. Behind each type of structure is the thought that polymers with high aromatic character and very strong bonds between rings produce more char on heating, retaining most of the potential fuel of the original polymer as residue. A good,

though impractical example, is polyphenylene, a crystalline, high-melting substance, with thermal degradation beginning at 500 to 550°C and continuing to 900°C with only 20-30 percent weight loss. Such intrinsically fire retardant materials unfortunately tend to be relatively expensive.

An inexpensive intrinsically fire retardant polymer is polyvinyl chloride. The first step in PVC degradation Is the release of hydrogen chloride and the formation of double bonds. The hydrogen chloride provides vapor phase inhibition and the double bonds crosslink to provide extensive char (rigid PVC).

At the other end of the scale from intrinsically fire retardant polymers are those polymers modified with monomeric fire retardant additives. Fire retardant additives used with synthetic polymers include organic phosphorus compounds, organic halogen compounds, and combinations of organic halogen compounds with antimony oxide. Inorganic fire retardants include hydrated alumina, magnesium hydroxide, and borates. Not all fire retardant additives function well in all polymers. Additives may interact with other resin formulation components such as fillers, stabilizers, and processing aids. To be effective, the fire retardant must decompose near the decomposition temperature of the polymer in order to do appropriate chemistry as the polymer decomposes, yet be stable at polymer processing temperatures [53-57].

An intermediate approach between intrinsically fire retardant polymers and adding simple additives to a resin formulation is the incorporation of fire retardant chemical units directly Into the polymer backbone. In this way one achieves permanent fire retardancy and is better able to maintain the desirable physical properties of the polymer. Monomeric additives may not be permanent, may come to the surface, and may change the polymer's physical characteristics. Fire retardant monomers used as coreactants in polymer synthesis contain appropriate functional groups for incorporation into the chain. Many are halogen compounds, the source of fire retardancy. Generally 10-25 percent halogen Is necessary to impart suitable fire retardancy in polymers, either by additive or backbone incorporation. Phosphorus comonomers have also been used, as have phosphorus-halogen comonomers [53-57].

2.4.1 Mechanisms of Flame Retardancy

There are two mechanisms of flame retardancy in polymers: (1) condensed-phase mechanism and (2) vapor-phase mechanism.

2.4.1.1 Condensed-Phase Mechanism

In condensed phase mechanism, the additive changes the nature of the products of degradation and combustion before volatilization [58]. In other words, flame retardancy is provided by the changes in the polymer substrates [48]. There are two main mechanisms in condensed-phase by which flame retardancy is achieved: (1) char-formation and (2) dehydration. Char-formation is a very important way of flame retardation since it forms a protective layer on the polymer surface which prevents the contact of the polymer with oxygen and heat therefore from further decomposition into fuels for combustion [48, 52]. In addition, char helps the polymer to preserve its structural integrity [48]. Another important flame retardancy mechanism in condensed phase is dehydration. As mentioned before, combustion of a polymer starts by the endothermic heating of the polymer to its decomposition temperature. Another way to decrease the flammability of a polymer is to increase the endothermic heat demand for the thermal decomposition of the polymer [48]. This can be achieved if the system evolves water which will decompose endothermically and cool the pyrolysis zone or other noncombustible gases which will dilute the combustible gases [48, 52].

2.4.1.2 Vapor-Phase Mechanism

In the vapor phase, the flame retardancy is achieved by the trapping of radicals interrupting the exothermic combustion process. In the radical trap theory of flame retardation, radical species from flame retardants compete with the H•, O•, and OH• radicals those are essential for the propagation of the flame [48, 49, 51, 52]. The most important example of radical trapping is in halogenated flame retardants. In halogen-based flame retardants, the bromine or chlorine molecules that are built into the polymer diffuse into the flame zone and create free-radical inhibitors. In the reactions, H•, O•, and OH• radicals are replaced with less reactive Br• and Cl• radical [48, 49]. The radical scavenge reactions can be seen in Equations below[49].

The combustion process in the vapor phase can also be prevented by the physical effects like the suppressant characteristic of an inert gas such as carbon dioxide or nitrogen [49, 52].

Some flame retardants act both in condensed and vapor phases for flame retardancy whereas some flame retardants act only in one phase [48].

$$CH^{+} + Br\bullet \longrightarrow HBr + CH_3 \quad (2.8)$$

$$H\bullet + HBr \longrightarrow H_2 + Br\bullet \quad (2.9)$$

$$OH\bullet + HBr \longrightarrow H_2O + Br\bullet \quad (2.10)$$

$$O\bullet + HBr \longrightarrow Br\bullet\ OH\bullet \quad (2.11)$$

2.5 Flame Retardant Additives

A wide range of flame retardant materials have been developed for polymers, around 150 to 200 different compounds being commercially available. Flame retardants can be classified as additive or reactive compounds. Additive compounds are mixed into polymer during processing, but do not chemically react with polymer. Reactive compounds are polymerized with a resin during processing to become integrated into the molecular network structure. In this study, all flame retardants used are in the class of additive compounds so detailed information is given about additive compounds [59].

Flame retardant additives can be classified as halogen, phosphorus, nitrogen, silicon, and boron containing flame retardants and miscellaneous inorganic additives [44, 52, 59, 60] **.**

Antimony trioxide and brominated flame retardants were used in this study. Accordingly, information is given only about these flame retardants in the following sections.

The specific functionality and modes of retardancy for fire retardant additives and comonomers are as follows [53, 54, 57].

Phosphorus additives: The thermolysis of phosphorus compounds yields phosphorous acids and anhydrides which promote dehydration leading to water vapor and

promotion of carbonaceous char. Reaction cooling is accomplished by the endothermic reduction of phosphorus species by carbon. Formation of a stable, glassy, protective mask of polymetaphosphoric acid is considered a mode of action of phosphorus fire retardants. Phosphorus compounds can also be volatile and Show effectiveness in the vapor phase.

Halogen additives: Halogens show activity in quenching the chain-carrying free radicals present in the flame (O• H• and OH•) In the solid state decomposition zone, halogen acids catalyze char formation OH• (particularly for polyolefins).

Halogen-antimony systems: A chain of reactions leading to volatile antimony halides and oxyhalides provides free-radical quenching in the vapor phase. The end product of the reactions occurring when antimony and halogen are present in the combustion zone is thought to be solid antimony oxide in a finely divided form in the flame. Injecting fine particles into the reaction zone is known to reduce flame propagation rates. Solid state catalysis directs formation of highly stable, intumescent, carbonaceous chars.

Phosphorus-halogen systems: Phosphorus halides and oxyhalides are flame free-radical quenchers and may be more effective than the halogen acids alone. When a single chemical moiety contains both halogen and phosphorus, the relative ease of breakdown of the phosphorus compound enhances the availability of the halogen species.

Phosphorus-nitrogen systems: Phosphorus-nitrogen interaction can alter the course of thermal decomposition to enhance char development. Not all polymers display responses to phosphorus-nitrogen interaction, but composites of plastics with cellulosic materials often show strong positive responses.

Inorganic materials: A number of filler materials of mineral origin contribute volume, structure, and thermal stability to carbonaceous chars once created by other routes. Vaporization of water of hydration is involved in cases like hydrated alumina. The detailed mechanism of the release of water during thermal decomposition of magnesium hydroxide has recently been reported [61]. In other additives catalysis of

dehydrochlorination reactions may occur. Nanocomposites, for example involving silica, have shown recent promise.

Metals and organometallic additives: A variety of metals and organometallic additives have been used. These range from platinum at the parts per million level in silicones, which involves changing decomposition chemistry to yield less energetic volatlles, to incorporation of ferrocene moieties into the backbone of polyurethanes and other polymers. In the ferrocene case char formation is enhanced without enhancement of smoke [62].

As noted above, many fire retardants have both solid phase and vapor phase activity. Identification of the precise mechanism is difficult given that one must uncover complex flame reactions, or reactions in the solid which are transient in nature or which are in an insoluble solid, degraded substrate or char.

2.5.1 Bromine Compounds in Elastomers

Bromine-containing additives have been used in SBR, natural rubber, polychloroprene, EPDM and other elastomers for wire and cable insulation, belts, tubing, seals, roofing, and coated fabrics. These additives are generally used with antimony oxide synergist, and sometimes with smoke suppressants such as a borate, stannate or molybdate. The levels of addition are generally lower than needed with chlorinated additives, and consequently physical properties are well maintained.

However, most of these brominated additives are solids which do not melt at elastomer-compounding temperatures, so that a thorough mixing is needed. Consequently it is helpful to charge the retardant early in the mixing sequence before any rubber-softening ingredients are added. Two mixing passes or predispersion may be helpful. Clays, silica or talc can have favorable effects on flame retardancy. Carbon black can cause extended afterglow in some tests and may need addition of a borate to suppress this. ATH usually has a favorable effect but calcium carbonate, magnesium hydroxide or carbonate may interfere with the action of the brominated flame retardant. Non-phosphate plasticizers will generally require more flame retardant.

Decabromodiphenyl oxide (Albemarle's Saytex 102E, Chemtura's DE83R and ICL Industrial Products FR-1210) is effective in almost all elastomers, generally with

antimony oxide. It is both efficient and inexpensive, and has good high temperature resistance. This additive does have a discoloration tendency when exposed to light, but this is often not a consideration in elastomers. Recent bromination process techniques for increasing purity (avoiding lower brominated analogs) have been patented by Albemarle [63-65] and Chemtura [66]. Ethylenebis(tetrabromophthalimide) (Albemarle BT-93) is more expensive but has advantages of better light and heat stability, and less blooming tendency. In EPDM blended with low density polyethylene, 30 phr of BT-93 and 10 phr antimony oxide gave a V-0 rating and lower levels could reach the wire insulation rating of vertical-wire flame test. By contrast, 30 phr of chloroparaffin and 10 phr of antimony oxide was required to reach V-0 was not achieved. Lower smoke compared to decabromodiphenyl ether is sometimes found with BT-93.

Decabromodiphenylethane is close to decabromodiphenyl ether in performance but avoids some environmental concerns about brominated diphenyl ethers, and has somewhat better thermal stability than the ether [67].

2.5.2 General Mechanism of Flame Retardant Additives

Flame retardant additives differ from each other in terms of chemical structure and certain general mechanisms of action. All flame retardants act chemically and/or physically in the condensed phase and/or in the gas phase by interfering with at least one of the individual stages of burning process [52, 68]. Normally an efficient flame retardant additive will affect more than one of these steps either in physical or in chemical way. The end result in the presence of flame retardant additive is the retardation and final elimination of burning process mechanism [46].

Gas phase active flame retardants act through scavenging free radicals responsible for the branching of radical chain reactions in the flame. This is the chemical action mechanism in the gas phase. Some of the flame retardants produce large amounts of noncombustible gases that dilute the combustible gases, decompose endothermically, and decrease the temperature by absorbing heat. This is the physical action mechanism in the gas phase [22, 68]. In condensed phase mechanism, flame retardant (FR) additives act in two different modes of action. First, flame retardants accelerate the degradation of polymer and increase the dripping of the polymer. By increasing the

dripping behavior of the polymer, fuel source is removed from the combustion zone. Second, flame retardants can leave a layer of carbon (charring) on the polymer surface [68]. The formed intumescent char acts as a physical barrier to reduce the heat and mass (fuel, oxygen) transfer between the gas and condensed phases so it protects the underlying material from the effect of flame. The amount and the properties (integrity, stability and foam structure) of the char determine the flame retarding effect of an intumescent system. The major advantage of this system is the decrease in the heat generated during the combustion due to the formation of carbon rather than formation of CO and CO_2 [69-72].

The schematic representation of general mechanisms of flame retardant additives is given in Figure 2.7 [73].

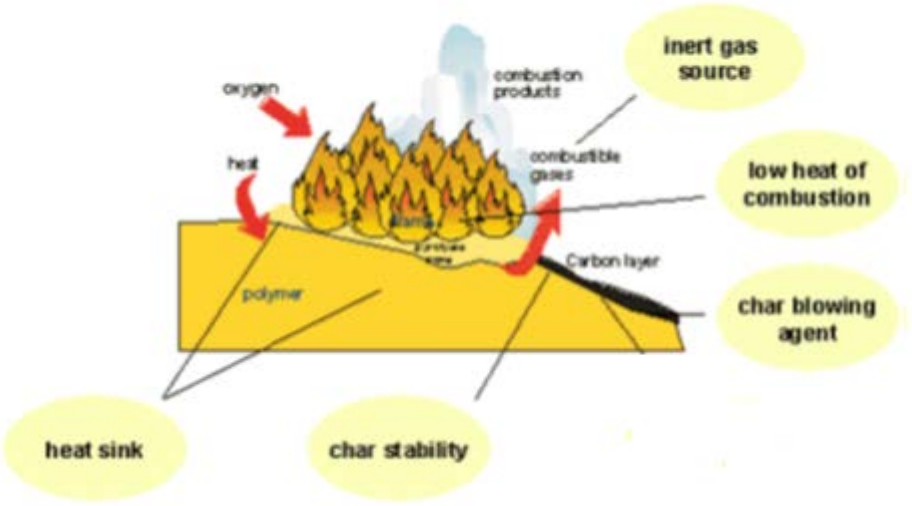


Figure 2. 7 General mechanisms of flame retardant additives [73]

When individual stages of burning process are considered, in the initial heating stage the presence of an effective flame retardant can result by the formation of a glassy layer. This coating is of low thermal conductivity and/or high reflectivity which enables to repel radiant heat from the external source before extensive decomposition of the substrate. Additives that swell on heating to yield an intumescent coating are examples of flame retardants yielding a surface layer with poor thermal conductivity [46, 68].

During the degradation and decomposition stages of the burning process, the flame retardant additive can chemically alter the thermo-oxidative decomposition of the flammable substrate. The desired result would be a lower concentration of combustible gases. This can be accomplished by promoting char formation, by hydrogenation or by dehydration, thus limiting the production of combustible hydrocarbon gases [46].

In the ignition stage of burning process, the candidate additive can be effective in a number of ways. Basically, any mechanism that tends to increase the concentration of noncombustible decomposition gases or decreases the production of combustible gases moieties will result in inhibiting the burning process at the ignition process. Besides these routes the flame retardant agent may also produce, by its own degradation or interaction with the substrate, free radical terminating species. These gaseous inhibitors reduce the flame speed by their interaction with the highly energetic chain-propagating species, such as OH radicals. An additive can also produce a very dense gas that can blanket the surface of the flammable substrate and exclude oxygen needed for the ignition process [46].

Even after the ignition of the substrate has occurred, the combustion and the propagation stages of the burning process can be inhibited by decreasing the heat transfer rate at the surface of the burning substrate. One notable way of achieving this would be from a flame retardant additive that on decomposing generates particulate matter in the pre-flame zone. These smoke particles provide a surface that attenuates the radiative thermal energy from the flame zone [46].

2.5.3 Synergistic and Catalytic Effects in Flame Retardancy of Polymeric Materials

Synergistic and antagonistic effects of two or more additives are often encountered in flame retardancy of polymeric materials. Halogen-antimony synergism is the best known. Evidence for bromine-ammonium, bromine-chlorine and bromine-phosphorus synergism has been observed in some systems [74].

The term synergism is defined as an effect greater than the addition of individual effects. Antagonism can be unequivocal if two flame retardants, each producing a positive result when used separately, produce, when added together, a result less than

the result which would have been obtained from either one alone at the same total concentration [42]. The phenomenon of synergism is widely encountered, described and discussed in the literatüre dealing with flame retardancy of polymers [46, 75, 76]. Synergistic effects are observed in vapor-phase as well as in condensed phase-active FR systems. Their modes of action in the various systems are different and involve a wide variety of interactions. They involve chemical interactions between the FR additive and the synergist, between the synergist and the polymer or between al three: polymer, FR additive and synergist, between two synergists and the FR additive and even between two polymers in a polymer blend. In some cases the synergist itself is not a flame retarding agent and becomes active only in the presence of an FR additive. This is the case with halogen-based additives and antmiony-trioxide. In other cases such as the bromine-phosphorus synergism, both, additives are active flame retardants. In certain cases the interaction between the ingredients in a formulation brings about a decrease in the flame retardancy parameters and are those antagonistic. This is encountered in the case of the application of phosphorus derivatives together with nitriles [76].

The term synergism, as currently used in the FR terminology is a poorly defined term. Strictly speaking, it refers to the combined effect of two or more additives, which is greater than that predicted on the basis of the additiviy of the effect of the components. The term synergistic effectiviy (SE) is meant to serve as a general tool for the characterization and for comparing synergistic systems. It is defined as the ratio of the FR effectivity (EEF) of the flame retardant additive plus the synergist to the EEF of the additive without synergist. EEF is defined as the increment in oxygen index (OI) for 1% of the flame retardant element. In the case when the synergism is between two or more flame retardants the SE is the ratio of the measured OI at a given mixture of the ingredients to the value calculated for the same mixture without the synergistic effect. The SE in the case is defined for the mixture of the flame retardants and not for the individual ingredients. The SE values are based in most cases on results obtained for additive / synergist ratios yielding the highest effect. It is realized that the synergistic effect at other ratios may be smaller or disappear. Thus the SE values may not represent the complete picture, which may be rather complex. It is, however, related

to the conditions of the maximum synergistic effect, which is utilized in practice. In the following, several synergistic systems will be briefly discussed and compared.

The differentiation between the synergistic systems and catalytic phenomena observed in FR technology is not straightforward. Some synergistic systems could easily be classified as catalytic and vice versa. The criterion adopted in this paper for a catalyst is its high effectivity at a low concentration in the formulation. The number of FR catalytic systems reported upon in the literature is until now relatively small, but the interest in catalytic approaches appears to be growing.

2.5.3.1 Halogen-Antimony Synergism

The halogen-antimony synergism has been first described for cellulosic fabrics treated with chlorinated paraffins and Sb_2O_3 [75], and has also been observed for polyesters, polyamides, polyolefins, polyurethanes, polyacrylonitrile and polystyrene [76].

The mechanism responsible for this synergism appears to depend both on condensed phase as well as vapor phase activities [77-79]. It ise believed that during the pyrolysis, some hydrogen halide is released in the decomposition of the halogenated compound either by interaction with antimony trioxide or with the polymer. The HX reacts with the Sb_2O_3 producing either SbX_3 or SbOX [77, 78]. Although some SbX_3 is found in the first stage of the pyrolysis, the weight loss pattern requires the information of less volatile Sb-containing moieties, obtained by progressive halogenation of Sb_2O_3 [79]. SbOCI was found to decompose in several endethermic stages: at 245-280°C to $Sb_4O_5X_2$; at 410-475°C to Sb_3O_4X; above 685°C solid Sb_2O_3 is reformed. During the transformantions gaseous SbX_3 ise evolved and released to the gas phase, whereas SbOX, which is a strong Lewis acid, operates in the condensed phase, facilitating the dissociation of the C-X bonds [80]. 3rd Lowering the charring temperature by adding Sb_2O_3 to cellulosic fabrics treated with chlorine compounds was observed [81]. Adding Sb_2O_3 to polyolefins treated with Dechlorane Plus was found to substantially increase the char yield [82]. The main effect of Sb_2O_3 is, however, in the gas phase. The antimony halides, after reaching the gas phase, react with atomic hydrogen producing, HX, SbX, SbX_2, and Sb. Sb reacts with atomic oxygen, water and hydroxyl radicals, producing, SbOH and SbO, which in turn scavenge H atoms. SbX_3 reacts with water

producing SbOH and HX. A fine dispersion of solid SbO and Sb is also produced in the flame and catalyzes and the H recombination. In addition it is believed that the antimony halides delay the escape of halogen from the flame, and thus increase its concentration, and at the same time also dilutes the flame.

2.5.3.2 Antimony Trioxide Synergist

Antimony trioxide is a solid white powder which sinks in water, slowly dissolving. Antimony trioxide is produced by exposing molten antimony sulphide and/or pure antimony to air at 600-800°C.

Antimony trioxide is used mainly as a fire prevention additive and pigment (concentration: 1-13%). The substance comes in various grades, depending on particle size. The breakdown of particle size affects both physical properties and pigment property. The finer fraction is used for pigmentation.

Antimony oxide (Sb_2O_3) has long been known as a synergistic agent with halogen, which is widely used as a flame retardant in plastics, rubber, textile, and coatings [4]. At present, its applications have been limited by the problems of the scope of the large size, more additive amount, heavier smoke in burning, and lower mechanical properties of synthetic materials. Therefore it is necessary to study the ultrafine, functional and composition Sb_2O_3 [83, 84].

The flame-retardant property, however, is not affected by particle size. This property is based on antimony trioxide reacting in the event of a fire with the surrounding material, with the result that a protective layer of various antimony compounds covers the combustible materials. Since the formation of these compounds consumes heat and because they are generally difficult to ignite, they protect the underlying material from ignition. The presence of thermally unstable halogen compounds accelerates the protective impact of antimony. Antimony trioxide is therefore nearly always used together with high-halogenated organic compounds such as chloroparaffins.

Antimony trioxide is used as a fire prevention additive in a number and variety of materials, e.g. polystyrene (present, for example, in the casings of computer display screens), in fire-retardant paint for application to wood, and in PVC plastic in cables.

Another use for antimony trioxide is as a trace element additive to phosphorescent light sources such as fluorescent tubes and TV/computer screens. Antimony reinforces the photogenic capacity of phosphorus.

In glass manufacturing, antimony trioxide is used instead of arsenic as a plaining agent. When the paraison of glass is heated, antimony trioxide is gasified, whereupon bubbles of gas are formed which serve to create a remixture of the molten glass and also to trap other substances in the gas bubbles formed and to remove them from the glass [85].

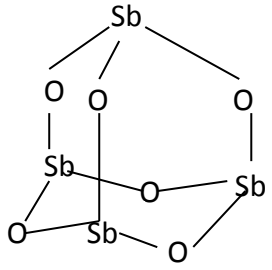


Figure 2. 8 Molecular structure of Sb_2O_3 [85]

Antimony trioxide is used in conjunction with decabromodiphenylethane (DBDPE) at a ratio of roughly three parts DBDPE to one part antimony trioxide (ATO). ATO is not a flame retardant itself, but a synergist for halogenated flame retardants. This means that the flame retardant effect is greater when the flame retardant is used with ATO than without ATO [47].

The synergistic effect occurs in the following way. To be efficient, Br^- radicals must reach the flame in the gas phase to react with volatile (combustible) parts of the polymer. The addition of antimony trioxide facilitates the breakdown of halogenated flame retardants into active molecules. Antimony also reacts with the halogens to produce volatile antimony halogen compounds (such as $SbBr_3$), which are themselves directly effective in removing the high-energy H^+ and OH^- radicals that feed the flame phase of the fire. Removing these free radicals slows the combustion process, reducing heat generation and lessening further thermal decomposition One notable exception to the use of ATO as a synergist for DBDPE is in polycarbonate resins. Use of ATO in polycarbonate can significantly degrade the material's structural properties [47].

2.5.4 Decabromodiphenylethane

This is a white solid containing 82.3% Br and melting at 361 °C. It is Albemarle's DBDPE and more recently, Chemtura's Firemaster® 2100. It can be made by direct bromination of diphenylethane [86, 87]. It is fairly close in performance to decabromodiphenyl oxide but permits compounding a "PBDE-free" formulation. It also has less blooming tendency than decabromodiphenyl oxide [67].

It is well known that brominated flame retardants can effectively improve the fire retardant property of many polymer materials. Decabromodiphenyl oxide (DBDPO) has high bromine amount and excellent thermal stability, and its thermal decomposition temperature is close to that of many polymers. Unfortunately, it has been pointed out that DBDPO can release polybrominated dibenzo-p-dioxine (PBDD) and polybrominated dibenzofuranes (PBDF) that are toxic and carcinogenic gases. Therefore it has been forbidden to use by some countries recently [88]. Decabrom-bromodiphenylethane (DBDPE) is also called 1, 2 bis (pentabromophenyl) ethane developed by American Albemarle Corporation. It is equivalent with DBDPO in the molecular mass, thermal stability and bromine amount. International organization has evaluated the human health and environmental risk for DBDPE [89, 90]. It can not release PBDD and PBDF during combustion [91], and its light stability and anti-dialysis are better than DBDPO. Especially, polymers flame retarded by DBDPE can be recycled without great loss in the flame retarding. In China, bromine-containing flame retardants as the important flame retardants are widely used and DBDPE will be the most promising substitute of DBDPO.

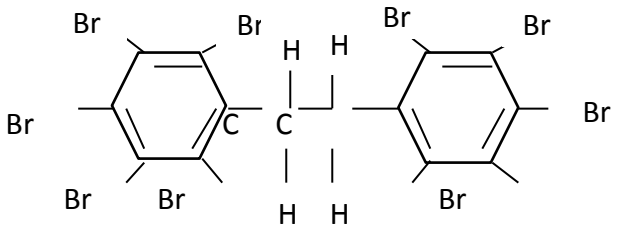


Figure 2. 9 Molecular structure of decabromodiphenyl ethane [92]

DBDPE flame retardant can be used in a wide range of high performance applications. In particular it finds use in styrenic polymers, engineering resins, wire & cable and elastomers. DBDPE flame retardant has very good thermal stability and high bromine

content making it a prime candidate for high temperature applications. It exhibits good UV resistance and hence is suitable for use in many applications requiring color stability. Because of its very good thermal stability and low blooming characteristics, DBDPE flame retardant is suitable for use in systems where recycling is anticipated. DBDPE flame retardant is not acutely toxic, it is not teratogenic, and it is not harmful to fish. DBDPE flame retardant can be used in the formulation of products meeting European dioxin ordinances [92].

2.6 Flame Retardancy and Mechanical Properties

Additive-type flame retardants, physically incorporated into polymers, provide the most convenient and economical way of introducing flame retardancy into commercial polymers. However, a variety of problems, such as poor compatibility, diffusing out on to the surface of the resulted products and reduction in the mechanical or other physical properties of the polymers, restrict the application of most of the commercially available additive-type flame retardant [52]. To overcome the aforementioned problems, several techniques have been employed and a large number of halogen-free flame retardants have been synthesized.

2.7 Compounding Basics (Production Methods of Polymer Composites)

Basic rubber compounding processing can be seen in Figure 2.10.

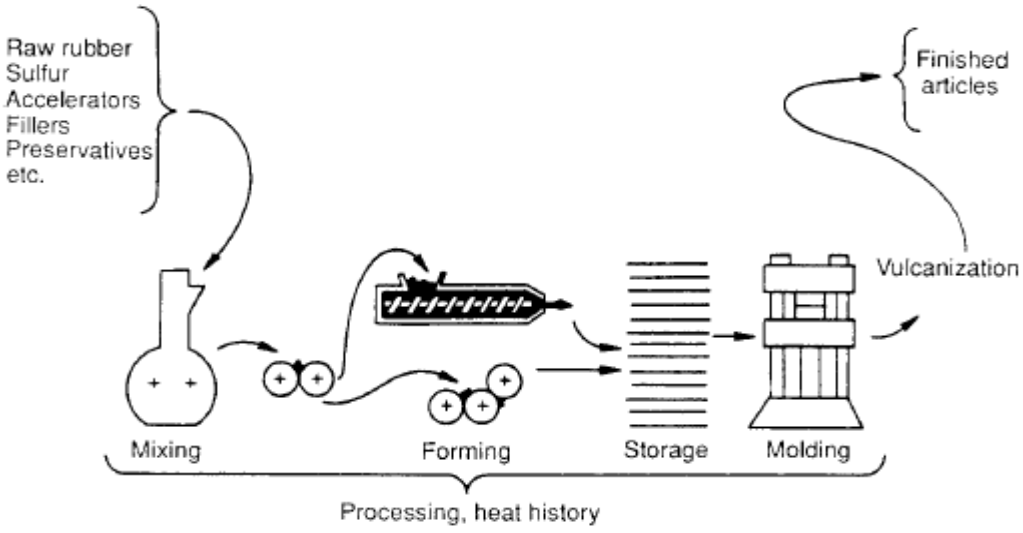


Figure 2. 10 The effect of processing on heat history [93]

2.7.1 Compound

Rubber compounding can be defined as the science of mixtures. An elastomer compound is a mixture of an elastomer and a wide variety of chemicals, soluble and insoluble, which have been mixed according to a specific formula in a closed chamber (e.g., Banbury, Shaw, Moriyama mixers) or on a two roll mill. The gigantic thermoplastic lump of mixed compound is subsequently formed into sheets, tubes or other shapes, and vulcanized (crosslinked) in its final form [93].

A rubber compound is made up of three major classes of chemicals: elastomers, fillers and curatives. Additional classes include antioxidants and processing chemicals such as oils and resins. Fillers include reinforcing materials such as carbon black and precipitated silica, and extender minerals such as clay, talc and whiting. Curatives are those chemicals responsible for vulcanization or crosslinking. They include sulfur, accelerators, and activators such as zinc oxide and stearic acid. Without these modifying ingredients an elastomer alone is generally useless for commercial applications. Table 2.2 contains a list of the major material classes and the compound properties each group supplies. Compounding research and development consists of evaluating the properties of compounds in which materials and their concentrations have been systematically varied. The objectives are to determine the mechanisms by which each material functions, and to develop compounds with certain well defined properties [93].

Table 2. 2 Formula components and associated properties [93]

Formula Component	Associated Properties
Elastomer	Resilience
a) Natural rubber	Environmental Resistance: Temperature; oil; UV; Ozone; solvents
b) Synthetic elastomer	Reinforcement
c) Blend	Processing requirements
	Cost
Filler	Reinforcement (Abrasion, Tear)
a) Carbon Black	Durometer hardness
b) Silica	Processing (viscosity)
c) Extenders	Color – translucence
	Cost
Crosslinking (Cure) System	Cure state: (Rheometer); Hardness; Modulus; Set; Heat build-up
a) Sulfur; peroxide	Cure Rate
b) Accelerators	Scorch safety
c) Activators	Heat and Aging resistance
	Cost
Plasticizer (Softoner)	Processing: Viscosity; Mixing; Extrusion; Calendering
a) Oils	Hardness
b) Esters	Elastomer Compatibility
c) Resins	Low temperature flexibility
	High tempereture stability
	Cost
Antidegradant	Heat resistance
	Ozone resistance
	Staining; Color
Miscellaneous	Adhesion promoter
	Cell formation
	Coupling silica to elastomers

2.7.2 The Formula

The formula defines the compound and determines its properties. It is a list of the ingredients and the amount of each, by weight, expressed as parts per hundred (phr) of elastomer. Thus, each formula begins with 100 parts of elastomer. Filler contents range from 30 to 70 phr for reinforcing materials, to 300 phr for extender materials.

Softener oils, which control compound hardness and processing properties, can range from 5 to 150 phr. Most sulfur cured formulas contain from 0.3 to 3.0 phr sulfur. Lower concentrations are supplemented with sulfur donating accelerators. Sulfur or other types of crosslinkers are required to transform the thermoplastic compound to its final thermoset, crosslinked or cured state.

Each rubber blend doesn't require the use of all the substances mentioned above. But the rubber and the substances composing the vulcanization system certainly must be present [93].

2.7.3 Formula Mixing

The mixed formula is called the compound. Mixing of formula ingredients takes place in a closed container under mechanical pressure. The mixing chamber contains two rotors with surface fins, which rotate in opposite directions. Dispersion of ingredients takes place by a shearing action between rotor and chamber wall surfaces. The most frequently used machine is the Banbury mixer, named after its inventor, Fernley Banbury. Mixing can also be carried out on open mill equipment where two parallel, smooth surface, counter rotating rolls disperse ingredients by shear in the narrow space (nip) between the rolls. The open mill generally provides superior dispersion, but is limited in batch size. Each internal mixer discharges mixed compound onto a two roll mill which transforms compound from lump to sheet form [93].

2.8 Rubber Processing Techniques

Rubber blends and composites are prepared in order to enhance the polymer's properties like physical, mechanical, thermal and flammability properties. Rubber processing includes the mixing of the polymer with the additives and vulcanization of rubber by the molding of the mixture to the final shape [94].

2.8.1 Mixing

Usually rubber processors have a system of mixing where the raw rubber, carbon black, oil, curatives, etc. are all mixed together. This mixing will generally ocur in an internal mixer [95].

The working part of an internal mixer consists of a cylindrical chamber holding two rotors as shown schematically in Figure 2.11 [96]. The rotors are driven by a motor and gears. In small mixers the speed may be adjustable but in large mixers the rotor speed is usually limited to one or two values. The rubber and solid components are fed into a hopper or drop door in the side of a chute which opens into the mixing chamber. Liquid components may be added through the hopper or injected directly into the chamber. A hydraulically-operated ram closes the top of the chamber, subjecting the rubber mix to a controlled pressure. In the operating cycle, the components are added to the chamber with or without rotor movement. The cycle begins when the ram squeezes the rubber into the region between the rotors. After the mixing time, a drop door at the bottom of the chamber opens and the batch falls out of the mixer and is transported to the next processing operation [97].

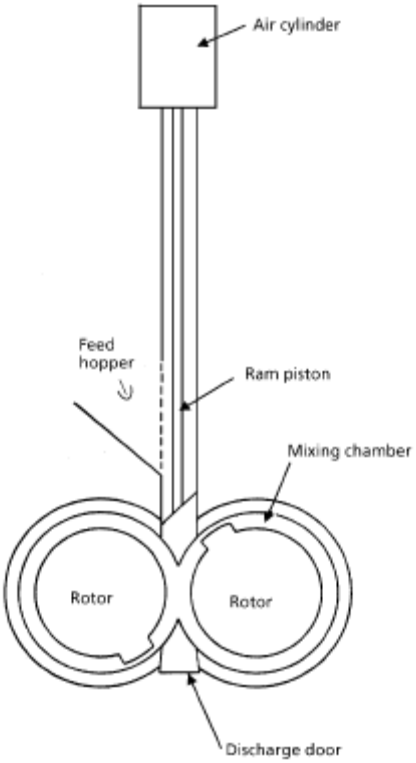


Figure 2. 11 Schematic view of an internal mixer [97]

2.8.2 Vulcanization Techniques

Vulcanization process is carried out under high temperature and high pressure by using various techniques. The most important methods of curing;

- Press vulcanization
- Open vulcanization
- Continious vulcanization
- Cold vulcanization

In this study the press vulcanization curing method was used.

2.8.2.1 Press Vulcanization

As the name suggests, press vulcanization is made by using pressure and temperature supported molds. Curing press includes two or more plates seperated by hydraulic pressure. The plates are heated by steam or electrically. The rubber part is vulcanized between the heated plates and under pressure with different molds.

Compression molding is a widely used method for molding of polymeric materials (especially thermosets). The principle of compression molding is quite simple. The molding material is generally preheated in an open, heated mold cavity. After the mold is closed, pressure is applied to force the material into contact with all mold areas, while heat and pressure are maintained until the molding material is finished. In this study, stainless steel plates, of which the inner parts are cut out into desired shape, are used as mold. Teflon film is used to prevent the adhesion of polymer melts onto the heated upper and lower plates of the hydraulic press [98].

2.9 Characterization Methods

Numerous test methods are used for evaluating the fire retardant and thermal properties of polymers. In this study, Limiting Oxygen Index (LOI), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC) tests are used for polymer composite materials. For the characterization of flame retardant behavior of polymers,

Tensile Test are also used for understanding the tensile properties of polymers. The Alpha Technologies MDR 2000 Moving Die Rheometer is also used to measure cure properties of EPDM compound.

2.9.1 UL-94

UL-94 is the most commonly used test method for measuring the ignitability and the flame spread of polymeric materials exposed to a small flame at vertical position which is practical and easy to apply. The schematic view of the UL-94 test is shown in Figure 2.12 [99].

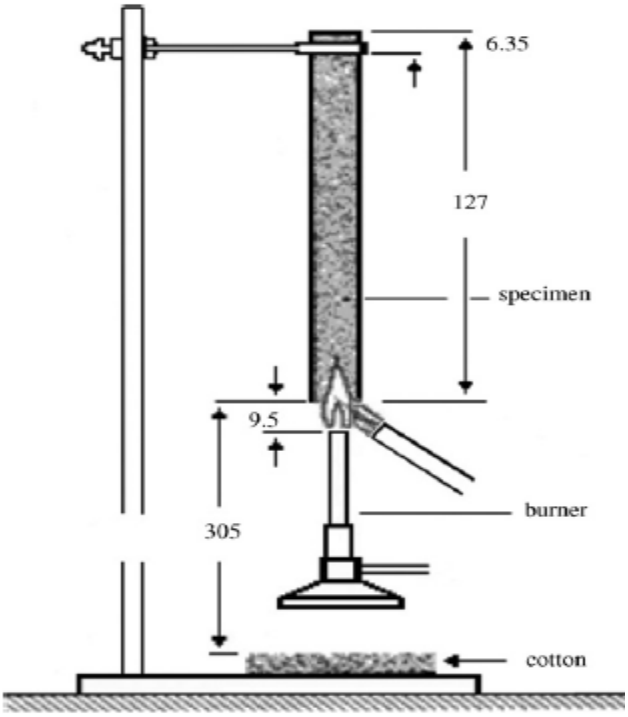


Figure 2. 12 The schematic view of the UL-94 test [99]

The flame is applied to the bottom of the specimen and the top of the burner has to be located at 10 mm from the bottom edge of the specimen. The flame is applied for 10 seconds and removed. The after flame time t_1 (the time required for the flame to extinguish) is noted. After extinction, the flame is applied for another 10 second. The after flame time t_2 is noted, together with the afterglow time t_3 (the time required for the fire glow to disappear). During the test, the presence of burning drops, causing a piece of cotton located under the sample to ignite, must be noted. In view of these data, the flammability of material is classified into three categories (V-0, V-1, V-2) depending on their performance regarding the individual duration of burning for each specimen, total burning time for all specimens and the presence or absence of burning drips [99, 100, 101]. Criteria for UL-94 Classifications are shown in Table 2. 3 [99, 101].

The classification V-0 is the best flame retardancy in which the material should stop burning within 10 s without dripping after two applications [52].

Table 2. 3 Criteria for UL-94 classifications [99, 101].

Time, (second)	V-0	V-1	V-2
t_1	< 10	< 30	< 30
t_2	< 10	< 30	< 30
$t_1 + t_2$ (for five samples)	< 50	< 250	< 250
$t_2 + t_3$	< 30	< 60	< 60
Cotton ignited by burning drips	No	No	Yes
Afterglow or afterflame up to the holding clamp	No	No	No

2.9.2 Limiting Oxygen Index (LOI)

LOI is widely used to quantify the flammability of polymers. LOI test was proposed in 1966 and was standardized as NF T 51-071 (in France), ASTM D 2863 (in the United States), ISO 4589 (international standard) [99, 100, 101]**.** The schematic representation of LOI test is shown in Figure 2.13 [100]. Slow stream of oxygen/nitrogen mix is supplied from the bottom of the tube. The ratio of oxygen and nitrogen is changed throughout the test to determine the oxygen concentration that will support the combustion of the material for at least 3 minutes or the combustion of 50 mm of the sample. The LOI value is calculated as $[O_2/(O_2+N_2)]*100$. As air contains 21 % oxygen, material with an LOI below 21 are classified as combustible, LOI above 21 are classified as self-extinguishing. The higher the LOI is the better the flame retardant property [99, 100, 101]. Despite its widespread use, the LOI method has several deficiencies; (1) The test condition has never been correlated to any aspect of full size fires, (2) The use of downward flame spread for a distance of 50 mm to define the oxygen index of a material. In real fires, the downward spread of flame is of little importance, (3) LOI test is conducted at oxygen concentration usually above the normal oxygen content of air, which again does not occur in most fires [59].

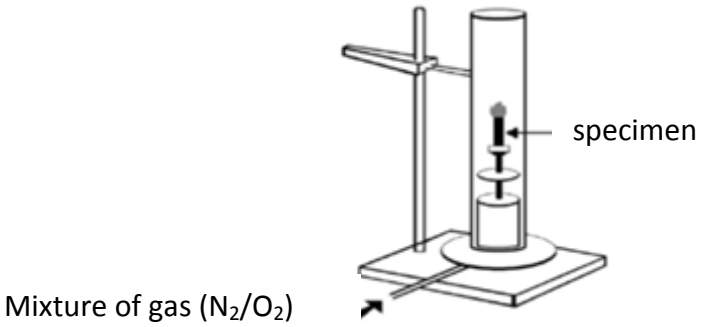


Figure 2. 13 The schematic representation of LOI test [100]

2.9.3 Rheological Measurements

Compound characterization is generally divided into two sections: processing and physical test properties. Processing refers to the behavior of the uncured, thermoplastic compound in terms of viscosity, cure rate and crosslinking. The instrument used to determine curing properties is a *rheometer*. In the present work, crosslinking is defined as the difference between rheometer minimum and maximum values, and reflects the extent of polymer chain bonding by sulfur or carbon linkages. This is also referred to as "state of cure." Cure rate, in contrast, reflects the speed of the crosslinking reaction in terms of the slope of the middle part of the rheometer curve. The initial part of the curve indicates the tendency to crosslink prematurely, a reaction called *scorching*. The final section of the rheometer curve is generally a plateau. The extent to which this plateau drops in value at long cure times is called *reversion*, which relates to losses in hardness and reinforcement properties in the compound after long cure times [101].

The oscillating disc curemeter or rheometer (ODR) solves the problem of not being able to make any rheological measurements after the scorch time, by changing the rotor from a rotating mode to an oscillating one. Since cured rubber can stretch to some extent without breaking, the oscillations are kept within this limit. The magnitude of the oscillation is measured in degrees of arc, 1° and 3° are most common, and the rate of oscillation is suggested as 1.7 Hz. The curemeter is an essential piece of equipment and used extensively in the rubber laboratory. The machine plots a graph of torque versus time for any given curing temperature. The full extent of cure and beyond can now be recorded. For example reversion, the point at

which the vulcanized compound breaks down due to prolonged heating can now be measured [102].

Testing Procedure: A piece of uncured compound rubber is placed on the heated rotor, and the heated top die cavity is immediately brought down on to the lower die thus filling the cavity. In Figure 2.14, the curve shows an immediate initial rise in torque upon closure of the heated cavity. At the top of this first 'hump', the compound has not had much chance to absorb heat from its surroundings, and since viscosity is temperature dependent it will be somewhat higher in these first few seconds. As the compound absorbs heat from the instrument, it softens. Its temperature then stabilizes, and its viscosity has a constant value prior to the onset of cure. This assumes that it is not masked by a very short scorch time. This is the first important feature on the curve. It is the minimum viscosity of the rubber at the chosen temperature and degree of oscillation; and it has the symbol ML.

After a certain time, the viscosity (torque) begins to increase, indicating that the curing process (vulcanization or cross-linking) has begun. The time from the closure of the cavity to this moment is the next important property, the scorch time. The torque continues to increase, until there is no more significant rise. At this point the compound is vulcanized, and this maximum torque value is designated by the symbol MH.

The last major piece of information to be extracted is the time it takes to complete the cure, known as the cure time. This is defined with some precision as “the time taken for the curve to reach a height expressed as the value of ML plus a “percentage” of the difference between MH and ML. If we think of this ‘percentage’ as a decimal, then 90% is 0.9 (this number is commonly chosen), and mathematically this height would be expressed as 0,9(MH-ML)+ML. This “cut off” at 90% is often known as the technical cure time of the compound, and has the symbol t’90 [102].

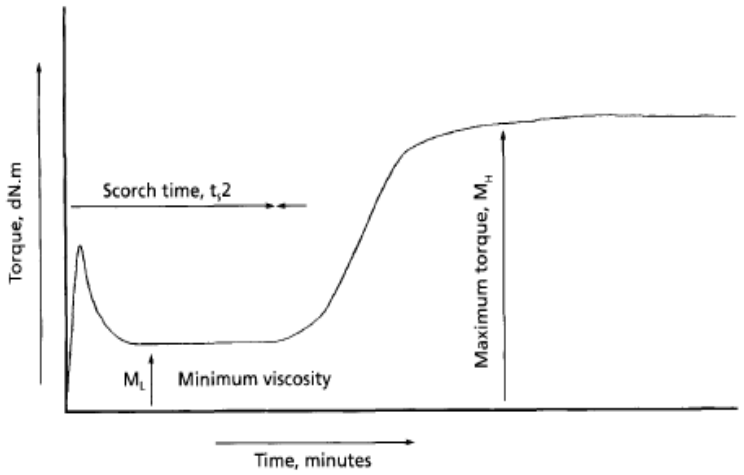


Figure 2. 14 Typical oscillating disc curemeter curve [102]

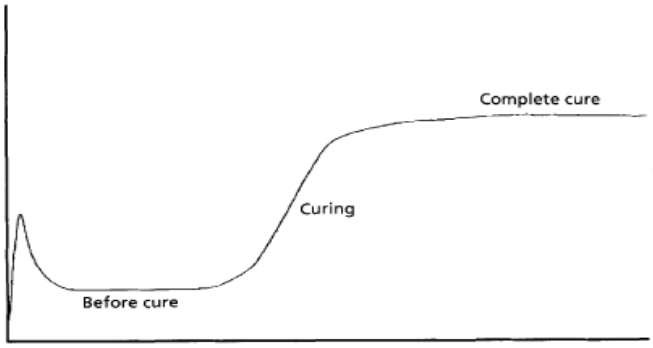


Figure 2. 15 Normal ODR curve [102]

Vulcanization curve is obtained by the rheometer and comments are made on the curve.

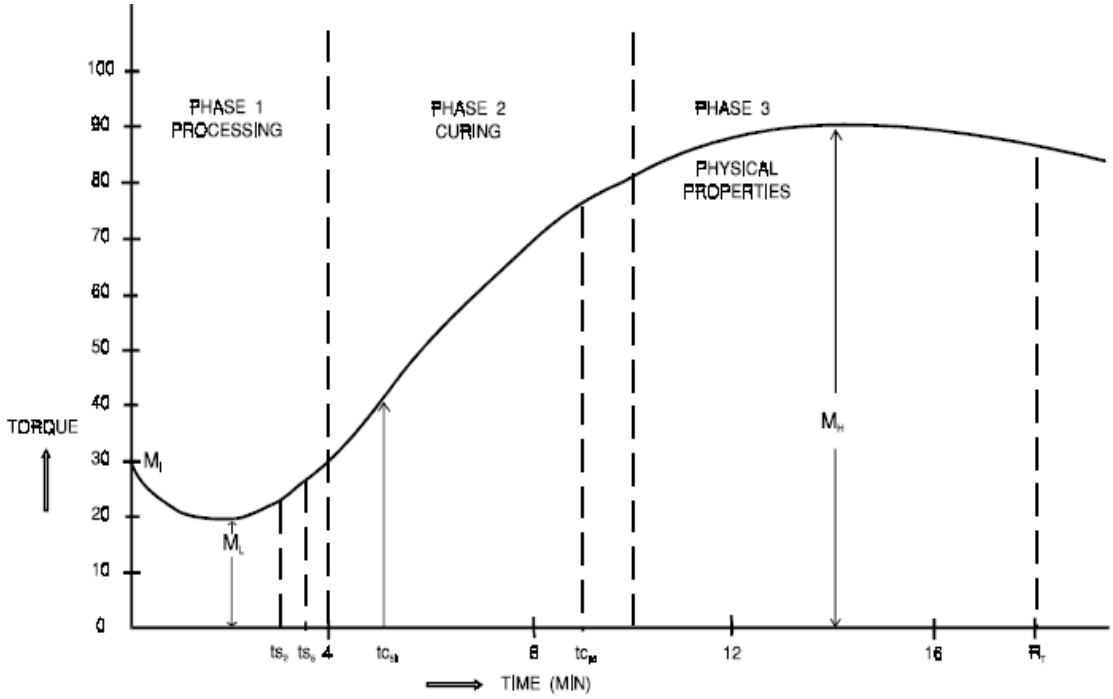


Figure 2. 16 Detailed oscillating curve [103]

Figure 2.16 shows a typical “Cure Curve” obtained with a oscillating disc rheometer. From this curve of Torque Vs Cure Time, all the vulcanization characteristics of the Rubber Compound can be determined directly. XY Plot of Torque (force) against real cure time is called “Rheograph”. Rheograph is divided into 3 phases :

A) Phase - 1. It gives an indication of processing behavior of the rubber compound.

B) Phase - 2. It describes the curing characteristics of the rubber compound.

C) Phase - 3. It gives good indication of physical properties of the rubber compound.

The plot of torque against time is analysed to obtain the various results. In oscillating disc rheometer, The rheograph is displayed in real time and at the end of test time, computer analyses the graph and results are automatically computed and displayed on the screen. Displayed results are categorized into three columns:

1. Torque values with units lbin.

2. Time values with unit minutes

3. Derived values.

The significance of these displayed values are:

Torque values:

i) MI (Initial Torque). It is the torque recorded at time zero at the start of the test.

ii) ML (Minimum Torque): As the compound gets heated under pressure, the viscosity decreases and the torque falls. The lowest value of Torque recorded is called ML. Basically, it is a measure of the stiffness and viscosity of unvulcanized compound.

iii) MH (Maximum Torque): As the curing starts, the torque increases proportionately. Depending upon the type of compound, the slope of rising torque varies. After a while the torque typically attains maximum value and it plateaus out. It is called "Plateau Curve". If test is continued for sufficient time, the reversion of cure occurs and torque tends to fall. This type of curve with reversion is called "Reverting Curve". At times the torque shows continuous rising trend during the period of record. Such type of curve is called "Rising or Marching Curve". MH (Max. torque) is the highest torque recorded in plateau curve. In reverting curve, the Max. torque recorded is abbreviated as MHR.

Time value:

i) ts2 (Induction time). After attaining minimum torque, during cure phase, as the torque rises, ts2 is scorch time for viscosity to rise 2 units above ML.

ii) ts5 (Scorch time). It is the time for viscosity (torque) to rise 5 units above ML. Both ts2 are ts5 are measures of initial slope of curing phase of Rheograph i.e. these are measures of processing safety. Scorch is premature vulcanization in which the stock becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is the result of both the temperatures reached during processing and the amount of time the compound is exposed to elevated temperatures. This period before vulcanization starts is generally referred to as "Scorch time". Since scorching ruins the stock, it is important that vulcanization does not start until processing is complete.

iii) tc50 (Optimum cure time). It is the time at which 50% of cure has taken place.

iv) tc90 (Optimum Cure time). It is the time at which 90% of cure has taken place.

Derived values :

i) Cure Rate: CR = 100/(tc90-ts2)

The cure rate is an essentially a measure of the linear slope of the Rising Curve. The rate of cure is the rate at which cross-linking and the development of stiffness (Modulus) of the compound occur after the scorch point. As the compound is heated beyond the scorch point, the properties of the compound changes from a soft plastic

to a tough elastic material required for use. During the curing phase cross links are introduced which connect the long polymer chains of the rubber together. As more cross links are introduced, the polymer chains become more firmly connected and the stiffness (modulus) of the compound increases. The rate of cure is an important vulcanization parameter since it determines the time the compound must be cured i.e. the cure time.

ii) Thermoplasticity : Tp = (MI-ML)

The Thermoplasticity is derived from the difference of initial viscosity & minimum viscosity.

iii) Reversion time (RT) : It is the time to reach 98% MH after passing MH. The reversion time is recorded in minutes. It gives us an indication of the quality of the compound as to how long it retains its physical properties when subjected to heat ageing. Reversion occurs with over cure and the Modulus & Tensile Strength decreases [103].

2.9.4 Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is commonly used in the characterization of polymers based on their thermal properties. In TGA, the change in the mass of the material with time and temperature is obtained [104]. The TGA curve is recorded either weight loss of the sample versus temperature or the change of sample weight with time versus temperature. In addition to mass loss data, decomposition temperature of the material can be obtained from TGA curve [104]. TGA is also important in the determination of flame retardancy of a material since char yield can be determined from TGA. Another important characteristic of TGA is that since each polymer has a different decomposition profile, the material can be distinguished from TGA curves [104].

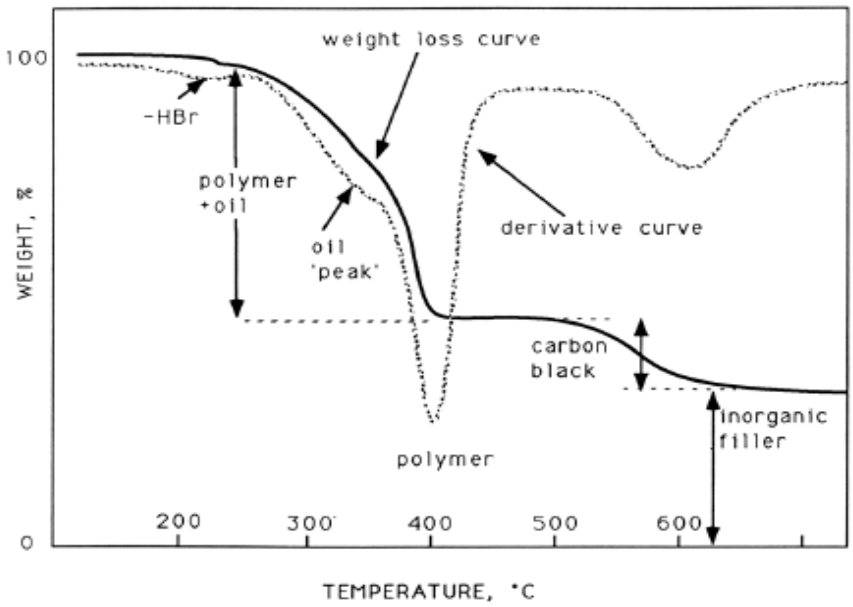


Figure 2. 17 Shows a TA thermogram of an elastomer compound [105]

2.9.5 Differential Scanning Calorimetry

Differential scanning calorimetry is an important analysis in polymer characterization since it determines the energy changes in a system resulted from either chemical or physical reasons. Its working principle is to measure the heat necessary to maintain the same temperature in the sample versus a reference material with a known specific heat. It also measures the enthalpy changes in the system due to a change of state of the sample. DSC analysis is very commonly used to determine important physical changes in the samples such as the glass transition temperature (T_g), the crystallization temperature (T_c), the melt temperature (T_m) and the decomposition temperature (T_D). In addition to the physical changes in the system, chemical changes as a result of polymerization and degradation reactions can also be determined by using DSC analysis [104]. A typical DSC curve showing the determination of T_g, T_c, T_m and T_D can be seen in Figure 2. 18.

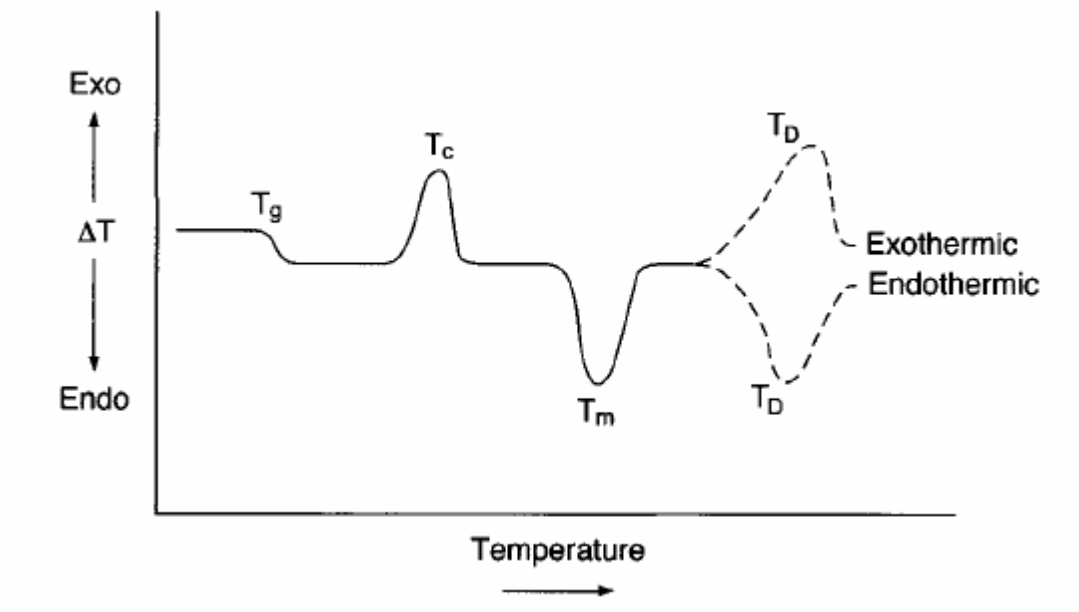


Figure 2. 18 Typical DSC curve showing the transitions in a system [104]

2.9.6 Tensile Test of Elastomers

Tensile test method was used to determine mechanical properties of the material by loading a machined or cast specimen of specified cross-sectional dimensions in uniaxial tension until it breaks; the test is used principally to determine tensile strength, yield strength, ductility (elongation and reduction of area), and modulus of elasticity. Also known as a pull test [106].

The most used strain mode in the quality control rubber laboratory is tensile. In this test, a piece of rubber is stretched until it snaps (tensile at break). The test piece often goes through a considerable amount of elongation before break occurs (up to around 900 %**,** depending on the compound). It is interesting that this test is so popular, since there are very few product applications where the rubber is stretched so much.

Tensile testing is accomplished by first molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces are die cut. (See Figure 2.19)

The test pieces are then stretched in a tensile testing machine and the force required to stretch the samples is measured. Values of stress (force divided by the unstretched cross sectional area of the straight portion of the dumbbell) are recorded at various levels of extension, up to the break point. The extension is measured as percent elongation and is defined as:

$$\frac{L-L_o}{L_o} * 100 \qquad (2.12)$$

Where: L is the stretched length.

L_o is the original length.

Tensile values before the sample breaks, give the modulus of the sample. For the rubber chemist, modulus means the tensile value (stress) at a given elongation. Modulus numbers at 100%, 200% and 300% elongation are commonly measured. Note that the modulus, as defined here, is not equivalent to the modulus as understood by an engineer, which is equal to stress over strain.

An important function of tensile testing is to determine how well ingredients are dispersed in the rubber compound, during the mixing stage. For example, if carbon black is is poorly dispersed, the tensile strength (at break) of the cured compound will be lower than it should be. A low state of cure, due to insufficient curative, as well as inadequate cure time or temperature, will also give a lowered tensile strength.

If a compound has too much carbon black, not enough oil, or too high a state of cure, perhaps due to excessive sulfur or accelerator, it will be reflected in a higher modulus value. Compounds used in the rubber industry have tensile strengths from less than 7 MPa to around 28 MPa. There are cases where tensile strength is specifically relevant to an application, for example an elastic band. A higher tensile strength is also preferred for highly dynamic applications [102].

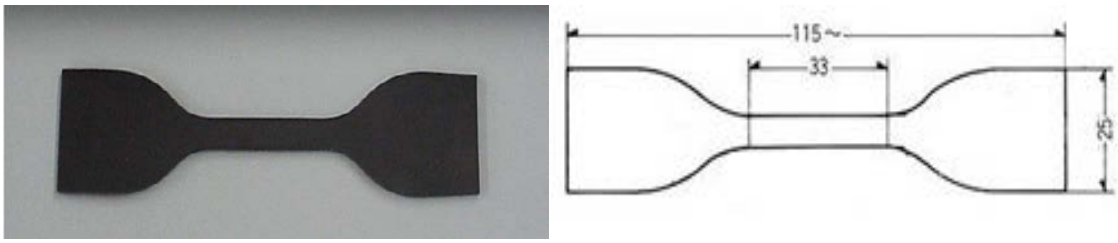


Figure 2. 19 Rubber "dumbbell" tensile test sample [102]

Table 2. 4 Tensile test parameters

Elongation at break	%	ASTM D 412-87
Tensile Strength	MPa	ASTM D 412-87
% 300 Modulus	MPa	ASTM D 412-87

2.9.7 Hardness Test

Durometer, like many other hardness tests, measures the depth of an indentation in the material created by a given force on a standardized presser foot. This depth is dependent on the hardness of the material, its viscoelastic properties, the shape of the presser foot, and the duration of the test. ASTM D2240 durometers allows for a measurement of the initial hardness, or the indentation hardness after a given period of time. The basic test requires applying the force in a consistent manner, without shock, and measuring the hardness (depth of the indentation). If a timed hardness is desired, force is applied for the required time and then read.

60 Shore A is softer than 70.

70 Shore A is the standard.

90 Shore A is very stiff.

The surface indentation or hardness usually does not bear any relation to the ability of an elastomeric part to function properly. Hardness is a measure of an elastomer's response to a small surface stress.

2.9.8 Density Test

Density is the mass of the unit volume of a elastomeric material at a certain temperature. This test is done according to the standard of ASTM D 297/15. Measuring density is important to determine of gram-weight of elastomer and to calculate of elastomer cost. For this test, test samples at least 2.5 grams of weight with smooth surfaces, cracks and dust-free are taken and weighted firstly in the air and then in the water. In this way, the density measurement were made automatically by density measuring device. For each trial, four times the density is measured and the measurements were averaged.

CHAPTER 3

EXPERIMENTAL

Experimental part of this study is divided into two parts. In the first part, the materials and experimental procedures used to prepare flame retardant EPDM blends were mentioned. In the second part, characterization methods were explained.

3.1 Production of Flame Retardant EPDM Blends

For the production of flame retardant EPDM blends, two different commercial flame retardants, antimony trioxide (Sb_2O_3) and decabromodiphenylethane (DBDPE), were used with EPDM rubber, carbon black and inactive white fillers, sulphur as curing agent for vulcanization, zinc oxide and stearic acid as activators and process oil as plasticizer for flexibility and also accelerators. For flame retardant EPDM blends, the combustion and the thermal degradation characteristics were investigated by using limiting oxygen index (LOI), UL-94, thermogravimetric analysis (TGA), differential scanning calorimeter (DSC). Rheometer was used to investigate curing properties. And also mechanical properties were investigated by using tensometer and durometer.

3.2 Materials

3.2.1 Ethylene Propylene Diene Monomer

Keltan EPDM was supplied by Lanxess, Gmbh (25038-36-2).

3.2.2 Fillers

3.2.2.1 Carbon Black

Birla Carbon N550 was supplied by Alexandria Carbon Black Company, Egypt (1333-86-4). Carbon black is the predominant reinforcing filler used in rubber compounds. Through the addition of carbon black to the rubber compound, durability and strength are significantly improved. Improvement in rubber properties is a function of the physical and chemical characteristics of carbon black. Carbon black's most important fundamental characteristics are aggregate size and shape (structure), particle size and surface activity [108].

3.2.2.2 Inactive filler

Inactive white filler was supplied by Omya Company. This filler already has a long history of use in plastic and rubber. Its use can decrease costs, and it can improve the heat resistance, size stability, and hardness of the base material. Inactive filler is the filler first used by the rubber industry, and is still used in the greatest quantity. Adding large amounts of white filler to rubber can increase the product's volume, which inhibit the use of expensive natural rubber and thereby cuts costs. The addition of white filler to rubber increases tensile strength, abrasion resistance, and tear resistance even more than vulcanization. White filler also has a significant reinforcing effect in both natural and synthetic rubber and can improve consistency [108].

3.2.3 Curing Activators

3.2.3.1 Zinc Oxide and Stearic Acid

Laboratory grades zinc oxide (ZnO) and stearic acid were used as curing activators/ process aids. They were supplied by Natural Oleochemicals Sdn Bhd (57-11-4) and Brüggemann Chemicals (8051-03-04).

Vulcanisation activators are products which have a strong activation effect on the cross linking reactions of diene rubbers.

3.2.4 Process Oil

Process oil was supplied by Sah Petroleums.

Rubber process oils are used during the processing and production of rubber compounds. The oil helps in improving the dispersion of fillers and flow characteristics of the compound during further processing.

Depending on the type of rubber and the end product applications, aromatic types, naphthenic types, paraffinic types are selected.

3.2.5 Decabromodiphenylethane

Decabromodiphenylethane flame retardant was supplied by Albemarle Corporation. This flame retardant has very good thermal stability and high bromine content which makes it a prime canditate for high temperature applications. It exhibits good UV resistance and hence is suitable for use in many applications requiring color stability.

Table 3. 1 Typical properties of decabromodiphenylethane [92]

% Bromine (theoretical)	82,3
Initial melting point (by DSC), °C	350
Molecular weight, g/mole	971,2
Appearance/form	white/powder
Dielectric constant (1 MHz)	1,15
Dissipation factor (1 MHz)	0,19
Average particle size (μ)	5,63
Solubility (weight % at 25°C)	
in water	<0,01
in acetone	<0,01
in methanol	<0,01
in toluene	<0,01
in chlorobenzene	<0,01
in methylene dibromide	<0,01
in dimethyl Formamid	<0,01
TGA (TA Instruments, model 2950, 10°C/min under N_2)	
1% weight loss, °C	314
5% weight loss, °C	344
10% weight loss, °C	359
50% weight loss, °C	402
90% weight loss, °C	423

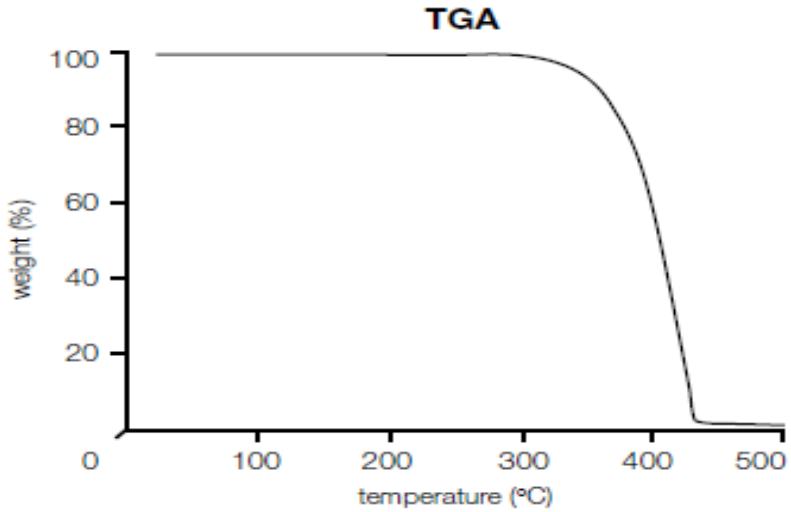


Figure 3. 1 TGA curve of decabromodiphenylethane [92]

3.2.6 Antimony Trioxide

Campine antimony N 08, antimony trioxide (Sb_2O_3) was supplied by Campine Company. Antimony trioxide is a toxic, inorganic compound that is primarily used as a flame retardant in combination with halogenated materials, produced as a white, odorless crystalline powder.

Table 3. 2 Typical properties of antimony trioxide [92]

Melting point	656°C (Sb_2O_3)
Boiling point (sublim.)	1550°C (Sb_2O_3)
Autoflammability	not available
Solubility in water (20°C) (pH 8, loading 100 mg Sb_2O_3/l, 24 h)	1.86 mg Sb/l
Appearance	Wetted white powder
Odour	Characteristic
Colour	Natural
Density (20°C)	not available
Bulk density (20°C)	not available
Flashpoint	not available
pH – value	not available

3.2.7 Accelerator

The curing accelerators was supplied by Rheinchemie.

The curing accelerator provides a considerably long scorch time, great processing safety and a fast full cure. It is used as a sole accelerator for the low sulphur vulcanization or in combination with dithiocarbamate or thiuram accelerators.

3.2.8 Sulphur

Sulphur granule was supplied by Treco. The properties of rubber can be dramatically altered by cross linking the polymer chains. This process, carried out with sulfur, is known as vulcanization.

3.3 Preparation of Flame Retardant EPDM Blends

Each chemicals seen in Table 3. 3, were weighted according to the calculation of the sample formula in the below and then mixed in the 1,8 L laboratory intensive mixer at 80 °C. YI-TZUNG laboratory intensive mixer can be seen in Figure 3. 2.



Figure 3. 2 YI-TZUNG laboratory intensive mixer

Calculation for untreated EPDM formula:

Total mass = Mikser volume*%70 capacity*density of mixture

=1800 mL*0,70*1,273 =1603,98 g

Coefficient=total mass / total phr

= 1603,98 / 356,9 =4,4942

EPDM = 4,4942*100 phr= 449,42 g

ZnO= 4,4942*6 phr= 26,9652 g

Table 3. 3 Mixing formulas of untreated and treated EPDM

INGREDIENTS	Untreated EPDM Phr	ALFT 398 Phr	ALFT 399 Phr	ALFT 400 Phr	ALFT 401 Phr	ALFT 402 Phr
EPDM	100	100	100	100	100	100
ZnO	6	6	6	6	6	6
Stearic Acid	2	2	2	2	2	2
Carbon Black	100	100	100	100	100	100
DBDPE	0	20	0	20	20	20
Sb_2O_3	0	0	10	10	5	7
Inactive white filler	80	80	80	80	80	80
Process Oil	65	65	65	65	65	65
Curing accelerators	3,9	3,9	3,9	3,9	3,9	3,9
TOTAL phr	356,9	376,9	366,9	386,9	381,9	383,9

Untreated EPDM: 0 phr Sb_2O_3 and 0 phr DBDPE, ALFT 398; 20 phr DBDPE and 0 phr Sb_2O_3, ALFT 399; 0 phr DBDPE and 10 phr Sb_2O_3; ALFT 400; 20 phr DBDPE and 10 phr Sb_2O_3; ALFT 401; 20 phr DBDPE and 5 phr Sb_2O_3; ALFT 402; 20 phr DBDPE and 7 phr Sb_2O_3.

EPDM rubber, carbon black, white filler, process oil, other chemicals, activators and accelerators were added to mixer respectively. The reactive blendings of the polymers was carried out until 190 °C for 10 min in the intensive mixer.

Then the blending was took to the two roll mixing mill (YI-TZUNG MT2-2 Basic Model) to achieve better mixing and obtain homogeneity and prevent scorching. Two roll mixing mill can be seen in Figure 3.3. The mixing mill had the rolls of 155 mm in diameter with adjustable nip gape between rolls ranging from 0.2 mm to 1 cm. The mill was equipped with cooling water to control the temperature of the mill to the specified temperature in order to avoid premature vulcanization (scorching).



Figure 3. 3 YI-TZUNG MT2-2 basic model laboratory mill

To get a vulcanization curve and also minimum and maximum torque values, (ML and MH) and t90–ts2 burning periods, Alpha Technologies MDR 2000 Moving Die Rheometer was used. Test machine can be seen in Figure 3.4. The test was done according to ASTM D 2084-95. After getting the homogeneous mixture in two-roll mixing mill, 5 grams of mixture was taken and placed to the rheometer test machine. At the end of the reological control at 200 °C and 5 minutes by using Alpha Technologies MDR 2000 Moving Die Rheometer, vulcanization curves and parameters were recorded.



Figure 3. 4 Alpha Technologies MDR 2000 Moving Die Rheometer

Table 3. 4 Rheological parameters of rubber

Minimum Torque (ML)	dNm	ASTM D 2084-95
Maximum Torque (MH)	dNm	ASTM D 2084-95
Scorch Time (ts2)	min:s	ASTM D 2084-95
Vulcanization Time (t90)	min:s	ASTM D 2084-95

The granules of EPDM blends were used to mold plates at 180 °C, pressure of 13 MPa and, an exposure of optimum curing time, 9 min. Vulcanization of the compounds was carried out in compression type laboratory-press can be seen in Figure 3.5. The optimum curing time (t90) had been determined by using Alpha MDR2000.



Figure 3. 5 Compression type laboratory-press

The vulcanized test plates with dimensions of 2.00*1450*1450*mm cutted according to the ASTM D 412 was tested in Zwick Z010 tensometer and tensile strength, elongation at break and %300 modulus values were obtained. Zwick Z10 tensometer can be seen in Figure 3. 6.



Figure 3. 6 Zwick Z10 tensometer

The same vulcanized plates have been used to do other physical measurements, hardness and density controls.

3.4 Characterization Techniques for Polymer Blends

3.4.1 UL-94 Tests

UL-94 rating was obtained according to ASTM D3801 where V-0 indicates the best flame retardancy and V-2 is the worst. Bar specimens of 130 × 13 × 3.25 mm^3 were tested.

3.4.2 Limiting Oxygen Index Test (LOI)

As mentioned in the previous sections, LOI is the minimum oxygen concentration (volume percent of oxygen in an oxygen/nitrogen mixture) that will sustain burning. LOI test was performed according to the ASTM D2863 standards in the FTT Fire Testing Technology, Elevated Temperature Oxygen Index Analyzer instrument on test bars of size 130*65*2.00mm^3.



Figure 3. 7 FTT fire testing technology, elevated temperature oxygen index apparatus

During LOI test, the specimen was positioned in the vertical position in the transparent column. The concentration of oxygen in the column was set by adjusting the flow rates of oxygen and nitrogen gases that were moving upward through the column. The polymer was ignited from the top [107]. The schematic drawing of LOI can be seen in Figure 3. 8.

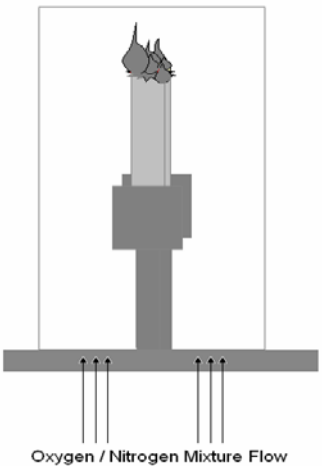


Figure 3. 8 The schematic drawing of LOI

3.4.3 Rheological Measurements

Rheological tests were used to characterize the flow properties of the rubber blends. Rheological test of the blends were performed by using an Alpha MDR 2000 rheometer machine which can be seen in Figure 3.4. 5 grams of piece was taken as a sample for testing. We set the temperature of measurement as 200 °C and 5 minutes**.** We get the vulcanization curve by the rheometer and find the vulcanization time (t90) of rubber.

3.4.4 Thermogravimetric Analysis (TGA)

The decomposition temperature of flame-retarded EPDM was observed using a Perkin-Elmer thermogravimetric analyser under nitrogen atmosphere, with sample masses of about 4 mg and a heating rate of 20 °C/min. The range of temperature was 30-800 °C.

3.4.5 Differential Scanning Calorimetry (DSC)

DSC was carried out on Mettler Toledo DSC 1 Star System at a heating rate of 10°C/min up to 400°C under nitrogen flow of 50ml/min.

3.4.6 Tensile Test of Elastomers

Tensile test of the vulcanized EPDM rubber sheets were performed according to the ASTM D 412-87 standard by using Zwick Z10 tensometer machine with a load cell of 5kN. The specimen used in the tensile test had a gauge length, L_0, of 20 mm, width of 4mm and thickness of 2 mm. All the tests were done at about 25 °C. The specimen can be seen in Figure 3.9. During the test, the crosshead speed of the testing instrument

was set to 20 mm/min. As a result of the test, tensile stress at yield and at break, Young's modulus and elongation at break and %300 modulus values were calculated. Each set was repeated for 5 specimens and the average values and standard deviations were reported.

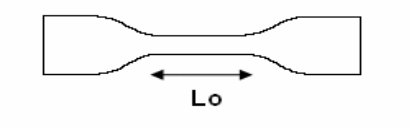


Figure 3.9 Tensile test specimen

3.4.7 Hardness Test

Hardness test of the blends were performed according to the ASTM D2240 standard by using Durometer that can be seen in Figure 3. 10.



Figure 3. 10 Durometer

3.4.8 Density Test

Density of blends was performed according to the ASTM D 297/15 by using of a pycnometer, by hydrostatic weighings, or by compressed volume densimeter. The pycnometer can be seen in Figure 3. 11.



Figure 3. 11 Pycnometer

CHAPTER 4

RESULTS

In results and discussion part, the flammability characteristics of different flame retardant containing EPDM rubber blends are discussed and the flammability, rheological, thermal and mechanical results are given for flame-retardant EPDM blends.

In this study by using halogen-antimony synergism, flame retardant EPDM based rubber was produced. Sulphur vulcanization was used as curing system. Amounts of flame retardant chemicals DBDPE and antimony trioxide were changed for each trial. Physico-mechanical properties of flame retardant EPDM rubber were investigated. At semi-finished stage rheometer tests were done and vulcanization curve were obtained. At final stage, flammability tests UL-94 and limiting oxygen index (LOI) tests and also density, hardness, tensile-elongation tests were performed. Temperature stability of samples were examined by TGA ve DSC.

4.1 Rheological Properties

Rheometer test which has very importance in rubber industry provides information for the changing characteristics during vulcanization. Rheological properties has an important role to control vulcanization variables and to determine spesific vulcanization requirements for mixture and operating conditions.

Rheometer test results of flame-retardant EPDM formulations are given in Table 4. 1.

Table 4. 1 Rheometer test results of flame-retardant EPDM formulations

Test Parameters	untreated EPDM	ALFT 398	ALFT 399	ALFT 400	ALFT 401	ALFT 402
Rheometer Test Temperature, °C	200	200	200	200	200	200
Rheometer Test Time, minute	5	5	5	5	5	5
ts2, second	00:24	00:29	00:29	00:29	00:28	00:28
t90, second	00:52:00	01:26:00	01:26:00	01:43:00	01:28:00	01:20:00
ML, N.m	1.4	2.28	1.92	2.26	2.2	1.89
MH, N.m	11.81	21.33	19.17	20.67	21.21	18

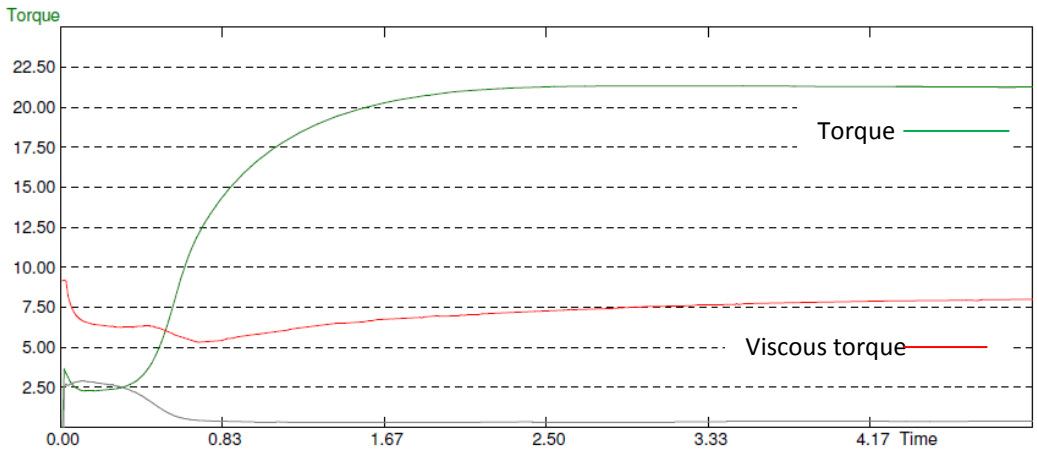


Figure 4. 1 Rheometer curve of ALFT 398 sample

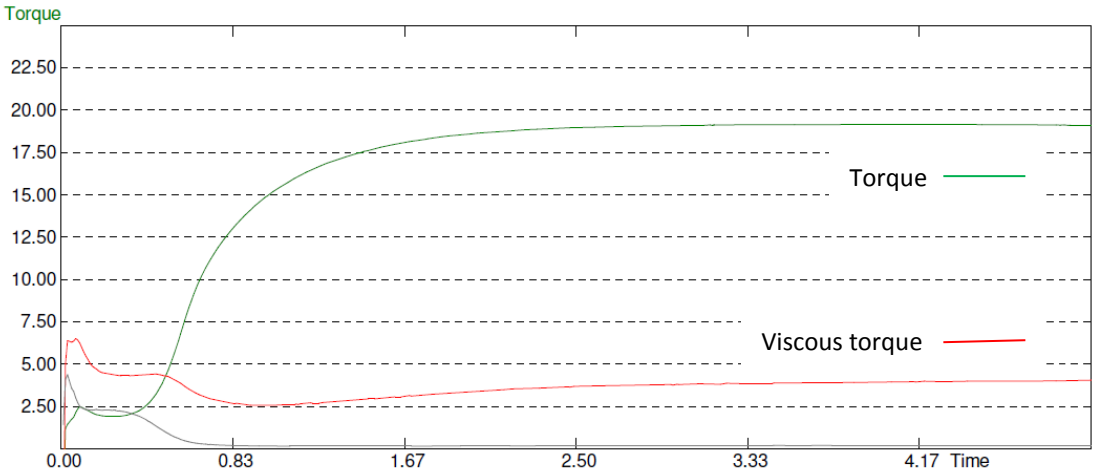


Figure 4. 2 Rheometer curve of ALFT 399 sample

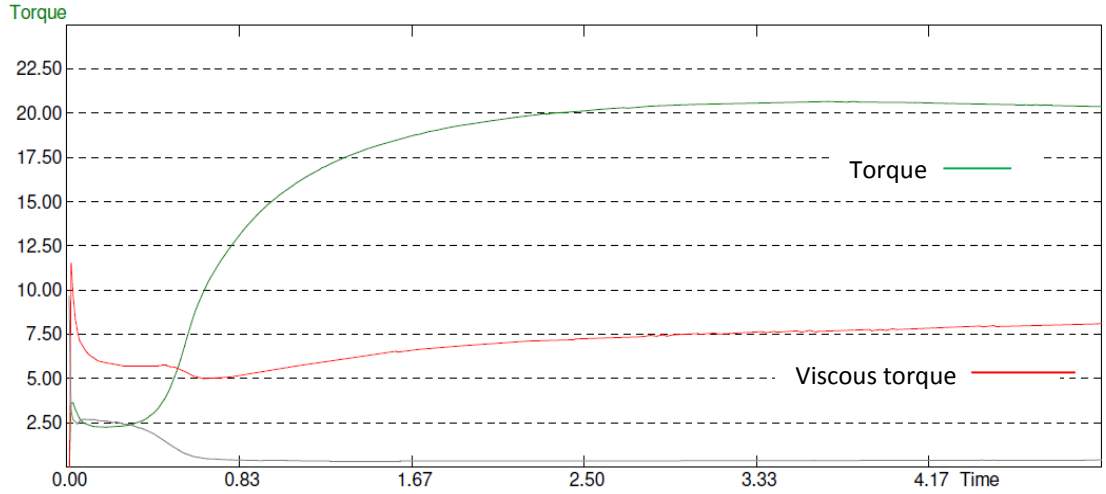


Figure 4. 3 Rheometer curve of ALFT 400 sample

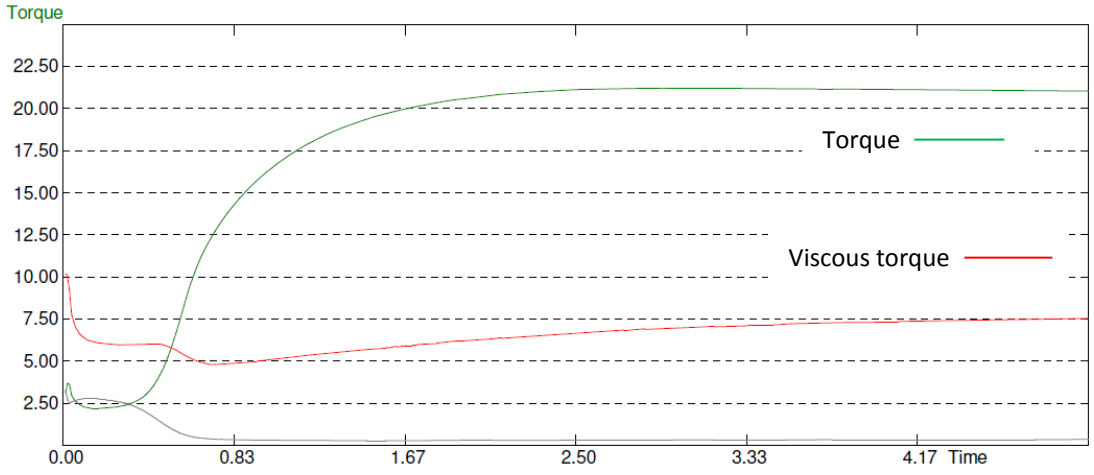


Figure 4. 4 Rheometer curve of ALFT 401 sample

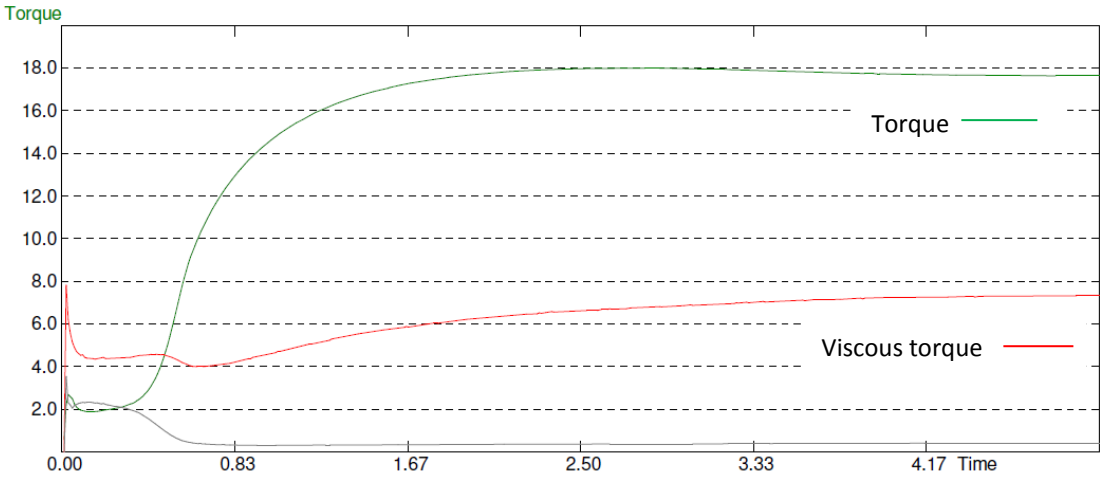


Figure 4. 5 Rheometer curve of ALFT 402 sample

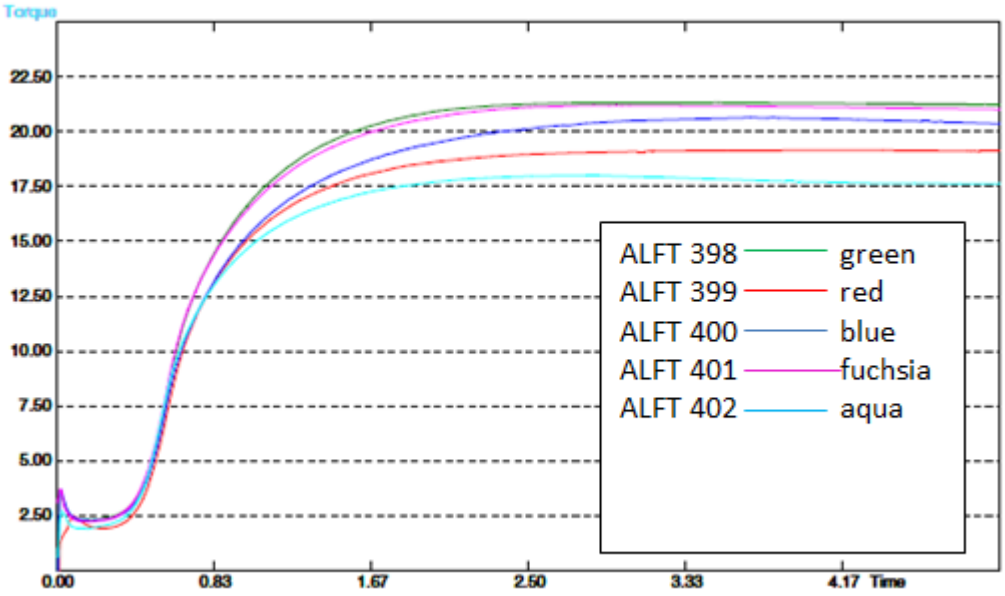


Figure 4. 6 Comparison of rheometer curves

The parameters most commonly used in rubber industry, the minimum torque (ML) scorch time (ts2), optimum cooking time (t90) and the maximum torque (MH). ML value are changed according to the raw rubber and chemical ratios used in the mixture. So this is a physical property.

Scorch is the point of starting vulcanization. In the scorch time, accelerators and activators create complexes and then vulcanization starts. It is known today that this accelerators creates which complexes, but it is not known exactly that what are that

complex behaviours and their effects in the vulcanization mechanism. Basis vulcanization complex is as follows [108].

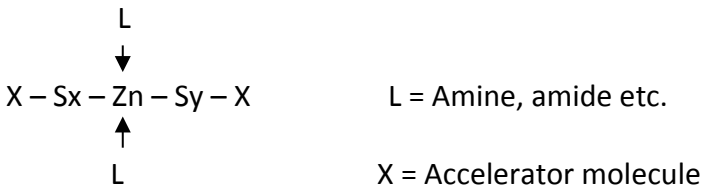


Figure 4. 7 Cross-linked complex

Crosslinking of a small portion of polymer molecules severely disrupts the flow properties. (at least 5% of the polymer molecules). This situation makes it difficult to subsequent processes, will affect physical properties and surface appearance of the final product.

In this case, the mixture must be known that how it is sensitive to the early vulcanization. This period of time known as scorch time is important information for the process.

Scorch time is required to be a certain range according to operating conditions. If scorch time is too short, it will lead early cooking problem which causes instability of shape and surface roughness problems. If scorch time is too long, there is late cooking (leaving from the cooking line without exact cooking) will lead measurement disturbances.

In sulphur vulcanization of EPDM it can be said that scorch time is unchangable with changing DBDPE and Sb_2O_3. Scorch time is generaly changes with carbon black amount.

Optimum cooking time, t90, is named as %90 of time that been spent to reach to MH. It is corresponding to 90% of curing. It is important for determining that how long time it should take in cooking line.

Because of the synergism occured between DBDPE and Sb_2O_3, t90 is getting higher. The desired state in the rubber industry is fast and secure cooking. So long scorch time and short optimum cooking time is desired.

Maximum torque, MH, is named as the time corresponding to 90% of curing. It is a module related with polymer type, cross-link type, cross-link density and density of mixture and also hardness of mixture. At this point vulcanisation is completed.

MH has increased with increasing total bond number (monosulfudic+ disulfudic+polisulfudic bonds). Besides this, mono and disulfudic bonds are stronger than the polisulfudic bonds so with increasing of this bonds MH further increases.

MH's rise can't directly interpreted as the increase in hardness.

Because hardness is directly related with filler and oil ratio. So then while the hardness increases, MH remains constant, or vice versa. When the hardness is constant and increased MH, tensile strength or elongation at break or both of them can increase.

This change is relevant with bond structure. If MH was increased due to the mono and disulfudic bonds, tensile strength is expected to raise. If MH was increased due to the polisulfudic bonds, elongation at break is expected to raise [108].

4.2 Flammability Properties

4.2.1 LOI Results

Brominated flame retardant and antimony trioxide are blended with EPDM in order to improve the flame retardancy of polymer.

The total amount of flame retardants, decabromodiphenylethane (DBDPE) and antimony trioxide (Sb_2O_3) compounds, mixed with ethylene propylene diene monomer (EPDM) were maintained at 0 phr, 5 phr, 7 phr and 10 phr Sb_2O_3 compound addition correspond to 20 phr and 0 phr in the amount of DBDPE respectively. The composition of formulations and UL-94 ratings and LOI values of flame retardant EPDM are listed in Table 4. 2.

The results showed that untreated EPDM had low resistance to combustion. After addition of DBDPE, LOI value increased slightly. With increasing amounts of DBDPE the value was raised from 18.5 to 19.4. The results indicate that DBDPE alone is not a very effective flame retardant towards EPDM. The presence of a small amount of Sb_2O_3 could increase the LOI value of EPDM, as the value was raised from 18.5 to 20.3 but

the LOI value had little significant variation from 5 to 10 phr. Therefore, the flame retardation of Sb_2O_3 towards EPDM also was not very good. There were higher LOI values as Sb_2O_3 was incorporated with DBDPE because of synergism. Antimony trioxide acted as a synergist with halogens, particularly with bromine, while it was almost totally ineffective when used without halogen. Synergism occurred through a series of reactions; the basic reaction in the case of brominated flame retardant was [109].

$$Sb_2O_3 + 6HBr \longrightarrow 2SbBr_3 + 3H_2O \quad (4.1)$$

where the HBr was produced resulting from the decomposition of brominated flame retardant. Antimony tribromide formed a dense white smoke that snuffed the flame by excluding oxygen from the front of the flame.

In order to determine properly if two kinds of flame retardant have synergism, it could be compared L_{AB} with L_{A+B}. L_{AB} is the LOI value when two kinds of flame retardant are commonly used. $L_{A+B}= L_A+L_B -L_P$, L_A or L_B is the LOI value when flame retardant is used alone, L_P is the LOI value of polymer matrix [110]. When $L_{AB} > L_{A+B}$, two kinds of flame retardant have synergism. When $L_{AB} = L_{A+B}$, two kinds of flame retardant have additional role. When $L_{AB} < L_{A+B}$, two kinds of flame retardant have opposite role. The ΔLOI ($\Delta LOI = L_{AB} – L_{A+B}$) values of Sb_2O_3 incorporated with DBDPE are listed in Table 4. 3. The results showed that ΔLOI > 0, so DBDPE incorporated with Sb_2O_3 had synergism. The stronger the synergism, the bigger the ΔLOI value was. When we added 20 phr DBDPE and 10 phr Sb_2O_3, ΔLOI value was biggest.

Table 4. 2 The ΔLOI value of EPDM containing DBDPE and Sb_2O_3

DBDPE (phr)	Sb_2O_3 (phr)	L_F	L_S	L_P	L_{F+S}	L_{FS}	ΔLOI
20	5	19.4	-	18.5	-	24	-
20	7	19.4	-	18.5	-	25.1	-
20	10	19.4	20.3	18.5	21.2	25.6	4.4

L_F, L_S, L_{FS} are the LOI values of EPDM, respectively, flame retarded by DBDPE, Sb_2O_3, DBDPE/ Sb_2O_3.
L_P is the LOI value of untreated EPDM.
$L_{F+S} = L_F+L_S - L_P$.
ΔLOI value is the difference of LOI value between L_{FS} and L_{F+S}.

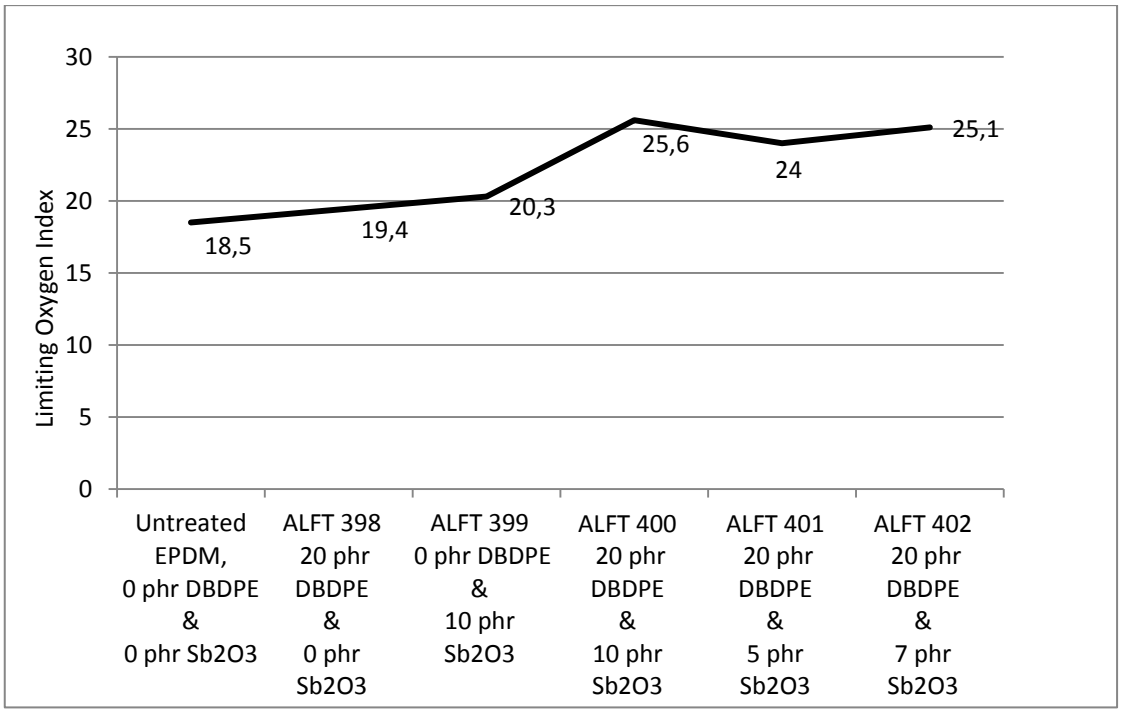


Figure 4. 8 LOI values of EPDM Blends

4.2.2 UL-94 Results

According to UL-94 test, total burning time (t1+t2) of ALFT 400 and ALFT 402, is less than 10 seconds. t1 and t2 are the afterflame time after first and second ignitions, respectively. Total burning time of ALFT 401 is 10 seconds, then classified as V-1. Total burning time of ALFT 398, ALFT 399 and untreated EPDM is more than 15 seconds and classified as V-2.

Table 4. 3 UL-94 and LOI values of untreated and treated EPDM

SAMPLE NAME	DBDPE, phr	Sb_2O_3, phr	UL-94 value	t1 (s)	t2 (s)	LOI value
Untreated EPDM	0	0	V-2	10.5 ± 1	15 ± 3.5	18.5
ALFT 398	20	0	V-2	8.5 ± 1	9.0 ± 2.5	19.4
ALFT 399	0	10	V-2	7.5 ± 1.2	9.0 ± 1.9	20.3
ALFT 400	20	10	V-0	2.5 ± 1	5 ± 1.5	25.6
ALFT 401	20	5	V-1	4.5 ± 1	5.5 ± 1.5	24.0
ALFT 402	20	7	V-0	3 ± 1.8	5 ± 1.8	25.1

4.3 Thermal Properties

4.3.1 Thermogravimetric Analysis Results

Thermogravimetric analysis (TGA) is used in order to get thermal stability of the EPDM rubber blends with different DBDPE and Sb_2O_3 loadings and compared with that of samples.

When the so-called flame retardant elements are incorporated into polymeric materials, the weight loss pattern of the polymers is altered. TGA can serve as a useful indicator of polymer flammability. TGA curves of compositions are shown in Figure 4.9. TGA data of all composites are listed in Table 4.4.

The difference in degradation behaviour of the EPDM containing various flame retardant elements could be clearly seen from the differential thermogravimetric (DTG) thermograms. Based on the numbers of peaks in the DTG thermograms, the weight loss processes of EPDM were considered as several stages. Owing to the action of the flame retardant elements, very different degradation behaviour was observed and different numbers of weight loss stages were found in Figure 4.9. The temperatures at the maximum weight loss rate (T_{max}) and the value of the maximum weight loss rate (R_{max}) for every stage of weight loss were read from the peak values of the DTG thermograms (Table 4. 4).

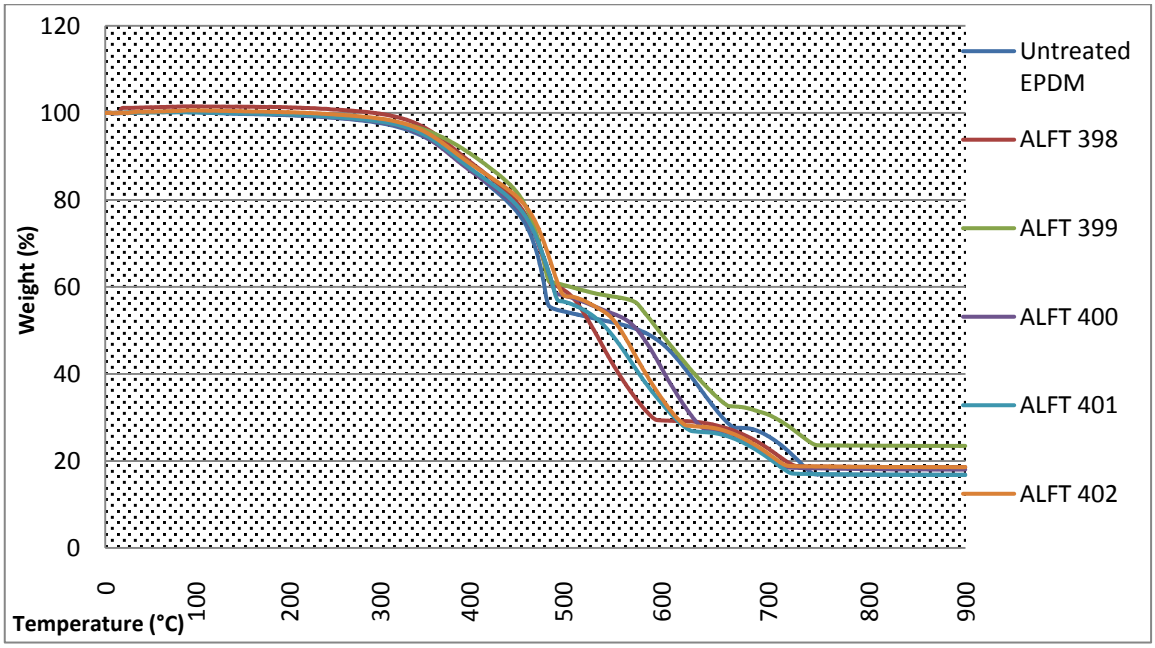


Figure 4. 9 TGA curves of EPDM blends

Table 4. 4 Typical TGA thermograms of EPDM blends: untreated EPDM; ALFT 398, ALFT 399, ALFT 400, ALFT 401, ALFT 402

Sample Name	**$T_{5\%}$ (°C)**	**$T_{50\%}$ (°C)**	**T_{max}^{1} (°C)**	**R_{max}^{1} (%/°C)**	**T_{max}^{2} (°C)**	**R_{max}^{2} (%/°C)**	**T_{max}^{3} (°C)**	**R_{max}^{3} (%/°C)**	**T_{max}^{4} (°C)**	**R_{max}^{4} (%/°C)**	**T_f (°C)**	**Char Ratio (%)**
untreated EPDM	344	575	413	84.8	484	59.35	642	36.5	731	19.76	750	16.91
ALFT 398	362	539	372	93.3	486	63.77	550	45.71	709	21.45	732	18.76
ALFT 399	363	601	-	-	484	64.33	596	51.47	732	26.13	754	23.57
ALFT 400	345	577	384	89.15	489	60.83	602	42.13	704	20.54	728	18.41
ALFT 401	350	551	387	89.49	491	60.06	579	41.89	708	19.58	735	17.03
ALFT 402	356	566	377	91.99	489	64.5	583	43.95	708	20.54	771	18.67

$T_{5\%}$ represents the onset decomposition temperature of 5% weight loss.

$T_{50\%}$: 50% decomposition temperature.

T_{max} represents the temperature of maximum weight loss rate in the n-stage decomposition.

R_{max} represents the maximum weight loss rate in the n-stage decomposition.

T_f represents the final decomposition temperature.

In nitrogen, the untreated EPDM showed a mass loss stage at temperature about 344°C. Introducing DBDPE into EPDM would increase the initial decomposition temperature of EPDM. The depressed initial decomposition temperature of the DBDPE containing EPDM might possibly result from the decomposition of C-Br bonds or the evaporation of DBDPE.

The thermogram of the Sb_2O_3-containing EPDM was the same as that of untreated EPDM except for the char ratio at 750 °C. The char ratio at 750 °C of the Sb_2O_3-containing EPDM was 23.57 wt% and was nearly proportional to the addition of Sb_2O_3 which mostly did not evaporate on heating. So Sb_2O_3 was not an effective flame retardant towards EPDM. From the results of limiting oxygen index and thermogravimetric analysis, Sb_2O_3 mostly played a filling role in EPDM.

If we introduced DBDPE and Sb_2O_3 into EPDM, much more complicated mass loss behaviours were observed. The char ratio at 771 °C was 18.67 wt%, which was higher than those of untreated EPDM and DBDPE containing EPDM. As mentioned previously, Sb_2O_3 had converted $SbBr_3$. From a promotion of charring after the main stage of weight loss, we can infer that $SbBr_3$ had both flame chemistry and a condensed phase effect.

It is found that the masses of the char residues of flame retarded composites containing DBDPE and Sb_2O_3 increase slightly, which illustrates that Sb_2O_3 could promote the char formation of the composites.

4.3.2 Differential Scanning Calorimetry Results

The DSC analysis is done in order to assess the effect of the additives on the thermal properties of the blends. The DSC curves of the polymer blends containing DBDPE and Sb_2O_3 can be seen in Figures 4.10. In addition, the melting points of the blends are presented in Tables 4.5. The DSC curves for all composites can be seen in Appendices B.

It can be seen from Table 4.5 and Figure 4.10 that the DSC results of the blends with flame retardants are very similar to each other having nearly the same melting temperatures.

Table 4. 5 Melting points of EPDM blends

SAMPLE	**T_m (°C)**
Untreated EPDM	484.206
ALFT 398	451.826
ALFT 399	483.572
ALFT 400	485.662
ALFT 401	489.394
ALFT 402	494.274

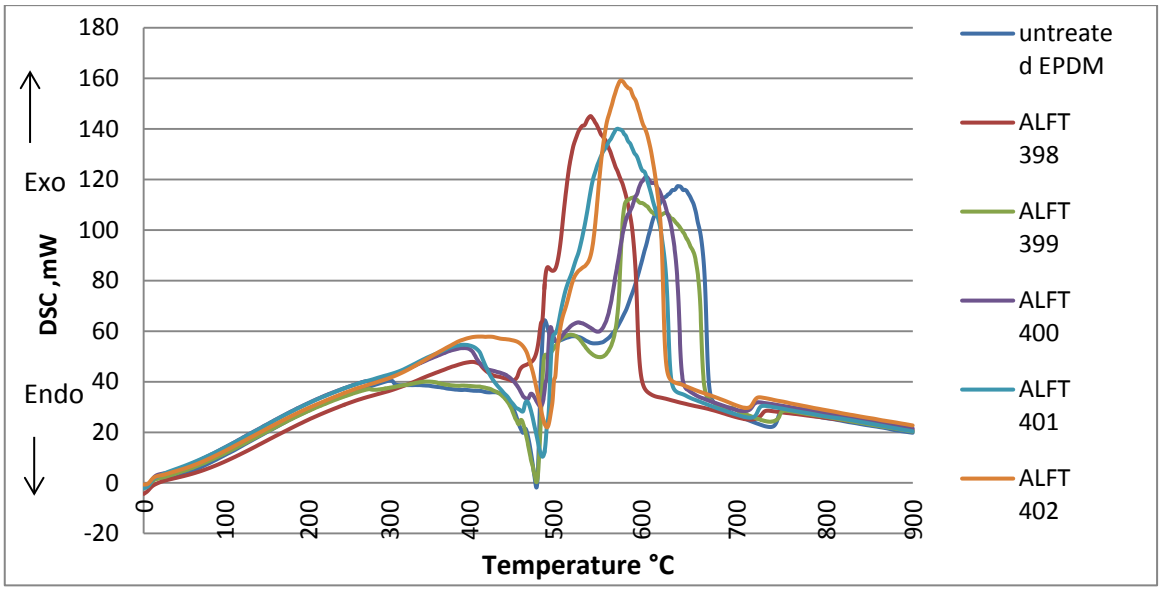


Figure 4. 10 DSC curves of polymer blends

4.4 Mechanical Properties

4.4.1 Tensile Test Results

After the rheological, flammability and thermal properties of the blends are completed, mechanical tests are applied to the polymer blends in order to see the effect of flame retardant addition to the mechanical properties of EPDM. The tensile properties of the blends are investigated by evaluating the tensile strength, 300% modulus and elongation at break results.

Table 4. 6 Mechanical properties of untreated and treated EPDM samples

Test Parameters	Untreated EPDM	ALFT 398	ALFT 399	ALFT 400	ALFT 401	ALFT 402
Vulcanization Temperature at Laboratory Press, °C	180	180	180	180	180	180
VulcanizationTime at Laboratory Press, minute	09:00	09:00	09:00	09:00	09:00	09:00
LOI	18.5	19.4	20.3	25.6	24	25.1
UL-94	Fail	V-2	V-2	V-0	V-1	V-0
Tensile Strength, MPa	12.85	11.64	11.61	10.27	11.33	11.19
Elongation at Break, %	535.83	341.1	323.3	348.18	345.23	341.15
%300 Modulus, MPa	6.74	10.2	10.79	8.85	9.85	9.82
Hardness, Shore A	69	74	73	75	75	74
Density, g/cm^3	1.273	1.319	1.312	1.349	1.339	1.344

The tensile properties of the blends with decabromodiphenylethane (DBDPE) and antimony trioxide (Sb_2O_3) are shown in Table 4.6 and Figures 4.11.

Agglomeration of fillers in the system reduces the tensile properties of the materials. However, theoretically there are other factors that might influence tensile properties such as shape of particles, filler dispersion and filler–matrix adhesion [112-116].

The shape of the filler particle also may affect the properties of the composites. It is reported that spherical filler reinforced composite has higher tensile strength while the composite reinforced with irregular filler showed lower tensile strength [117, 118].

With increase in DBDPE content, the tensile strength at 100% elongation present a decreasing trend except for the elongation at break. Unteated EPDM sample has the tensile strength at 100% elongation of 12.85 MPa, the ALFT 399 sample has the tensile strength at 100% elongation of 11.61 MPa and 323.3% elongation at break value. In the ALFT 400 sample increasing with DBDPE content, has the tensile strength at 100% elongation of 10.27 MPa and %348.18 elongation at break.

Increase in DBDPE content greatly impairs the mechanical performance of flame retardant EPDM material. This can be explained by the plasticization effect of DBDPE with matrix EPDM. So, increase in DBDPE content can improve the flame retardancy but with the expense of mechanical properties.

Adding Sb_2O_3 decreased the mechanical properties, as the tensile strength was reduced from 11.64 to 10.27 MPa. Sb_2O_3 is a mineral and can create interfaces with, which may lead to a deterioration of tensile strength.

When we added 20 phr DBDPE and 10 phr Sb_2O_3, the tensile strength dropped to 10.27 which is not adequate for the application of EPDM. In order to obtain a better combination of mechanical properties and flame retardation, the combination of 20 phr DBDPE and 7 phr Sb_2O_3 seemed to be a suitable solution.

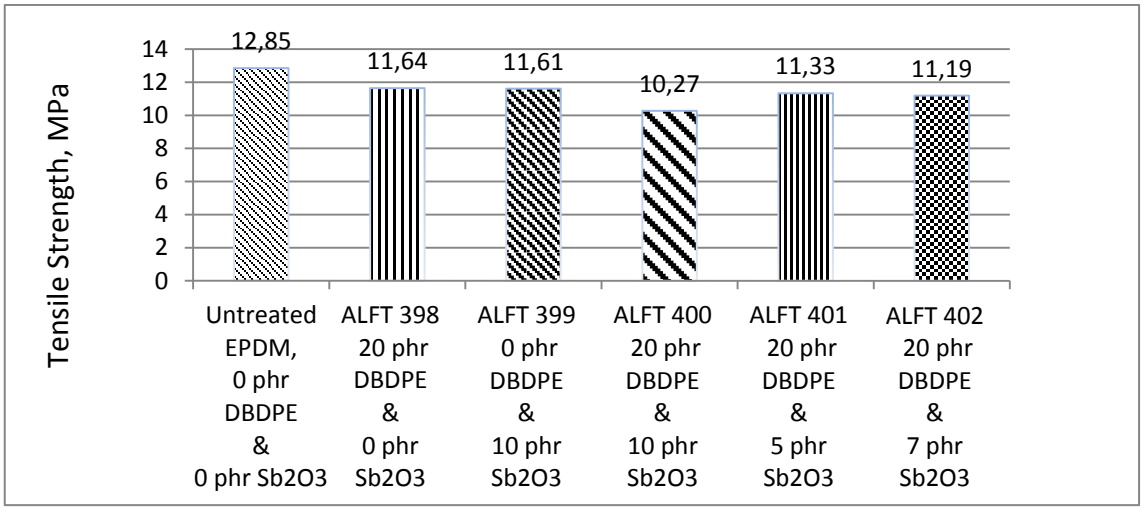


Figure 4. 11 Tensile strength of EPDM/DBDPE and Sb_2O_3 blends at break

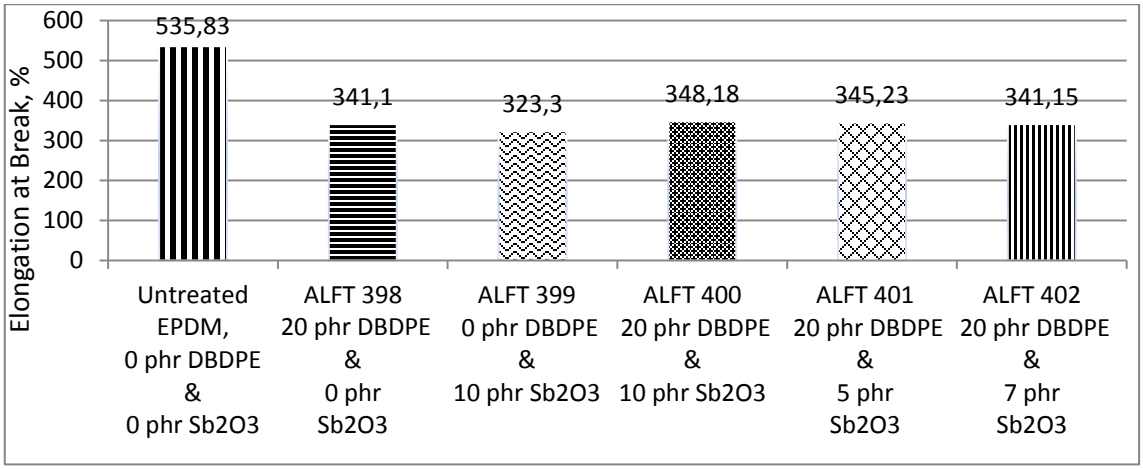


Figure 4. 12 Elongation at break values of EPDM/DBDPE and Sb_2O_3 blends

4.4.2 Hardness Test Results

Hardness is a measure of the resistance presented by a material when submitted to a local deformation [119, 120]. It depends, among other factors, on the amount of filler, the number of crosslinks and may be related to the modulus. Values of modulus at 100%, and hardness, also presented in Figure 4. 13, shown that they are not very sensitive to variations either in the type or the amount of DBDPE and Sb_2O_3.

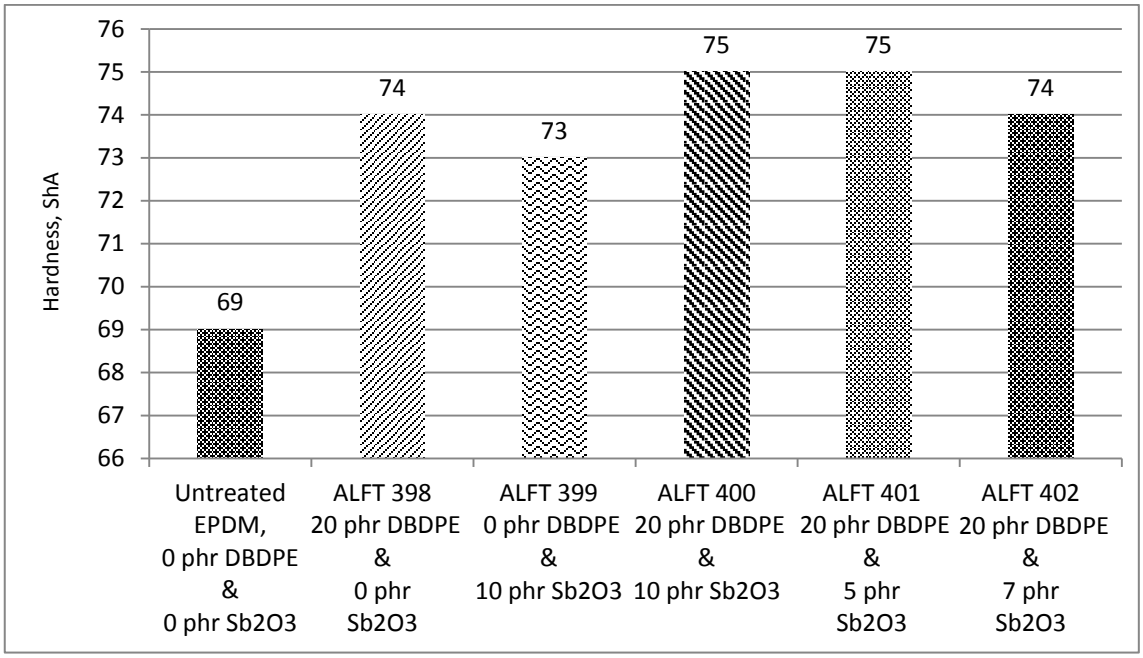


Figure 4. 13 Hardness of EPDM/DBDPE and Sb_2O_3 blends

4.4.3 Density Test Results

The density of a material is its mass per unit volume. Values of density presented in Figure 4.14, shown that it increases with increasing flame retardant amount.

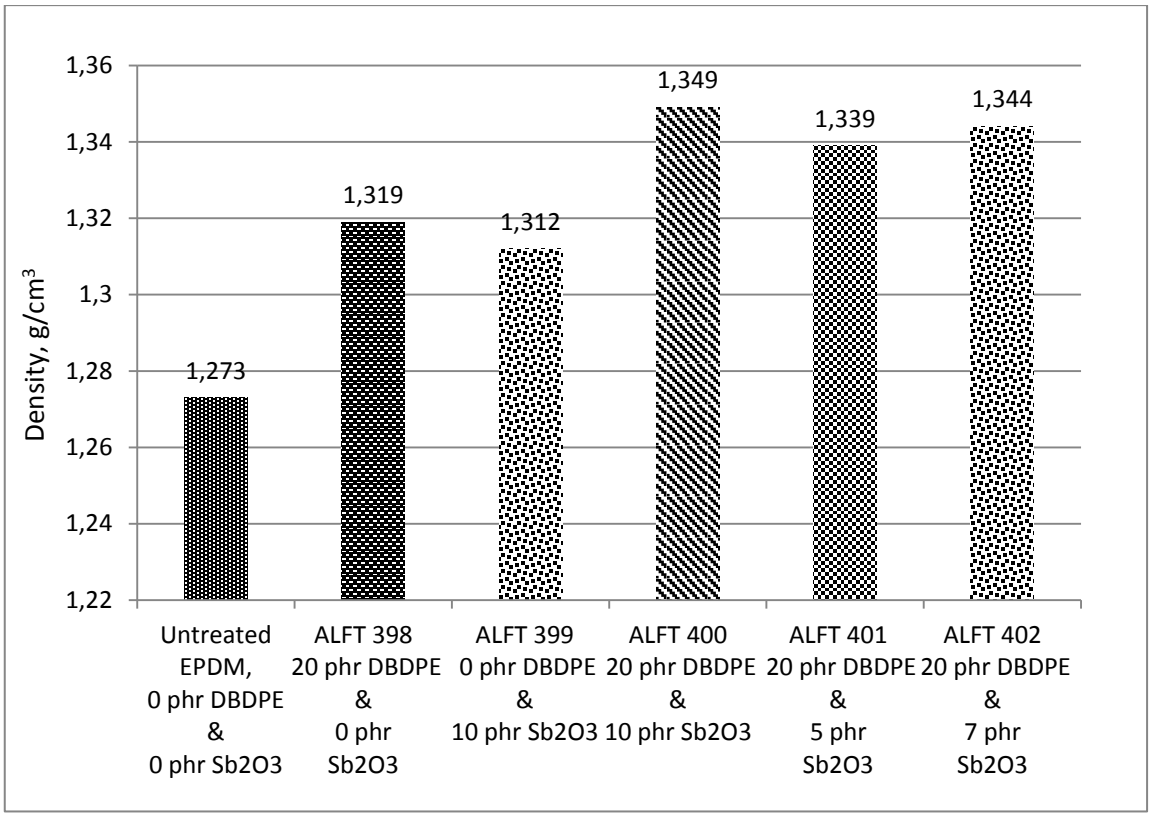


Figure 4. 14 Density values of EPDM/DBDPE and Sb_2O_3 blends

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

Different amount of decabromodiphenylethane (DBDPE) and antimony trioxide (Sb_2O_3) was added to the EPDM rubber, process oil, activators, accelerators, carbon black and other process aids. Taking the advantage of the halogen-antimony synergism, the effect of Sb_2O_3/DBDPE ratio on the flame retardancy and physico-mechanical properties of EPDM elastomer were investigated.

While rheometer tests were done in semi product step, flammability, density, hardness, tensile strength, elongation at break tests have been done to the final product for each formulation.

According to the analysis of the results of experiments, it was proved that untreated EPDM had low resistance to combustion. DBDPE and Sb_2O_3 when used alone produced little improvement in the flame retardation. The combination of DBDPE and Sb_2O_3 showed more effective flame retardation than the individual components. The maximum LOI value was 25.6, which was obtained from EPDM containing 20 phr DBDPE and 10 phr Sb_2O_3. But, if too much flame retardant was added in the compound, the tensile strength and elongation at break decreased rapidly (ALFT 399). It was seen that these flame retardants effected the thermal behaviour of EPDM, such as the degradation patterns, temperatures and rates of maximum mass loss.

ML, ts2, t90 and MH values are the most widely used process control parameters in rubber industry. It was also investigated that how Sb_2O_3/DBDPE ratio effects those control parameters. It was observed that ML increased with increasing rate of Sb_2O_3 /

DBDPE. It was also observed that MH, ts2 and t90 increased with increasing rate of Sb_2O_3/DBDPE.

Other important parameters that are valid in the rubber industry is hardness and density. It was observed that hardness and density increased while amount of DBDPE and Sb_2O_3 increased. Elongation at break and tensile strength for all mixtures was decreased, while amount of DBDPE and Sb_2O_3 increased.

As air contains 21% oxygen, material with an LOI below 21 are classified as combustible, LOI above 21 are classified as self-extinguishing. The higher the LOI is better the flame retardant property. As a result, generally EPDM rubber is flammable with the LOI value of 18.5. In this study it's LOI value was increased to 25.6 with DBDPE-Sb_2O_3 synergism.

REFERENCES

[1] Weil, E.D. and Levchick, S.V., (2008). "Flame Retardants in Commercial Use or Development for Polyolefins", Journal of Fire Sciences, 26: 5

[2] Beyer, G., (2001). "Flame Retardant Properties of EVA-nanocomposites and Improvements by Combination of Nanofillers with Aluminium Trihydrate", Journal of Fire Mater, 25(5): 193–197.

[3] Soh, A.K., Fang, D.N. and Dong, Z.X., (2004). "Analysis of Toughening Mechanisms of ZrO_2/Nano-SiC Ceramic Composites", Journal of Composite Materials, 38(3): 227–241.

[4] Yu-Xiang, O.U., (2002). Practical Flame Retardant Technology, Chemical Industry Press, Beijing.

[5] Snijders, E.A., Boersma, A. and Van Baarle, B., (2005). "Effect of Dicumyl Peroxide Crosslinking on the UV Stability of Ethylene-Propylene-Diene (EPDM) Elastomers Containing 5-Ethylene-2-Norbornene (ENB)", Journal of Polymer Degradation and Stability, 89:484–491.

[6] Ehsani, M., Borsi, H. and Gockenbach, E., (2004). "An Investigation of Dynamic Mechanical, Thermal and Electrical Properties of Housing Materials for Outdoor Polymeric Insulators" Journal of European Polymer, 40:2495–2503.

[7] Petsom, A., Roengsumran, S. and Ariyaphattanakul A., (2003). "An Oxygen Index Evaluation of Flammability for Zinc Hydroxystannate and Zinc Stannate as Synergistic Flame Retardants for Acrylonitrile-Butadiene-Styrene Copolymer", Journal of Polymer Degradation and Stability, 80:17–22.

[8] Chiu, S.H. and Wang, W.K., (1998). "Dynamic Flame Retardancy of Polypropylene Filled With Ammonium Polyphosphate, Pentaerythritol and Melamine Additives", Journal of Polymer, 39:1951-1955.

[9] Montezin, F., Lopez Cuesta, J.M., Crespy, A. and Georlette, P., (1997). "Flame retardant and mechanical properties of a copolymer PP/PE containing brominated compounds/antimony trioxide blends and magnesium hydroxide or talc", Fire and Materials, 21:245-252.

[10] Raghavan, J. And Krishnamurthy, V.N., (1998). "Insulation, Liner and Inhibition System in Propellants and Explosives Technology"; Edited: Krishnan, S., Chakravarthy, S.R. and Athithan, S.K., (1998) Allied Publishers, New Delhi.

[11] Morawetz, H., (1985). Polymers the Origins and Growth of Science, John Wiley and Sons.

[12] De, S.K. and Jim, R.W., (2001) . Rubber Technologist's Handbook, Rapra Technology, UK.

[13] Blow, C.M., (1971). Rubber Technology and Manufacture, Butterworth for the Institution of the Rubber Industry.

[14] Wikipedia, EPDM Rubber, http://en.wikipedia.org/wiki/EPDM_rubber, 26 December 2013.

[15] Jinzhu, T., Chao, Y.J., Wang, H., Gong J. and Vanzee J.W., (2009). "Chemical and Mechanical Stability of EPDM in a PEM Fuel Cell Environment", Journal of Polymer Degradation and Stability, 11:2072- 2078.

[16] Gamlin, C., Markovic, M.G., Dutta, N.K., Choudhury, N.R. and Matisons, J.G., (2003). "Structure Effects on the Degradation Kinetic of EPDM Elastomers by High-Resolution TGA and Modulated TGA", Journal of Thermal Analysis and Calorimetry, 59:319-336.

[17] Dick, J.S., (2001). Rubber Technology Compounding and Testing for Performance, Hanser Publisher.

[18] Du, A., Zhang, Z. and Wu, M., (2009). "The Effect of Pyrolytic Carbon Black Prepared From Junked Tires on Their Properties of The Ethylene-Propylene-Diene Copolymers (EPDM), Express Polymer Letters", 3:295-301.

[19] Su, J., Chen, S., Zhang, J. and Xu, Z., (2009). "Comparison of Cure, Mechanical, Electrical Properties of EPDM Filled with Sm_2O_3 Treated by Different Coupling Agents, Polymer Testing", 28:235-242.

[20] Clint, D.G., Dutta, N.K. and Choudhury, N.R., (2003). "Mechanism and Kinetics of The Isothermal Thermodegradation of Ethylene-Propylene-Diene (EPDM) Elastomers, Polymer Degradation and Stability", 80:525–531.

[21] Gwaily, S.E., Abdel-Aziz, M.M. and Madani, M., (1998). "Thermal and Electrical Studies on Irradiated Silica–Ethylene–Propylene Diene Monomer (SiO_2/EPDM) Composites Polymer Testing", 17:265–287.

[22] Morgan, A.B. and Wilkie, C.A., (2007). Flame Retardant Polymer Nanocomposites, Wiley, New York.

[23] Zhou, S., Wang, Z., Gui, Z. and Hu, Y., (2008). "A Study of The Novel Intumescent Flame-Retarded PP/EPDM Copolymer Blends", Journal of Applied Polymer Science, 110(6): 3804–3811.

[24] Lu, H., Yang, W., Zhou, S., Xing, W., Song, L. and Hu, Y., (2010). "Preparation and Flammability of EPDM/ PP/ $Mg(OH)_2$ Dynamic Vulcanizates", Polymers for Advanced Technologies, 21(2): 113–117.

[25] Bhowmick, A.K. and Stephens, H.L., (2000). Handbook of Elastomers, Second Edition, Marcel Decker, New York.

[26] John, A.R. and Vander Laan, R., (1990). "Ethylene Propylene Rubbers", The Vanderbilt Rubber Handbook; Vanderbilt R.T., Norwalk.

[27] Strate, G.V., (1986). “Ethylene Propylene Elastomers”, Encyclopedia of Polymer Science & Engineering, 6: 522-564.

[28] Boor Jr.J., (1979). “Ziegler-Natta Catalysts and Polymerization “, Academic Press, New York.

[29] Hofmann, W., (1989). Rubber Technology HandBook, Hanser, 3, New York.

[30] Morton, M., (1987). Rubber Technology, Second Edition, John Wiley, New York.

[31] ASTM D1418-06 Standard Practices for Rubber and Rubber Lattices-Nomenclature, 2006.

[32] Ver Strate G., Ethylene Propylene Elastomers, Encyclopedia of Polymer Science & Engineering, Vol. 6, pp. 522-564, 1986.

[33] ASTM D1566-09, (2011). Standard Terminology Relating To Rubber, ASTM.

[34] Wikipedia Free Encyclopedia, Vulcanization from Wikipedia, http://en.wikipedia.org/wiki/Vulcanization, 20 September 2013.

[35] Marton, J.M., Smith W.K., (2004). Handbook of Rubber Technology, CBS Publisher Delhi.

[36] Jian, T. and Carrie, W., (2004). Accelerator free nitrile gloves, Patent No. EP1435374.

[37] Morrison, N.J. and Porter, M., (1984). “Temperature Effects On The Stability of The Intermediates and Crosslinks In Sulfur Vulcanization”, Rubber Chemistry and Technology, 63- 85.

[38] Ferry, H.M. and Becker, A.V., (2004). HandBook of Polymer Science and Technology, 1, Oxford University Press.

[39] Eirich, F.R., (1978). Science and Technology of Rubber, Academic Press, New York.

[40] National Fire Programs, United States Fire Administration, http://www.fema.gov, 10 March 2012.

[41] Calamari, T.A. and Harper, R.J., (2000). “Flame Retardants for Textiles”, Kirk Othmer Encyclopedia of Chemical Technology.

[42] Grand, A.F. and Wilkie A.C., (2000). Fire Retardancy of Polymeric Materials, Marcel Dekker, Inc., New York.

[43] Lewin, M., Atlas, S.M. and Pearce, E.M., (1975). Flame Retardant Polymeric Materials, Plenum Press, New York and London.

[44] Lomakin, S.M. and Zaikov, G.E., (2003). Modern Polymer Flame Retardancy, VSP, Boston.

[45] Pearce, M.E. and Liepins, R., (1975). “Flame Retardants”, Environmental Health Perspectives, 11:59-69.

[46] Kuryla, W.C. and Papa, A.J., (1973). ”Flame Retardancy of Polymeric Materials”, 2, Marcel Dekker, New York.

[47] Pure Strategies, (2005). Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosures and Textile Applications, Massachusetts.

[48] Zhang, H., (2004). “Fire Safe Polymers and Polymer Composites”, Final Report, DOT-FAA-AR-04-11.

[49] Green, J., (1996). “Mechanisms for Flame Retardancy and Smoke Suppression, A review”, Journal of Fire Sciences, 14:426-442.

[50] Tsafack, M.J. and Levalois-Grützmacher J., (2006). “Plasma-Induced Graft-Polymerization of Flame Retardant Monomers onto PAN Fabrics”, Surface &Coating Technology, 200:3503-3510.

[51] Mazali, C.A.I. and Felisberti M.I., (2006). ”Vinyl Ester Resin Modified with Silicone-Based Additives Second Flammability Properties”, Journal of Applied Polymer Sciences, 99:644-649.

[52] Lu, S. and Hamerton, I., (2002). “Recent Developments in the Chemistry of Halogen-Free Flame Retardant Polymers”, Progress in Polymer Science, 27: 1661-1712.

[53] Nelson, G. L., (1978). “Chemistry”, 51:22-27.

[54] Nelson, G. L., (1979). Fire Retardants Polymers, Annual Review of Materials Science, 4:391-414.

[55] Troitzsh, J., (1983). International Plastics Flammability Handbook, Hansen: Munchen, Germany.

[56] Nelson, G.L., (1995). In Fire and Polymers II, Materials and Tests for Hazard Prevention, Washington D. C.

[57] Nelson, G.L., Kinson, P.L. and Quinn, C.B., (1974). “Fire Retardant Polymers”, Annual Review of Materials Science, 4:391-414.

[58] Atkinson, P.A., Haines, P.J. and Skinner G.A., (2000). “Inorganic Tin Compounds as Flame Retardants and Smoke Suppressants for Polyester Thermosets”, Thermochimica Acta, 360:29-44.

[59] Mouritz, A.P. and Gibson A.G., (2006). “Fire Properties of Polymer Composite Materials”, Springer, Dordrecht.

[60] Levchik, V.S. and Weil, E.D., (2000). “Featured Article Combustion and Fire Retardancy of Aliphatic Nylons”, Polymer International, 49:1033-1073.

[61] Lvov, B.V., Novichikhin, A.V. and Dyakov, A.O., (1998). “Mechanism of Thermal Decomposition of Magnesium Hydroxide”, Thermochimica Acta, 315: 135-143.

[62] Najafi-Mohajeri, N. and Nelson, G., (1998). “Polymer Preprints”, 39:380-381.

[63] Saadat, H. and Mack, A.G., (2008). PCT Patent Application WO 08/027781.

[64] Saadat, H., (2008). PCT Patent Application WO 08/027778.

[65] Mack, A.G. and McKinnie, B.G., (2008). PCT Patent Application WO 08/082709.

[66] Reitenbach, D., (2008). PCT Patent Application WO 08/008406.

[67] Weil, E.D. and Levchik, S.V., (2009). Flame Retardants for Plastics and Textiles Practical Applications, Hanser.

[68] Xanthos, M., (2005). “Funtional Fillers for Plastics”, Wiley-VCH, Weinheim.

[69] Li, Q., Pingkai, J. and Wei, P., (2005). “Thermal Degradation Behavior of Poly(propylene) with a Novel Silicon-Containing Intumescent Flame Retardant”, Macromolecular Materials and Engineering, 290:912-919.

[70] Bourbigot, S., Le Bras, M., Duquesne, S. and Rochery, M., (2004). “Recent Advances for Intumescent Polymers”, Macromolecular Materials and Engineering, 289:499-511.

[71] Xie, F., Wang, Y., Yang, B. and Liu, Y., (2006). “A Novel Intumescent Flame-Retardant Polyethylene System”, Macromolecular Materials and Enginnering, 291:247-253.

[72] Doğan, M. and Bayramli, E., (2011). “Synergistic Effect of Boron Containing Substances on Flame Retardancy and Thermal Stability of Clay Containing Intumescent Polypropylene Nanoclay Composites”, Polymers for Advanced Technologies, 22:1628-1632.

[73] Melamine based flame retardants mechanism of action, http://www.specialchem4polymers.com/tc/melamineflameretardants/index.aspx?id=4005, 05 May 2011.

[74] Lewin, M., (1999). “Synergistic and Catalytic Effects in Flame Retardancy of Polymeric Materials-An Owerview”, Journal of Fire Sciences, Brooklyn, 17:13-19.

[75] Little, R.W., (1947). Flameproofing Textile Fabrics, Reinhold, London.

[76] Khanna Y.P. and Pearce, E.M., (1978). “In Flame Retardant Polymeric Materials”, editors: Lewin M., Atlas S.M. and Pearce, E.M., 2:43.

[77] Hastie, J.W., (1973). “Molecular Basis of Flame Inhibition”, Combustion and Flame, 21: 178-401.

[78] Hastie, J.W. and McBee, C.L., (1975). “Mechanistic Studies Of Triphenylphosphine Oxide-Poly and Related Flame Retardant Systems”,75.

[79] Pitts, J.J., Scott, P.H. and Powell, D.G., (1970). “Journal of Cellular Plastics”, 6:6.

[80] Costa, L., Goberti, L., Paganetto, P., Camino, G. and Squarzi, P., (1989). “Proc. Meeting on FR Polymers”, Torino.

[81] Reed, N.J. and Highway-Berg, E.G., (1958). “Gested To Occur During the Pyrolysis and Combustion of Red Phosphorus”, Science Journal of Fire, 74:74.

[82] Weil, E.D., (1975). “In Flame Retardancy of Polymeric Materials”, Kuryla, W.C. and Papa, A.J., 3:185-203.

[83] Guo-Sheng, G., (2004). Ultrafine Power Technology, Chemical Industry Press, Beijing, 200.

[84] Li, F., Jiong-tian, L. and Yu-miao, M., (2005). "Preparation of Sb_2O_3/Mica Nanoparticles and Flame Retardant Principle", Journal of China University of Mining & Technology, 34(6): 750–755.

[85] KEMI, Information On Substances, http://apps.kemi.se/flodessok/floden/kemamne_eng/antimon_eng.htm, 05 February 2012.

[86] Hussain, S. and Mack, A., (2008). PCT Patent Application 08/115261.

[87] McKinnie, B.G., (2008). PCT Patent Application 08/115260.

[88] Stevens, G.C. and Mann, A.H., (1999). "Risks and Benefits In the Use of Flame Retardants in Consumer Products", London.

[89] National Academy of Sciences, (2000). National Research Council Subcommittee on Flame Retardant Chemicals, National Academy Press, Washington DC.

[90] European Chemicals Bureau, (2002). Institute for health and consumer protection..

[91] Hua, I., Kang, N. and Jafvert, C.T., (2003). "Heterogeneous Photochemical Reactions of Decabromodiphenyl Ether", Environmental Toxicology and Chemistry, 22(4): 798−804.

[92] Albemarle, Decabromodipehnylethane, http://albemarle.com/Home-3.html, 03 January 2012.

[93] Norman, H., (2007). Compounding Precipitated Silica in Elastomers, William Andrew Publishing/Plastics Design Library.

[94] Rosen S.L., (1993). "Fundamental Principles of Polymeric Materials", Second Edition, John Wiley & Sons, New York.

[95] Dick, J.S., (2003). Basic Rubber Testing - Selecting Methods for A Rubber Test Program

[96] Farrel Bridge Ltd., (1973). F-Series Banbury Mixer, Technical Bulletin.

[97] Funt, J.F., (2009). Mixing of Rubber, Smithers Rapra Technology Limited.

[98] Strong, A.B., (2006). Plastics Materials and Processing, Prentice Hall, New Jersey.

[99] Underwriters Laboroties Inc., (1997). UL-94-Test for Flammability of Plastic Materials for Parts in Devices and Appliances, Northbrook.

[100] Kiliaris, P., Papaspyrides, C.D., (2010). "Polymer/Layered Silicate (Clay) Nanocomposites: An Overview of Flame Retardancy", Progress in Polymer Science, 35:902-958.

[101] Laoutid F., Bonnaud L., Alexandre M., Lopez-Cuesta J.M., Dubois Ph., "New Prospects in Flame Retardant Polymer Materials: From Fundementals to Nanocomposites", Materials Science and Engineering R: Reports", vol.63, 100-125, 2009.

[102] Ciesiekski, A., (1999). An Introduction To Rubber Technology, Smithers Rapra Technology.

[103] FFInstruments Technology Systems Rheometer, http://www.ffinstruments.com/odrpdf/Oscillating, 13 Septermber 2013.

[104] Sandler, S.R., Karo, W., Bonesteel, J. and Pearce, E.M., (1998). "Polymer Synthesis and Characterization – A Laboratory Manual", Academic Press, San Diego.

[105] Cheremisinoff, N.P., (1996). Polymer Characterization - Laboratory Techniques and Analysis.

[106] Dictionary of Material and Testing. Second Edition, Joan L. Tomsic, With Contributions by Robert S. Hodder Manager, Metallurgical Services, Retired, Latrobe Steel, Society of Automotive Engineers, Inc.

[107] IDES The Plastics, Limiting Oxygen Index, http://www.ides.com/property_descriptions/ASTMD2863.asp, 20 June 2008.

[108] Standard Profil Factory, (2000-2005), Standard Profil Education Notes.

[109] La Rosa, A.D., Recca, A., Carter, J.T. and Me Grail, P.T., (1999). Polymer, 40.

[110] Hu, X., (1990). "Flame-Retardant", Material Technology, 1:48.

[111] Wu, C.S., Liu, Y.L. and Chiu, Y.C., (2002). Polymer Degradation and Stability, 78:41-48.

[112] Boudenne, A., Ibos, L. and Candau, Y., (2011). Handbook of Multiphase Polymer Systems, John Wiley & Sons Ltd, UK.

[113] Elleithy, R., Ali, I., Al-Haj Ali, M. and Al-Zahrani, S.M., (2011). "Different Factors Affecting the Mechanical and Thermo-Mechanical Properties of HDPE Reinforced with Micro-$CaCO_3$", Journal of Reinforced Plastics and Composites, 30(9):769–780.

[114] Liang, J.Z. and Li, R.K.Y., (2000). "Effect of Filler Content and Surface Treatment on the Tensile Properties of Glass-Bead-Filled Polypropylene Composites", Polymer International, 49(2):170-174.

[115] Saini, D.R, Nadkarni, V.M., Nigam, K.D.P. and Grover, P.D., (1987). "Tensile Properties of Highly Filled Magnetic Polymeric Composites", Journal of Composite Materials, 21(9):782–797.

[116] Ahmad, F.N., Jaafar, M., Palaniandy, S. and Azizli, K.A.M., (2008). "Effect of Particle Shape of Silica Mineral on the Properties of Epoxy Composites. Composites Science and Technology, 68(2):346–353.

[117] Leidner, J. and Woodhams, R.T., (1974). "Strength of Polymeric Composites Containing Spherical Fillers", Journal of Applied Polymer Science, 18(6): 1639–1654.

[118] Liang, J.Z., (2002). "Toughening and Reinforcing in Rigid Inorganic Particulate Filled Poly(propylene): A review", Journal of Applied Polymer Science,83(7): 1547–1555.

[119] Sheldon, R.P., (1982). Mechanical Properties of Composites, in Composite Polymeric Materials, Applied Science Publishers, New York.

[120] Shah, V., (1984). Mechanical Properties, in: Handbook of Plastics Testing Technology, John Wiley & Sons, New York.

APPENDIX-A

RHEOLOGICAL TEST REPORTS

ALFT 398 SAMPLE

AKTAS www.aktasgroup.com **TEST RESULTS** **06.07.2012 Page: 1**

Compound 201004 Description: DENEME 200

Preparation method: - None -
Ageing method: - None -

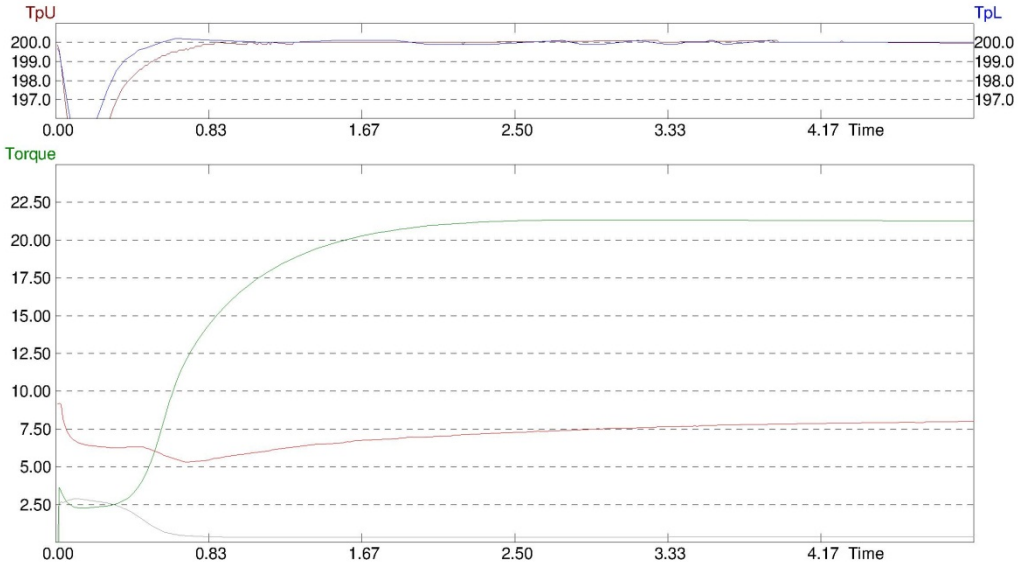
Orderno.: ALFT Batchno.: 398 Testno.: 1

Testcode: 41000 Descr.: Rheometer with curves ISO 3417

Variable		Value	Unit	LSL	USL
Test temp		200	°C		
Test time		10.0	min		
ML		2.28	dNm	1.00	2.50
MH	>	21.33	dNm	7.00	16.00
ts2	<	0:29	m:s	0:40	1:20
t90	<	1:26	m:s	3:00	4:00
t10		0:29	m:s		

Testdate	22.06.2012 16:19 AK
Validated by	AK
Limit version	0
Limits	Out of range
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	22.06.2012
Last changed	22.06.2012 AK

Status: **Fail**



ALFT 399 SAMPLE

AKTAS www.aktasgroup.com **TEST RESULTS** **06.07.2012 Page: 1**

Compound 201004 Description: DENEME 200

Preparation method: - None -
Ageing method: - None -

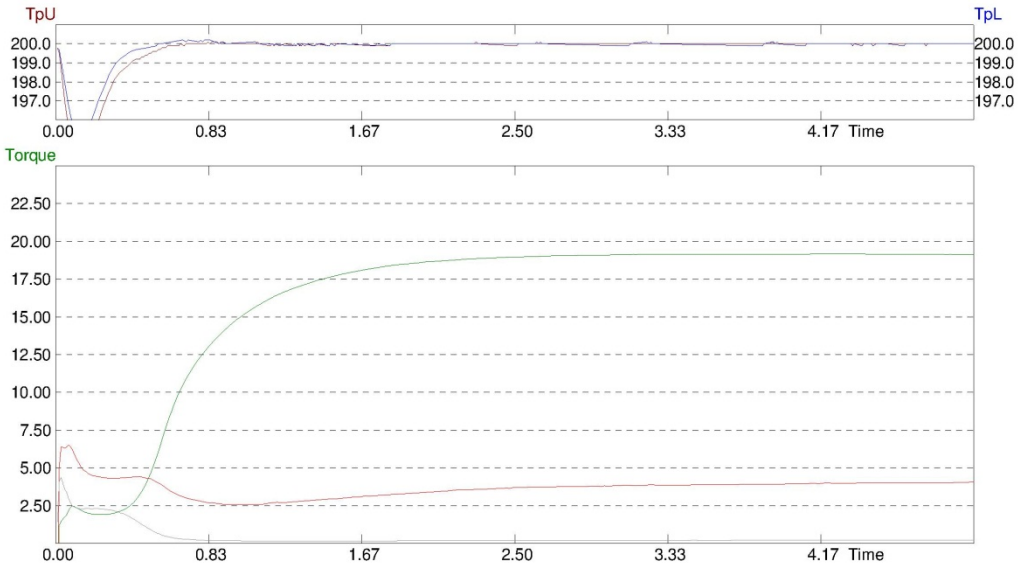
Orderno.: ALFT Batchno.: 399 Testno.: 1

Testcode: 41000 Descr.: Rheometer with curves ISO 3417

Variable		Value	Unit	LSL	USL
Test temp		200	°C		
Test time		10.0	min		
ML		1.92	dNm	1.00	2.50
MH	>	19.17	dNm	7.00	16.00
ts2	<	0:29	m:s	0:40	1:20
t90	<	1:26	m:s	3:00	4:00
t10		0:28	m:s		

Testdate	22.06.2012 16:25 AK
Validated by	AK
Limit version	0
Limits	Out of range
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	22.06.2012
Last changed	22.06.2012 AK

Status: **Fail**



ALFT 400 SAMPLE

AKTAS www.aktasgroup.com **TEST RESULTS** **06.07.2012 Page: 1**

Compound 201004 Description: DENEME 200

Preparation method: - None -
Ageing method: - None -

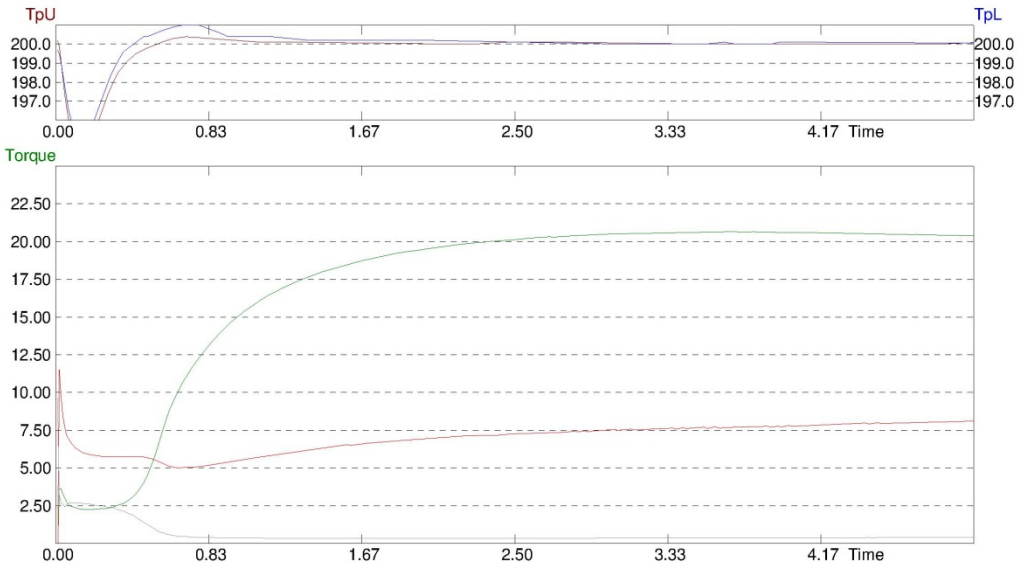
Orderno.: ALFT Batchno.: 400 Testno.: 1

Testcode: 41000 Descr.: Rheometer with curves ISO 3417

Variable		Value	Unit	LSL	USL
Test temp		200	°C		
Test time		10.0	min		
ML		2.26	dNm	1.00	2.50
MH	>	20.67	dNm	7.00	16.00
ts2	<	0:29	m:s	0:40	1:20
t90	<	1:43	m:s	3:00	4:00
t10		0:29	m:s		

Testdate	22.06.2012 14:16 AK
Validated by	AK
Limit version	0
Limits	Out of range
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	22.06.2012
Last changed	22.06.2012 AK

Status: **Fail**



ALFT 401 SAMPLE

AKTAS www.aktasgroup.com **TEST RESULTS** **06.07.2012 Page: 1**

Compound 201004 Description: DENEME 200

Preparation method: - None -
Ageing method: - None -

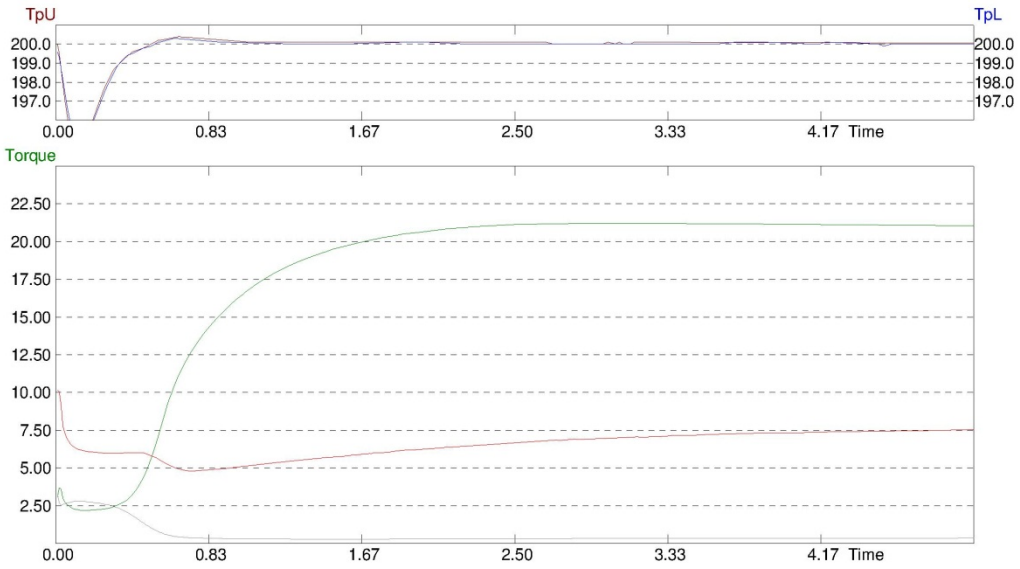
Orderno.: ALFT Batchno.: 401 Testno.: 1

Testcode: 41000 Descr.: Rheometer with curves ISO 3417

Variable		Value	Unit	LSL	USL
Test temp		200	°C		
Test time		10.0	min		
ML		2.20	dNm	1.00	2.50
MH	>	21.21	dNm	7.00	16.00
ts2	<	0:28	m:s	0:40	1:20
t90	<	1:28	m:s	3:00	4:00
t10		0:28	m:s		

Testdate	22.06.2012 16:12 AK
Validated by	AK
Limit version	0
Limits	Out of range
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	22.06.2012
Last changed	22.06.2012 AK

Status: **Fail**



ALFT 402 SAMPLE

AKTAS www.aktasgroup.com **TEST RESULTS** **06.07.2012 Page: 1**

Compound 201004 Description: DENEME 200

Preparation method: - None -
Ageing method: - None -

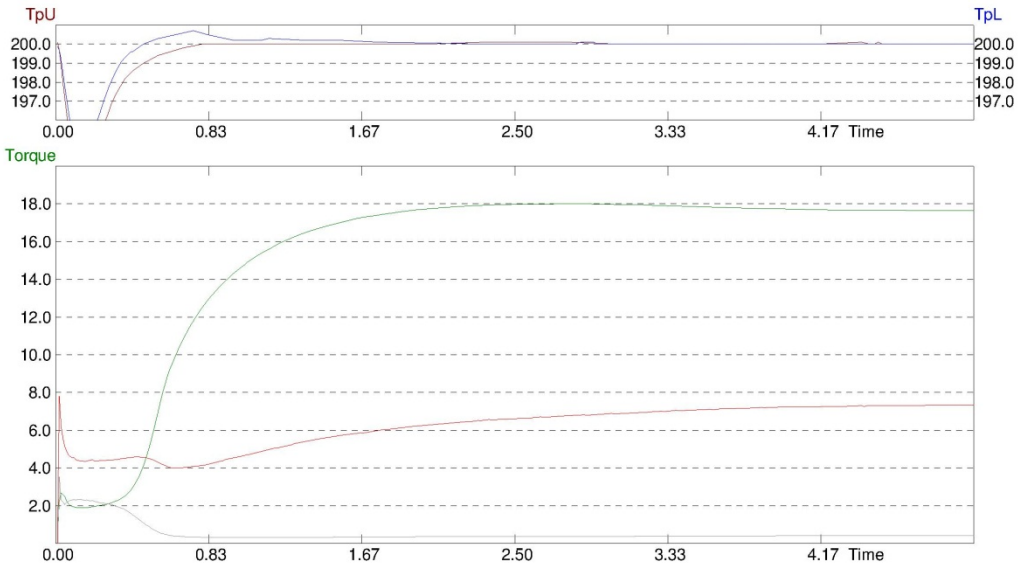
Orderno.: ALFT Batchno.: 402 Testno.: 1

Testcode: 41000 Descr.: Rheometer with curves ISO 3417

Variable		Value	Unit	LSL	USL
Test temp		200	°C		
Test time		10.0	min		
ML		1.89	dNm	1.00	2.50
MH	>	18.00	dNm	7.00	16.00
ts2	<	0:28	m:s	0:40	1:20
t90	<	1:20	m:s	3:00	4:00
t10		0:27	m:s		

Testdate	22.06.2012 08:33 AK
Validated by	AK
Limit version	0
Limits	Out of range
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	22.06.2012
Last changed	22.06.2012 AK

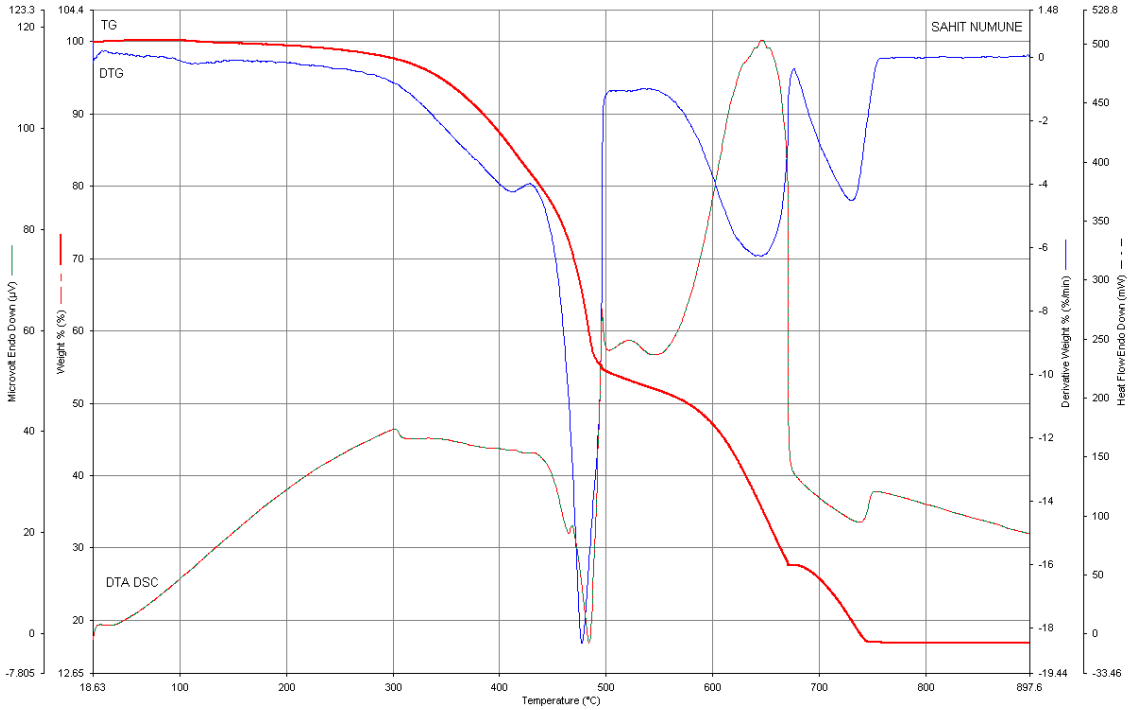
Status: **Fail**



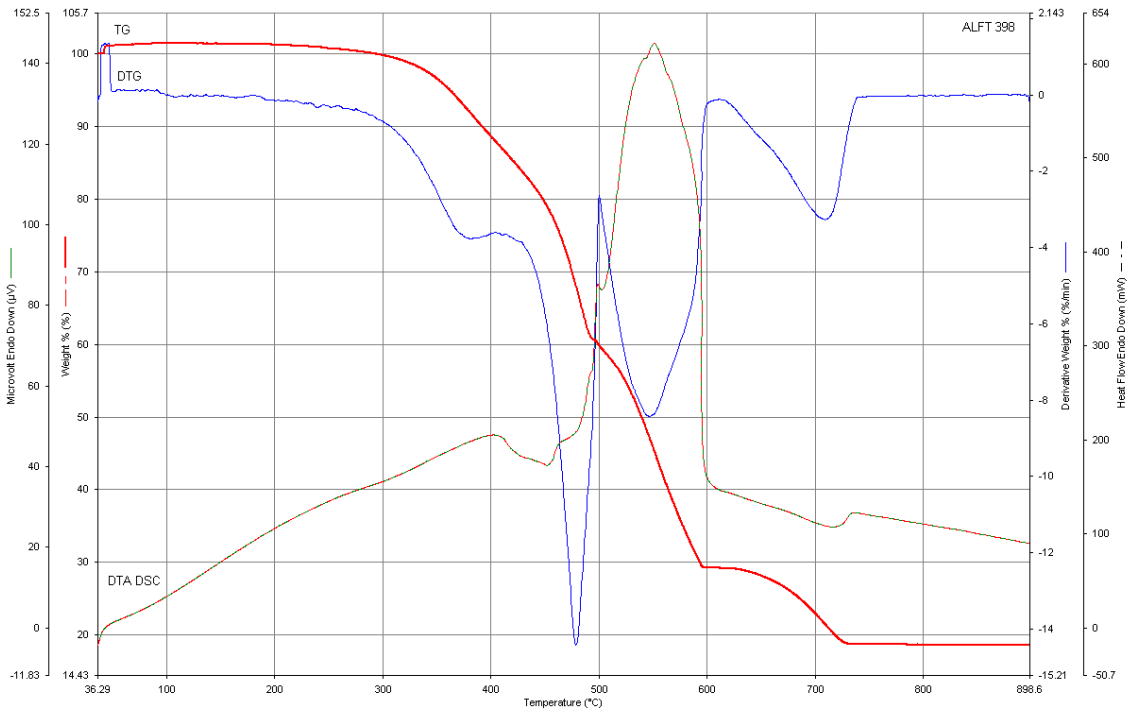
APPENDIX-B

TGA-DTA, DSC RESULTS

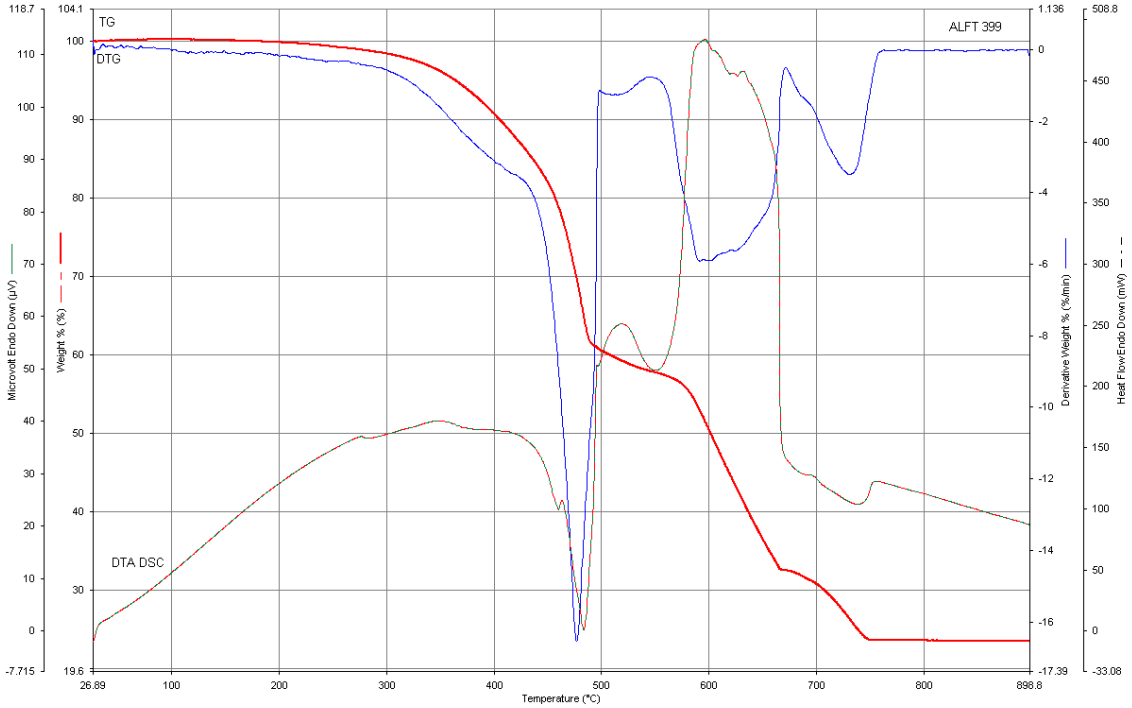
UNTREATED SAMPLE



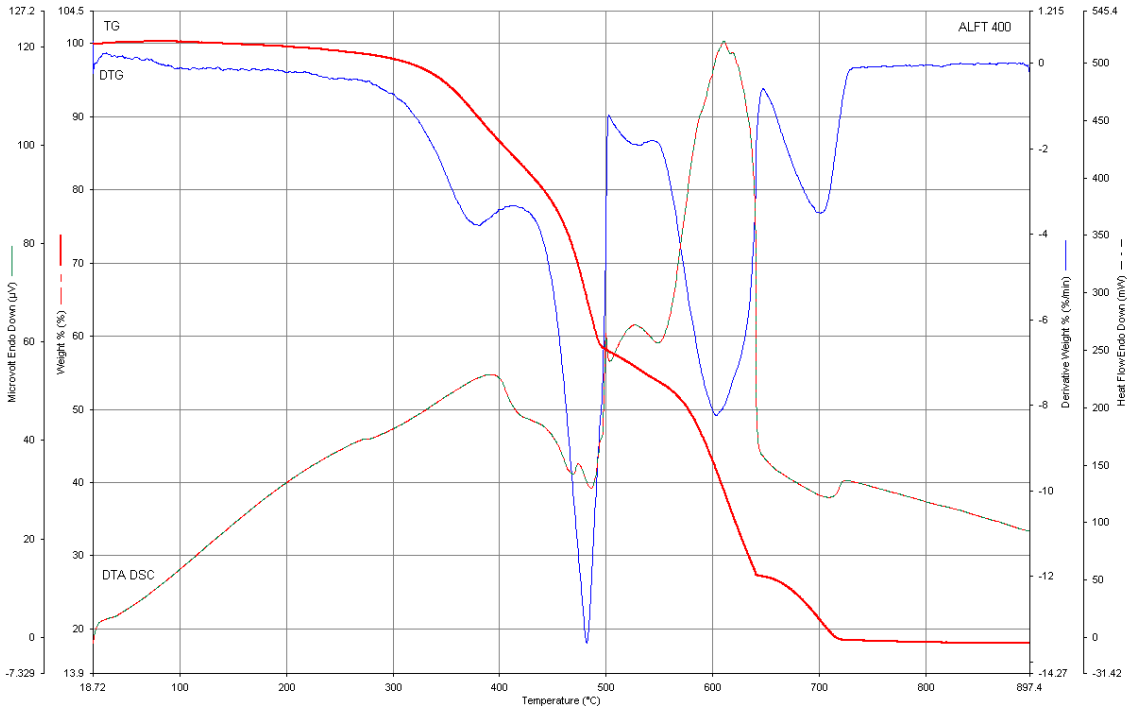
ALFT 398 SAMPLE



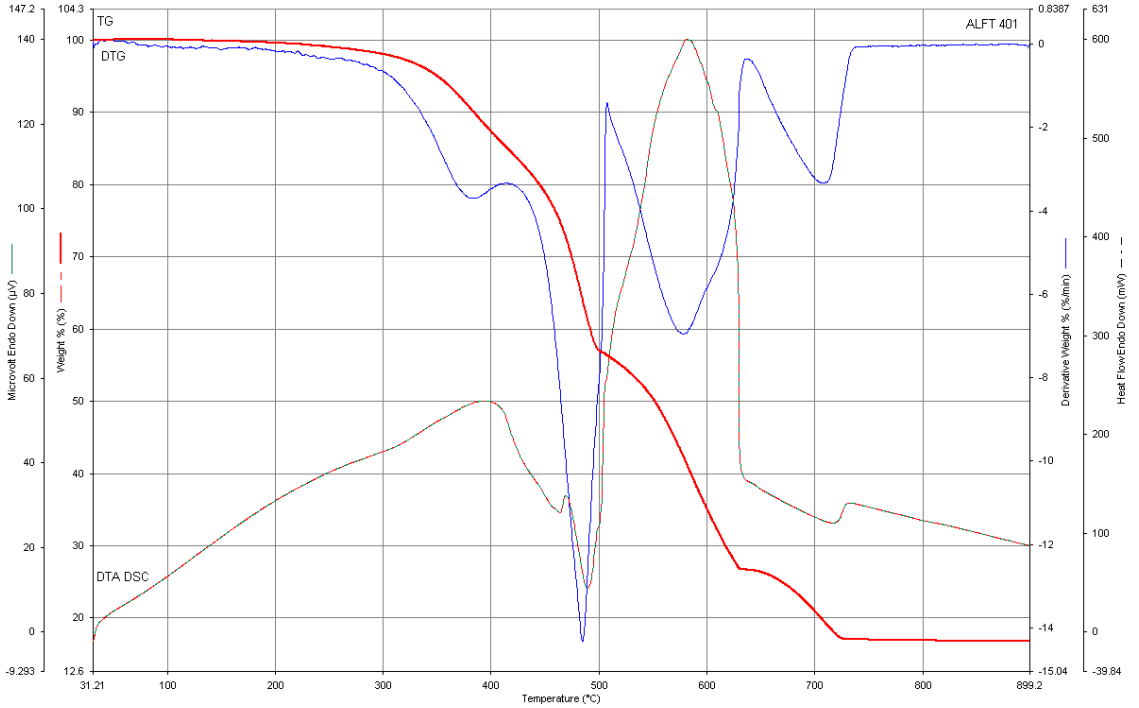
ALFT 399 SAMPLE



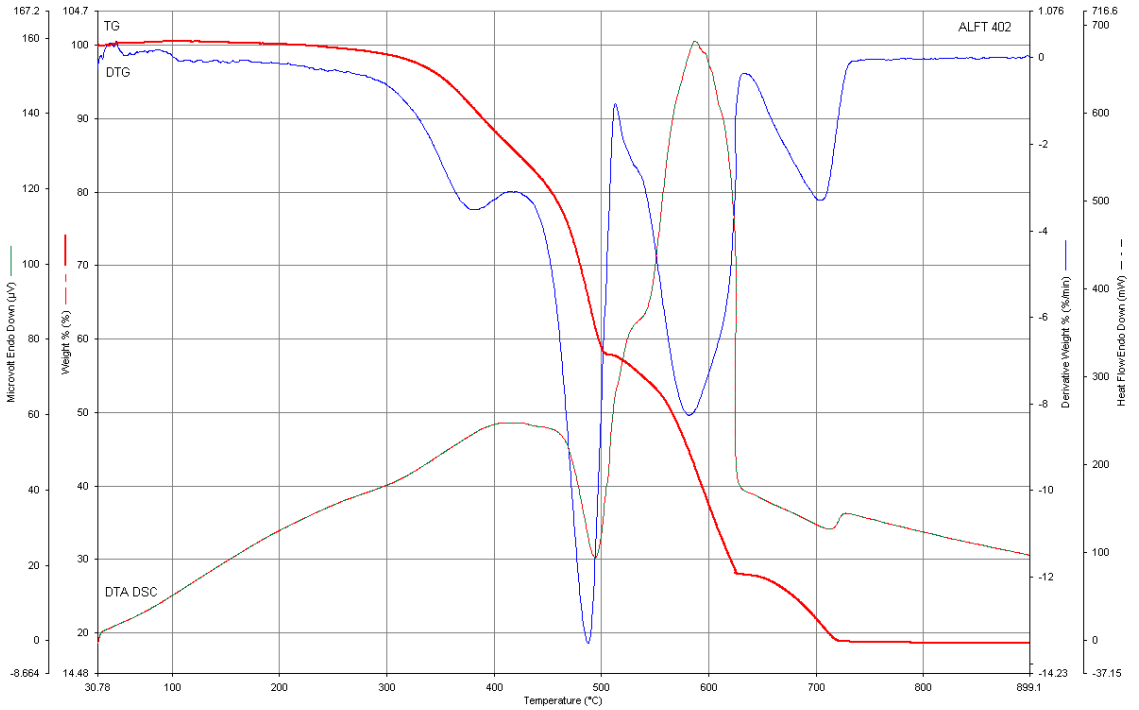
ALFT 400 SAMPLE



ALFT 401 SAMPLE



ALFT 402 SAMPLE



APPENDIX-C

MECHANICAL TEST RESULTS

Untreated EPDM

aktaş **MALZEME TEST RAPORU** **29.04.2013**

Zwick

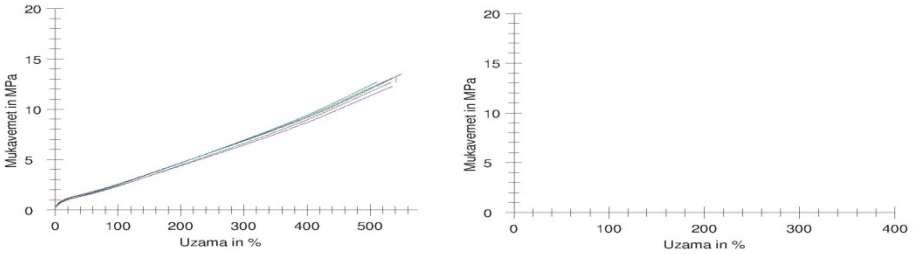
Parameter table:

Müşteri : AKTAŞ
Operatör : T.L
Malzeme kodu : ALFT katıksız şahit numune 50 gr 29042013
Çekme yönü : e-b
Yoğunluk : 1,273
Sertlik : 69
Şarj no : 29042013

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	16,41	13,47	13,46	551,23	6,84	6,2	69,68	2,08	12,9
2	13,20	13,25	12,65	543,18	6,88	6,2	70,77	2,35	14,57
3	11,16	12,65	12,65	534,95	6,60	6,2	70,51	2,27	14,07
4	12,68	12,65	12,60	512,51	6,93	6,2	70,46	2,29	14,2
5	12,55	12,26	12,26	537,28	6,43	6,2	70,43	2,24	13,89

Series graphics:



Statistics:

n = 5	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
x̄	13,20	12,85	12,72	535,83	6,74	6,2	70,37	2,246	13,93
Fmax.	16,41	13,47	13,46	551,23	6,93	6,2	70,77	2,35	14,57
min.	11,16	12,26	12,26	512,51	6,43	6,2	69,68	2,08	12,9
s	1,95	0,49	0,44	14,47	0,21	0,000	0,41	0,1011	0,6271

Page 1/1

AKTAŞ MALZEME TEST RAPORU 06.07.2012

Zwick

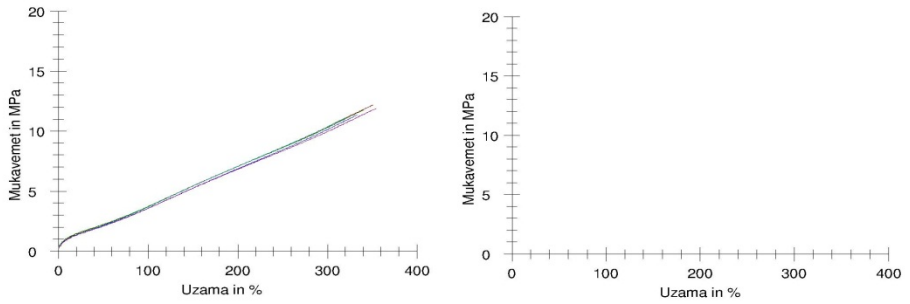
Parameter table:

Müşteri	: AKTAŞ	Yoğunluk	: 1,319
Operatör	: EK	Sertlik	: 74
Malzeme kodu	: ALFT 398 06072012	Şarj no	: 06072012
Çekme yönü	: e-b		

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	19,87	12,17	12,17	352,44	10,33	6,2	70,26	2,05	12,71
2	23,87	11,73	11,73	341,15	10,27	6,2	70,04	1,86	11,53
3	19,07	11,33	11,33	334,39	10,11	6,2	70,25	2,13	13,21
4	18,65	11,13	11,13	322,29	10,35	6,2	70,28	2,05	12,71
5	17,99	11,86	11,86	355,23	9,94	6,2	70,29	1,93	11,97

Series graphics:



Statistics:

n = 5	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
$\bar{x}$	19,89	11,64	11,64	341,10	10,20	6,2	70,22	2,004	12,42
Fmax.	23,87	12,17	12,17	355,23	10,35	6,2	70,29	2,13	13,21
min.	17,99	11,13	11,13	322,29	9,94	6,2	70,04	1,86	11,53
s	2,33	0,42	0,42	13,48	0,17	0,000	0,11	0,1076	0,6672

AKTAŞ MALZEME TEST RAPORU 06.07.2012

Zwick

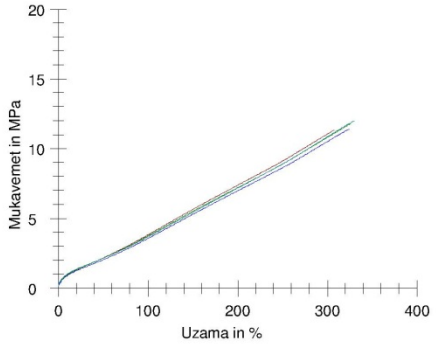
Parameter table:

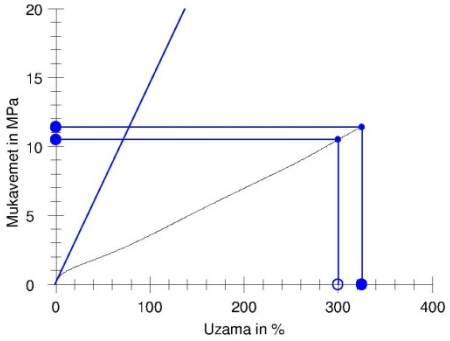
Müşteri	: AKTAŞ	Yoğunluk	: 1,312
Operatör	: EK	Sertlik	: 73
Malzeme kodu	: ALFT 399 06072012	Şarj no	: 06072012
Çekme yönü	: e-b		

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	18,26	11,29	11,29	308,93	11,03	6,2	70,28	1,95	12,09
2	18,86	11,78	11,78	327,34	10,79	6,2	70,23	2,13	13,21
3	14,51	11,40	11,40	326,08	10,49	6,2	70,71	2	12,4
4	22,49	11,96	11,95	330,83	10,83	6,2	70,14	2,19	13,58

Series graphics:





Statistics:

n = 4	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
$\bar{x}$	18,53	11,61	11,61	323,30	10,79	6,2	70,34	2,067	12,82
Fmax.	22,49	11,96	11,95	330,83	11,03	6,2	70,71	2,19	13,58
min.	14,51	11,29	11,29	308,93	10,49	6,2	70,14	1,95	12,09
s	3,26	0,31	0,31	9,78	0,22	0,000	0,25	0,1115	0,6911

AKTAŞ MALZEME TEST RAPORU 06.07.2012

Zwick

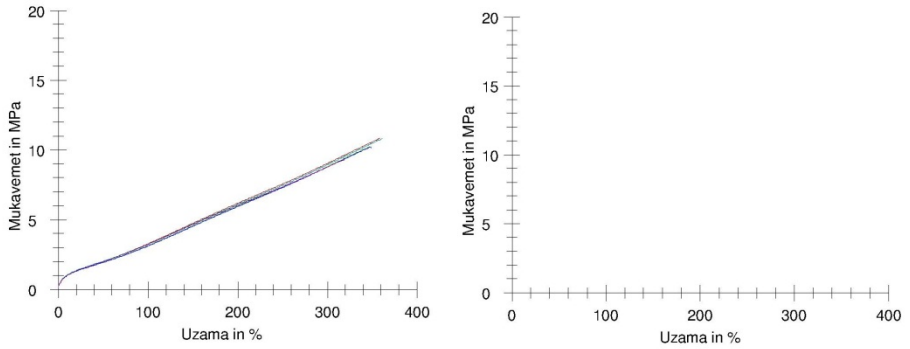
Parameter table:

Müşteri	: AKTAŞ	Yoğunluk	: 1,349
Operatör	: EK	Sertlik	: 75
Malzeme kodu	: ALFT 400 06072012	Şarj no	: 06072012
Çekme yönü	: e-b		

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	21,70	10,82	10,82	359,71	9,02	6,2	70,25	1,93	11,97
2	21,30	10,20	10,20	348,23	8,79	6,2	70,22	2,16	13,39
3	21,75	10,21	10,15	349,95	8,76	6,2	70,22	2,23	13,83
4	22,39	10,80	10,80	362,23	8,93	6,2	70,22	2,14	13,27
5	20,98	9,31	9,31	320,78	8,77	6,2	70,22	1,98	12,28

Series graphics:



Statistics:

n = 5	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
$\bar{x}$	21,62	10,27	10,26	348,18	8,85	6,2	70,23	2,088	12,95
Fmax.	22,39	10,82	10,82	362,23	9,02	6,2	70,25	2,23	13,83
min.	20,98	9,31	9,31	320,78	8,76	6,2	70,22	1,93	11,97
s	0,53	0,61	0,62	16,46	0,12	0,000	0,01	0,1272	0,7884

AKTAŞ MALZEME TEST RAPORU 06.07.2012

Zwick

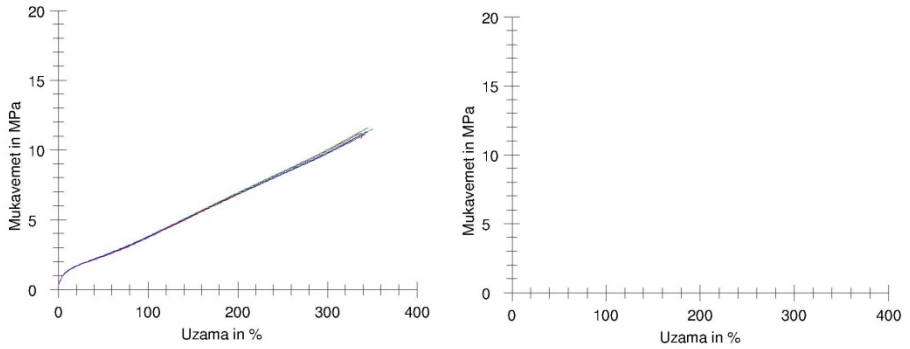
Parameter table:

Müşteri	: AKTAŞ	Yoğunluk	: 1,339
Operatör	: EK	Sertlik	: 75
Malzeme kodu	: ALFT 401 06072012	Şarj no	: 06072012
Çekme yönü	: e-b		

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	27,81	11,26	11,26	345,93	9,78	6,2	68,98	2	12,4
2	27,27	11,59	11,59	346,47	10,01	6,2	68,62	2,19	13,58
3	26,37	11,10	11,10	343,61	9,73	6,2	68,07	1,94	12,03
4	26,73	11,48	11,46	351,70	9,81	6,2	68,77	2,12	13,14
5	30,23	11,21	10,78	338,43	9,93	6,2	69,63	2,22	13,76

Series graphics:



Statistics:

n = 5	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
$\bar{x}$	27,68	11,33	11,24	345,23	9,85	6,2	68,82	2,094	12,98
Fmax.	30,23	11,59	11,59	351,70	10,01	6,2	69,63	2,22	13,76
min.	26,37	11,10	10,78	338,43	9,73	6,2	68,07	1,94	12,03
s	1,52	0,20	0,32	4,81	0,11	0,000	0,57	0,1207	0,7486

aktaş

MALZEME TEST RAPORU

29.04.2013

Zwick

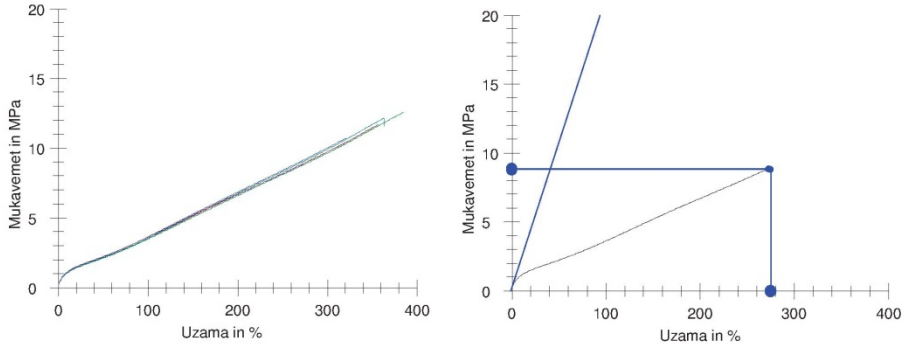
Parameter table:

Müşteri	: AKTAŞ		Yoğunluk	: 1,344
Operatör	: T.L		Sertlik	: 74
Malzeme kodu	: ALFT 402	29042013	Şarj no	: 29042013
Çekme yönü	: e-b			

Results:

Nr	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
1	20,52	11,67	11,67	357,68	9,73	6,2	70,26	2,14	13,27
2	20,66	12,56	12,56	386,02	9,63	6,2	70,22	2,2	13,64
3	20,72	10,70	10,70	322,23	10,01	6,2	70,23	2,24	13,89
4	20,18	12,14	11,57	364,28	9,90	6,2	70,19	2,25	13,95
5	21,22	8,85	8,80	275,56	-	6,2	70,22	2,1	13,02

Series graphics:



Statistics:

n = 5	E-Modulus MPa	Çekme Muk. MPa	Kopma Muk. MPa	Kopma Uzaması %	% 300 MPa	Genişlik mm	L0 mm	Kalınlık mm	S0 mm²
$\bar{x}$	20,66	11,19	11,06	341,15	9,82	6,2	70,22	2,186	13,55
Fmax.	21,22	12,56	12,56	386,02	10,01	6,2	70,26	2,25	13,95
min.	20,18	8,85	8,80	275,56	9,63	6,2	70,19	2,1	13,02
s	0,38	1,47	1,43	43,25	0,17	0,000	0,03	0,06465	0,4008

CURRICULUM VITAE

PERSONAL INFORMATION

Name & Surname	:Şirin ÇAVUŞOĞLU
Date and Place of Birth	:22.01.1987-Bulgaria
Foreign Language	:English
E-mail	:srn87@hotmail.com

EDUCATION

Degree	**Institution**	**Year**
M.Sc.	YTU, Chemical Engineering	2014
B.Sc.	Anadolu University Chemical Engineering	2009
High School	Turhan Tayan Anatolian High School	2005

WORK EXPERIENCE

Year	**Company**	**Position**
2010	Biesseci Bursa Textile Company	Responsible for Quality
2011-	Aktaş Holding-Akizo Insulation Systems	Responsible for Manufacture

PROJECT

1. ÇAVUŞOĞLU, Ş. (2009). "Production of Bio-oil by Pyrolysis of Biomass and Characterization by GC/MS ", Anatolian University.

AWARDS

1. TEV Honor Award