EFFECT OF DIFFERENT COMPOSITIONS ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPDM RUBBER

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EFFECT OF DIFFERENT COMPOSITIONS ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPDM RUBBER

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ABSTRACT

EFFECT OF DIFFERENT COMPOSITIONS ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPDM RUBBER

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In this work, EPDM rubber was compounded with increasing amount of filler (FEF N 550 type carbon black), process oil (saturated mineral oil), vulcanizing agent [di (t-butylperoxy) diisopropyl benzene, i.e., BBPIB] and diene [5-ethylidenebicyclo(2.2.1)-hept-2-ene, i.e., ENB] in order to investigate mechanical and rheological properties.

Effect of Increasing amount of filler was investigated by using FEF N 550 type carbon black in 35, 70, 87.5, 105 phr. Decrease in scorch times of vulcanization reactions, t_{s2} (25, 21, 19, and 18 s, respectively) and slight increase in rate constants for vulcanization reactions (0.0270, 0.0274, 0.0301 and 0.0302 s^{-1}, respectively) were explained in terms of nature of semi-active filler.

Effect of increasing amount of process oil was investigated by using saturated mineral oil (TUDALEN 3909) in 15, 30, 45 phr. Scorch time for vulcanization reaction and rate constants were measured as 95, 103, 97 s and 0.0277, 0.0274, 0.0291 s^{-1}, respectively.

Effect of increasing amount of vulcanizing agent was investigated by using BBPIB (PERKADOX 14/40 MB-gr) in 2.5, 5, 7.5, 10 phr. The compound with 5 phr vulcanizing agent gave optimum rheometer data, crosslink density,, ultimate tensile strength, hardness, deflection and damping. Vulcanization reaction rate constant reached 0.0335 s^{-1} with 7.5 phr vulcanizing agent.

Effect of increasing ENB ratio was investigated by using 4 different EPDM with ENB ratios 5.0, 5.6, 7.5, 8.9%. With two different cure systems, compounds with 5.6 and 7.5% ENB ratio gave optimum results. Vulcanization cure time, reaction rate constant and compression set properties changed in irregular manner.

Key words: EPDM, rheological properties, mechanical properties

ÖZ

FARKLI KOMPOZİSYONLARIN EPDM KAUÇUĞUN REOLOJİK VE MEKANİK ÖZELLİKLERİNE ETKİSİ

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Bu çalışmada artan dolgu (FEF N 550 karbon karası), proses yağı (doymuş mineral yağı), çapraz bağlayıcı [di (t-butylperoxy) diisopropyl benzene (BBPIB)] ve dien [5-ethylidenebicyclo(2.2.1)-hept-2-ene (ENB)] miktarının EPDM kauçuk karışımlarının reolojik ve mekanik özellikleri üzerindeki etkileri araştırıldı.

Artan karbon karası miktarı etkisi, FEF N 550 tip karbon karası 35, 70, 87.5, 105 phr oranlarında kullanılarak araştırıldı. Vulkanizasyon reaksiyonlarının scorch sürelerindeki (t_{s2}) (25, 21,19 ve 18 saniye) azalma vulkanizasyon reaksiyonu hız sabitlerindeki hafif artma karbon karasının yarı aktif doğasından kaynaklandığı yorumu yapıldı.

Artan proses yağı miktarı etkisi, 15, 30, 45 phr doymuş mineral yağı (TUDALEN 3909) kullanılarak araştırıldı. Vulkanizasyon reaksiyonu için scorch süreleri 95, 103 ve 97 saniye, hız sabitleri 0.0277, 0.0274 ve 0.0291 s^{-1} olarak ölçüldü.

Artan çapraz bağlayıcı miktarı etkisi 2.5, 5, 7.5, 10 phr BBPIB (PERKADOX 14/40 MB-gr) kullanılarak araştırıldı. 5 phr çapraz bağlayıcı kullanılan formül için reometre verilerinin, çapraz bağ yoğunluğunun, kopma mukavemetinin, sertliğin, baskı altında sıkışma miktarının ve damping miktarının optimum olduğu gözlendi. Vulkanizasyon reaksiyonu hız sabiti 7.5 phr çapraz bağlayıcı kullanılan karışım için 0.0335 s^{-1} değerine ulaştı.

Artan ENB oranı etkisi, 5.0, 5.6, 7.5, 8.9% ENB oranına sahip EPDM kauçuklar kullanılarak araştırıldı. İki farklı pişirici sistemi için de, 5.6 ve 7.5% ENB oranına sahip karışımların optimum değerleri verdiği görüldü. Vulkanizasyon reaksiyonu için hız sabitleri ve kalıcı deformasyon değerleri her iki pişirici sistemi için de düzensiz olduğu gözlendi.

Anahtar kelimeler: EPDM, reolojik özellikler, mekanik özellikler

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To my family

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EC1: EPDM compound with 35 phr FEF N 550 carbon black

EC2: EPDM compound with 70 phr FEF N 550 carbon black

EC3: EPDM compound with 87.5 phr FEF N 550 carbon black

EC4: EPDM compound with 105 phr FEF N 550 carbon black

EY1: EPDM compound with 15 phr saturated mineral oil

EY2: EPDM compound with 45 phr saturated mineral oil

EV1: EPDM compound with 2.5 phr di (t-butylperoxy) diisopropyl benzene

EV2: EPDM compound with 7.5 phr di (t-butylperoxy) diisopropyl benzene

EV3: EPDM compound with 10 phr di (t-butylperoxy) diisopropyl benzene

A1: 5% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 3 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 2 phr trimethylolpropane trimethacrylate

B1: 5.6% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 3 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 2 phr trimethylolpropane trimethacrylate

C1: 7.5% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 3 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 2 phr trimethylolpropane trimethacrylate

D1: 8.9% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 3 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 2 phr trimethylolpropane trimethacrylate

A2: 5% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 5 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 3 phr trimethylolpropane trimethacrylate

B2: 5.6% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 5 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 3 phr trimethylolpropane trimethacrylate

C2: 7.5% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 5 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 3 phr trimethylolpropane trimethacrylate

D2: 8.9% 5-ethylidenebicyclo(2.2.1)-hept-2-ene containing EPDM compound with 5 phr 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (45%) and 3 phr trimethylolpropane trimethacrylate

CHAPTER 1

INTRODUCTION

1.1 RUBBERS

Rubbers (elastomers) are class of materials like metals, fibers, concrete, wood, plastics or glass. They are differentiated from all other polymeric materials because of their special properties. Usage of elastomers is quite different from plastics. They are amorphous when unstretched and are above their glass transition temperature to be elastic while plastics are crystalline and are used below their glass transition temperature to preserve stability.

The first material known as caoutchouc (derived from the Aztek word “caa-o-chu” or weeping tree) is polyisoprene recovered from Hevea Brasiliensis. It can be reacted with sulphur and peroxides at high temperatures to form crosslinks. Thus it is transformed from caoutchouc to an elastomer or rubber. Today this material is known as natural rubber (NR).[1]

The first attempts to produce synthetic rubbers centered around the homopolymerization of dienes, particularly isoprene because it was known to be the monomer for natural rubber. It was found in the late nineteenth century that rubber like products could be made from isoprene by treating it with hydrogen chloride or allowing it to polymerize spontaneously on storage. These materials could be vulcanized with sulfur, becoming more elastic, tougher, and more heat resistant.[2]

Around 1900 it was discovered that other dienes such as butadiene and 2,3-dimethylbutadiene could be polymerized to rubber like materials spontaneously by alkali metals or by free radicals. Application was made of these facts during World War I in Germany, where 2,3-dimethybutadiene was polymerized spontaneously.[2]

Improvements in processing and properties were made in two ways: Copolymers of butadiene with vinyl monomers, notably styrene, were introduced and emulsion polymerization was adopted. By beginning of World War II, acceptable polymers were being produced Germany containing 68-70% butadiene and 30-32% styrene.[2]

The process by which crosslinks are introduced into elastomer is called vulcanization. Figure 1.1 illustrates crosslinking of a raw rubber.[1]

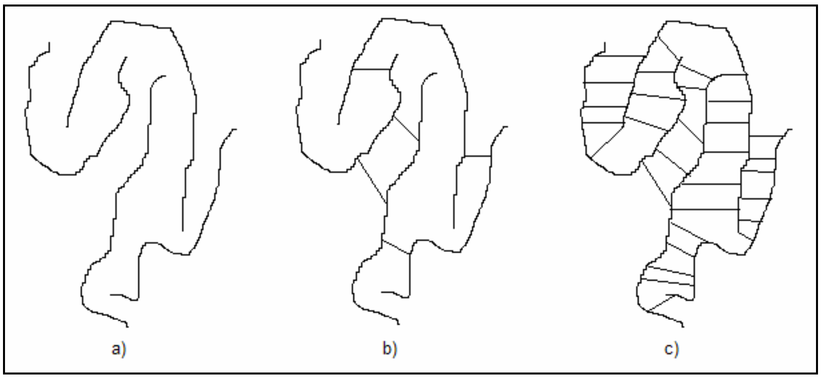


Figure 1.1 Crosslinking of raw rubber a) Plastomer (thermoplastic); no crosslinks b) Elastomer (soft elastomer); loosely crosslinked network structure c) Duromer (hard rubber); tightly crosslinked network structure

The chemistry of vulcanization is complex and has not been well understood throughout the century of practice of the process since its discovery by Goodyear in 1839. The profound effects of vulcanization, however, are clear: it transforms an elastomer from a weak thermoplastic mass without useful mechanical properties into a strong, elastic, though rubber.[2] Properties of natural rubber before and after vulcanization and reinforcement are given in Table 1.1 as an example.[3]

Table 1.1 Properties of natural rubber before and after vulcanization

Property	Raw Rubber	Vulcanized Rubber	Reinforced Rubber
Tensile Strength (MPa)	2.1	20.1	31
Elongation at break (%)	1200	800	600
Modulus (MPa)	-	2.7	17.2
Permanent set	Large	Small	
Rapidty of retraction (snap)	Good	Very good	
Water absorption	Large	Small	
Solvent Resistance (hydrocarbons)	Soluble	Swells only	

The deformation of ideal rubber like materials is an iso-volumetric process. In rubbery region and at constant levels of strain, the retractive force of an ideal rubber like material is proportional to the absolute temperature. In thermodynamic terms it can be expressed as follows.[1]

$$\delta = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V} \qquad (1.1.1)$$

and,

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = 0$$

where δ is retractive force, L is length and U is internal energy. Thus;

$$\delta = - T \left(\frac{\partial S}{\partial L}\right)_{T,V} \tag{1.1.2}$$

which means that the force or tension of a streched ideal rubber is proportional to the entropy S.

Consequently, the elastomers are polymeric networks with generally thermally stable crosslinks. When subjected to a small external force, they can be extended to at least double of their original length and after removal of the external force, they can retract immediately to their original length.

ASTM D1418 gives more than 50 standard abbreviations for natural and synthetic rubbers.[3] Table 1.2 shows various types of rubbers and their ASTM abbreviations together with their general properties.

Table 1.2 Polymer common names, ASTM designations and some general properties

Polymer Name	ASTM Designation	Minimum Hardness (Shore A)	Maximum Hardness (Shore A)	Maximum Tensile Strength (MPa)	Brittle Point ºC
Ethylene propylene diene monomer	EPDM	40	90	13.8	-58
Nitrile rubber	NBR	40	90	17.2	-51
Hydrogenated nitrile rubber	HNBR	45	90	20.7	-55
Polychloroprene	CR	40	90	17.2	-54
Natural rubber	NR	30	90	24.1	-58
Polyisoprene	IR	30	90	20.7	-58
Styrene butadiene rubber	SBR	40	90	17.2	-58
Butyl rubber	IIR	40	80	13.8	-58
Polybutadiene	BR	40	80	13.8	-73
Silicone	VMQ	40	80	10.3	-118
Fluoroelastomer	FKM	55	90	13.8	-40
Polyester urethane	AU	60	95	55.1	-51
Polyether urethane	EU	60	95	55.1	-51
Ethylene acrylic	AEM	40	90	13,8	-55
Polysulfide	T	20	80	10.3	-51
Epichlorohydrin	ECO	40	80	13.8	-40
Chlorosulfonated polyethlene	CSM	40	90	20.7	-55
Chlorinated polyethylene	CPE	50	90	20.7	-55
Polyacrylate	ACM	60	95	13.8	-34
Polyoctene	POE	65	95	27.6	-76

1.2 CLASSIFICATON OF RUBBER COMPOUNDING INGREDIENTS

Rubber compounding is the science of selecting various compounding ingredients and their quantities to mix and produce a useful rubber formulation for specific applications.

ASTM D5899 gives 18 different functional classifications for rubber ingredients.[3] Some of these functional classifications are given in Table 1.3.

Table 1.3 Functional classifications for rubber compounding ingredients

Rubber Compounding Ingredients	Function	Examples
Accelerators	Accelerate cure and reduce vulcanization time	Dithiocarbamates, sulfenamides, thiurams, thiazoles
Activators	Activate accelerator in a cure and improve its efficiency	Metal oxides
Antidegradant components	Retard deterioration of the cured rubber compound from exposure to oxygen, ozone, heat, light and mechanical flexing	p-phenylene diamines, substituded phenols, quinolines
Fillers, extenders, reinforcing agents	Improve cured physical properties and reduce cost	Carbon-black, clays, ground coal, flocs, silicas, reinforcing resins
Processing materials	Reduce compound viscosity and/or to improve the compound processing behavior	Petroleum oils, various ester plasticizers, and various soaps
Rubbers	Basic materials for rubber compounding	see Table 1.1
Vulcanizing Agents	Directly responsible for the formation of crosslinks during curing process	Sulfur, organic peroxides

1.3 MEASUREMET OF VULCANIZATION CHARACTERISTICS

The study of vulcanization process in crosslinkable rubber compouds is called curometry. The basic instruments for measurement of vulcanization characteristics are “Rheometers” which make it possible to plot the course of vulcanization process and evaluate crosslinking isotherms in terms of reaction kinetics.

The Mooney Viscometer which was developed by Melvin Mooney of U.S. Rubber Co., has been used to measure scorch by far[3]. It was the first instrument used to measure scorch safety of a mixed stock. The Oscillating Disk Rheometer (ODR) was introduced in 1963 and is considered a great improvement over the Mooney Viscometer because the ODR measures not only scorch, but also cure rate and state and cure. Even though thousands of ODRs have been used worldwide, the ODR itself has a design flaw which involves the use of ODR itself. The most problems by ODR were greatly reduced with the introduction of new rotorless curometers, i.e. Moving Die Rheometer (MDR) in 1985.[12]

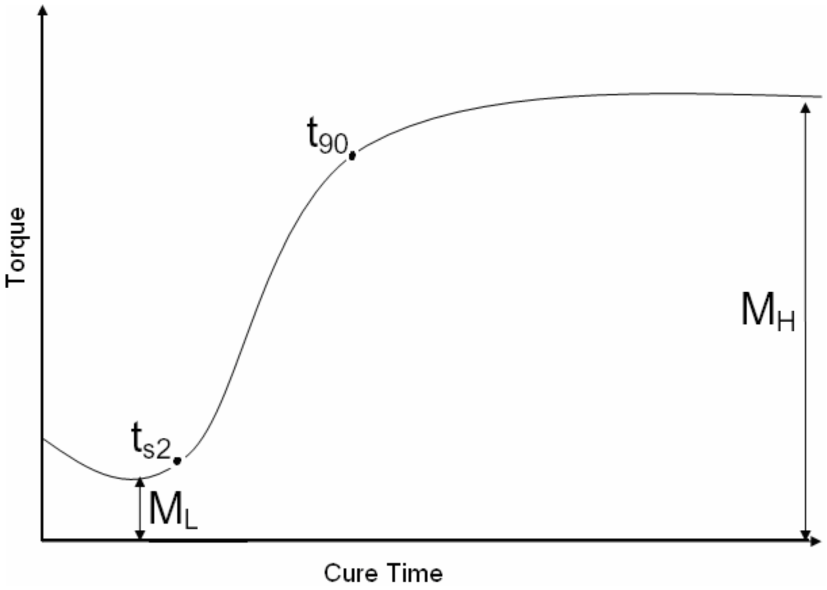


Figure 1.2 A typical crosslinking isotherm for elastic response during vulcanization of a rubber compound

In a crosslinking isotherm for elastic response (Figure 1.2) M_L is the minimum torque reading. M_H, is final rheometer indication constant in time, on completion of crosslinking reaction. t_{s2} (scorch time) is the time after two torque units above M_L is reached in an elastic torque curve. t_{90} is the time required for elastic torque curve to reach 90% of maximum torque time. Mt is the rheometer reading at any specified time.

From the crosslinking isoterms of an Moving Die Rheometer instrument one can also observe t10, t50, S''@ML, S''@MH, tg@ML, tg@MH ,i.e., time required for elastic torque curve to reach 10% of maximum torque, time required for elastic torque curve to reach 50% of maximum torque, minimum viscous torque reading, maximum viscous torque reading, ratio of minimum viscous torque and minimum elastic torque, and ratio of maximum viscous torque and maximum elastic torque, relatively.

The kinetic parameters such as activation energy, pre-exponential factor and the order of all reaction can be calculated by using moving die rheometer.[4] The differential equation under isothermal condition is given in Equation 1.3.1.

$$\frac{dY}{dt} = k_o \ (1\text{-}Y) \ \exp\left(- \frac{E}{RT} \right) \tag{1.3.1}$$

By integrating both sides;

$$\int \frac{dY}{(1\text{-}Y)} dy = \int k_o \ \exp\left(- \frac{E}{RT} \right) dt \tag{1.3.2}$$

$$-\ln(1\text{-}Y) = k_o \ t \ \exp\left(- \frac{E}{RT} \right) + A \tag{1.3.3}$$

where;

Y; ratio of Torque at time t and MH, i.e., Torque_t / MH
k_o; pre-exponential factor
E; activation energy
T; temperature

is obtained. When -ln(1-Y) vs t graph is drawn, then slope gives the k_ot, i.e. rate constant (k_T) of vulcanization reaction at selected temperature.

1.4 EPDM RUBBER

EPDM (Ethylene Propylene Diene Monomer) contains ethylene, propylene and also a third monomer which are typically non-conjugated dienes that has been incorporated into the polymer for the express purpose of enabling a sulfur crosslinking. Three different monomers are used commercially for this purpose.[3] They are given in Figure 1.3.

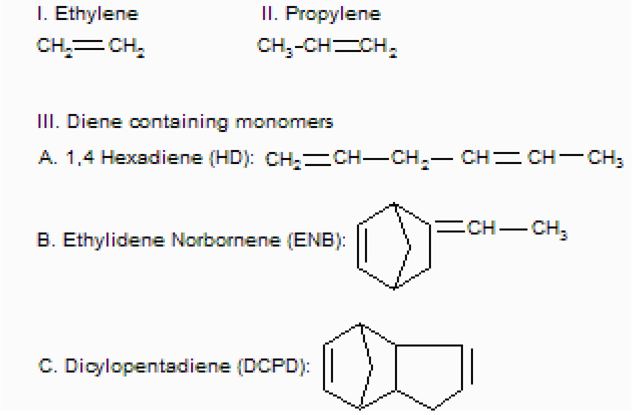


Figure 1.3 Ethylene, propylene and diene containing monomers

The description of homogeneous polymers is unambiguous, but for heterogeneous polymers further development of the SWP EOS theory is required.[5]

The SWP EOS (The Sako-Wu-Prausnitz Equation of State) is derived from the generalized Van der Waals partition function. For polymers Sako et al. assumed that the characteristic potential energy per segment is almost equal to that of saturated monomer. The segment number r is calculated from the number-average molecular weight of polymer, M_n; the molecular weight of the repeating unit M_{RU}; and a structural constant N_{Cseg}, that represents the number of carbon atoms per segment. The segment number is calculated according to,

$$r = \frac{M_n}{M_{RU}} \frac{N_{CRU}}{N_{Cseg}} \tag{1.4.1}$$

In Equation 1.4.1, N_{CRU} represents the number of carbon atoms of the repeating unit forming the polymer backbone.[5]

For homogeneous polymers, repeating unit estimation is straightforward such as in polyethylene, polypropylene, and polystyrene.[5] In polyethylene, for example, the repeating unit is ethylene, so the backbone of molecule has two units however for highly cross-linked or co- or ter-polymer, such as EPDM, a non ambiguous choice is not easily be made. For an EPDM grade with a ter-polymer with an ethylene/propylene ratio of 1:1, with 4.5 wt % ter-monomer ENB [5-ethylidenebicyclo(2.2.1)-hept-2-ene], resulting minimum polymer segment is depicted in Figure 1.4.[5]

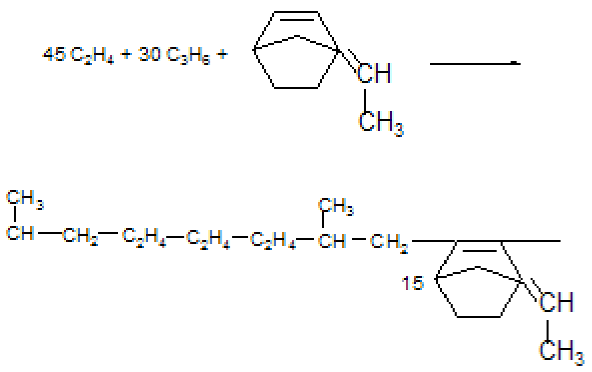


Figure 1.4 Schematic representation of the smallest EPDM polymer segment according to the SWP EOS theory

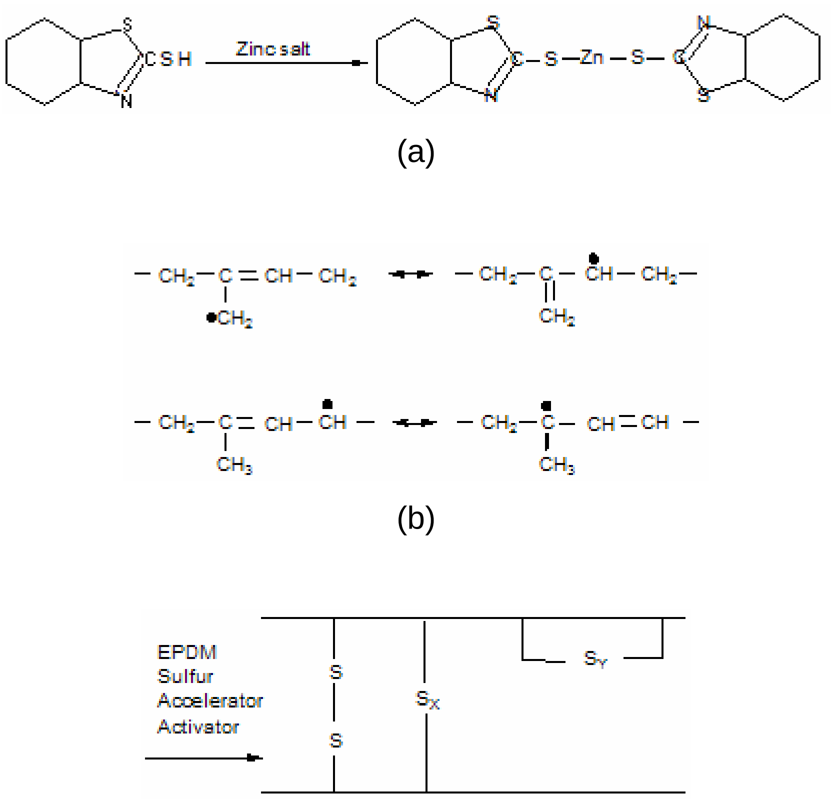
As it can be seen from Figure 1.4, this segment is extremely large, and no physical properties of this monomer can be found. It is therefore necessary to resize this segment to more comprehensible dimensions. However no solid theory on the implementation of non-homogeneous polymers in SWP theory exists, severe simplifications have to be made to define a repeating unit. It is assumed that no side chains are present in the polymer, that the influence of the third monomer can be neglected, and that the ethylene-propylene polymer can be regarded as a regularly alternating polymer.[5]

Typically EPDM polymers are classified as either semi-crystalline or amorphous. Semicrystalline grades generally have ethylene contents of 62% or greater, while amorphous grades generally have ethylene contents of less than 62%. As ethylene content increases the amount of crystallinity increases. The amount of crystallinity can be qualified by measuring the onset temperature of the crystalline melt, T_c, or the heat required to pass through the crystalline melt, (J/g). Amorphous grades, which have minimal crystallinity, are more flexible at low temperatures, lower in hardness, and more elastic. Semicrystalline grades, on the other hand, have several properties that are directly attributable to their crystallinity levels. When compared to amorphous grades, they exhibit higher green strength, higher tensile and modulus, and higher hardness.[3]

1.5 SULFUR CROSSLINKING OF EPDM POLYMER

Sulfur crosslinking of EPDM polymer is achieved due to double bonds of diene monomer on the side chain.[3]

The mechanistic details of chemistry of accelerated sulfur vulcanization are still widely debated..[2] Probable mechanisms in accelerated sulfur vulcanization is given in Figure 1.5.



(a)

(b)

(c)

Figure 1.5 Scheme for sulfur vulcanization of EPDM rubber (a) formation of zinc salt of accelerator (b) resonance (c) formation of crosslinks

In the presence of stearic acid, functional zinc salt of accelerator is formed. Functional zinc salt formation leads to the formation of zinc salt of accelerator (Figure 1.5 a). Zinc salt of accelerator, in turn, attacks the rubber chains, probably at the allylic hydrogen (Figure 1.5 b).[3-6]. Crosslinks are formed due to the activated double bonds of the polymer and sulfur (Figure 1.5 c).[3]

1.6 PEROXIDE CROSSLINKING OF EPDM POLYMER

Unlike the reaction mechanism of accelerated sulfur vulcanization, the basic chemistry of peroxide decomposition and subsequent crosslink-forming reactions is well established for the various unsaturated and saturated elastomers. Figure 1.6 provides a mechanistic scheme for peroxide vulcanization, describing both the desirable reactions which lead to effective crosslink formation and those competing reactions which detract from productive use of radicals.[7]

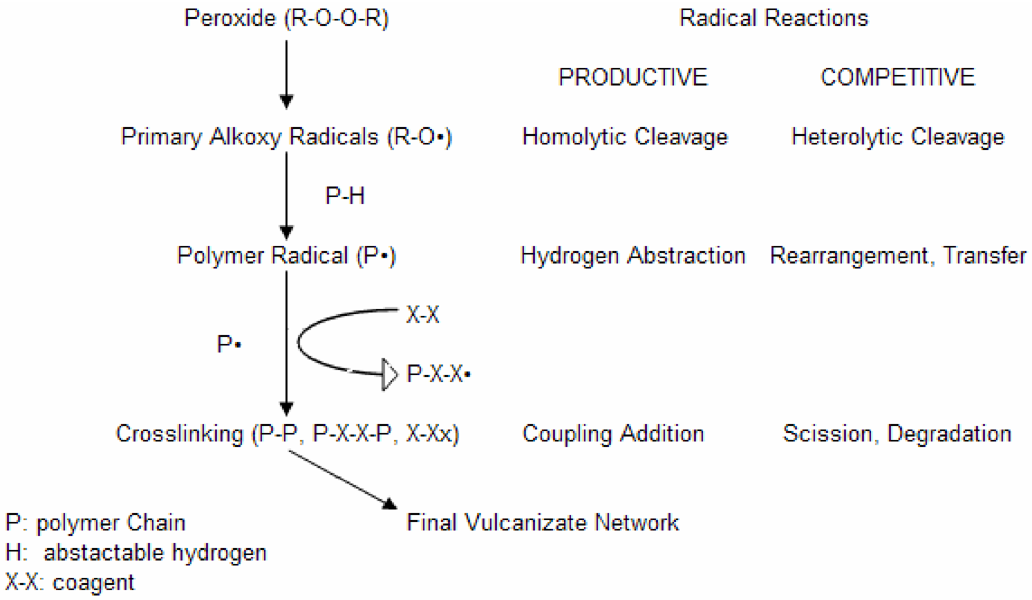


Figure 1.6 Scheme for peroxide vulcanization

Organic peroxides are used to produce free radicals. These free radicals create the desired crosslinked networks in the elastomer by adding to double bonds. Radical reactions, during decomposition of Perkadox 14/40 MB-gr ,i.e., di (t-butylperoxy) diisopropyl benzene (BBPIB) is given in Figure 1.7.[3]

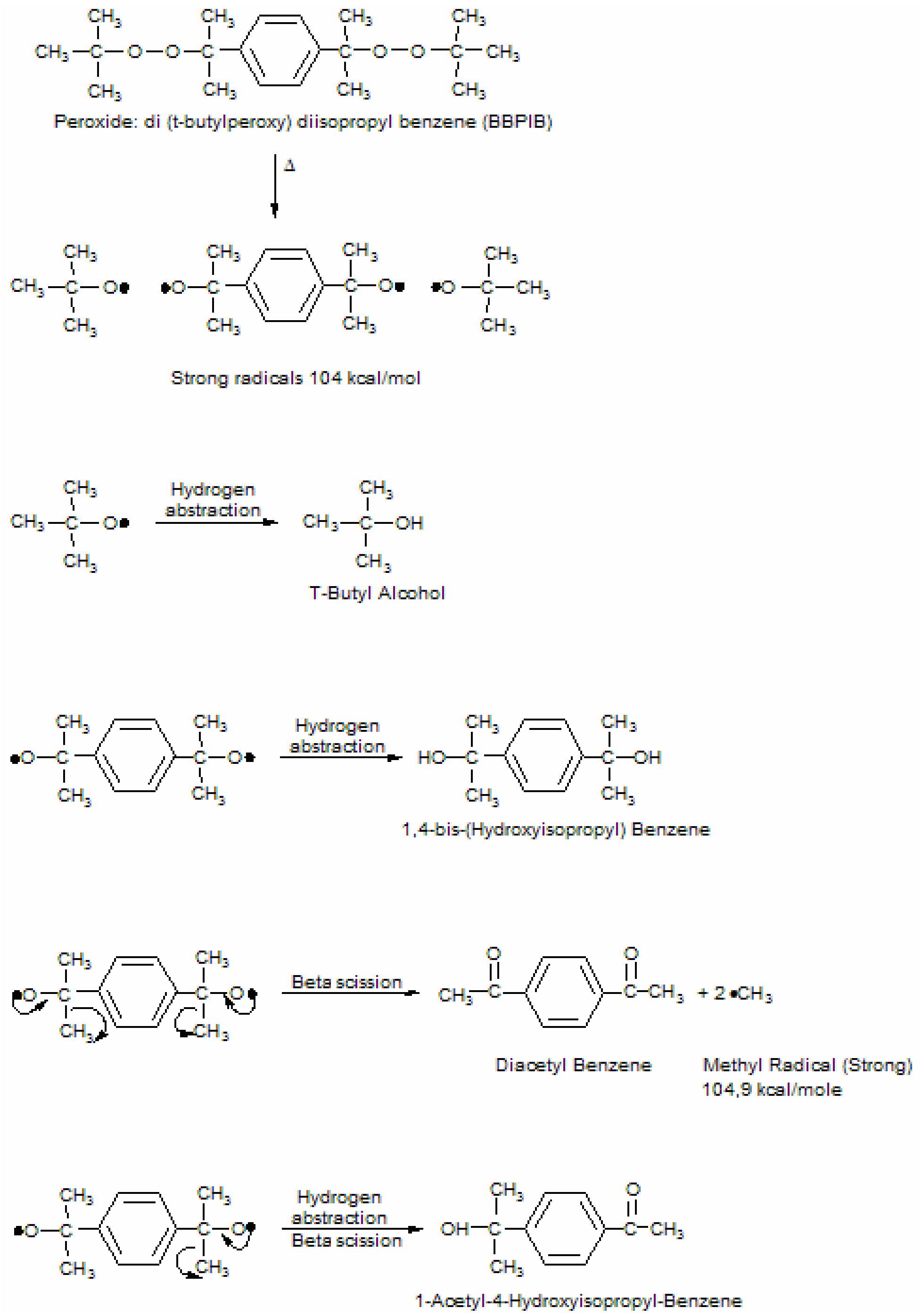
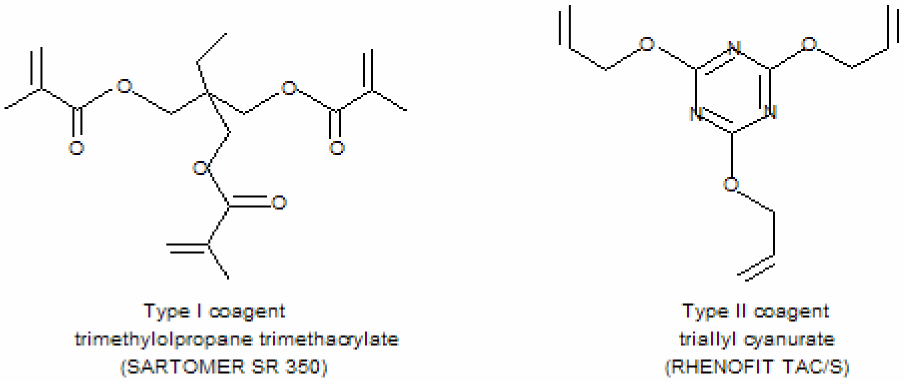


Figure 1.7 Radical reactions during decomposition of BBPIB

When monomeric coagents are added to an elastomer, unsaturation is added to the system. This provides higher cross-link densities for a given peroxide concentration. Higher cross-linking is possible because it is easier and more efficient to crosslink by free radical addition to unsaturation than hydrogen abstraction.[7]

Coagents are classified based on their contributions to cure. Type I coagents increase both the rate and state of cure. They are typically polar, multifunctional low molecular weight compounds which form very reactive radicals through addition reactions. Type II coagents form less reactive radicals and contribute only the state of cure. They include multifunctional acrylate and methacrylate esters and bismaleimides. Chemical structures of type I coagent trimethylolpropane trimetacrylate (Sartomer SR 350) and type II coagent trially cyanurate (Rhenofit TAC/S) are given in Figure 1.8 and in the presence of coagent triallyl cyanurate (TAC), crosslinking reaction of EPDM with dicumyl peroxide given in Figure 1.9.[7-8]



Type I coagent
trimethylolpropane trimethacrylate
(SARTOMER SR 350)

Type II coagent
triallyl cyanurate
(RHENOFIT TAC/S)

Figure 1.8 Chemical structures of type I coagent trimethylolpropane trimetacrylate and type II coagent trially cyanurate

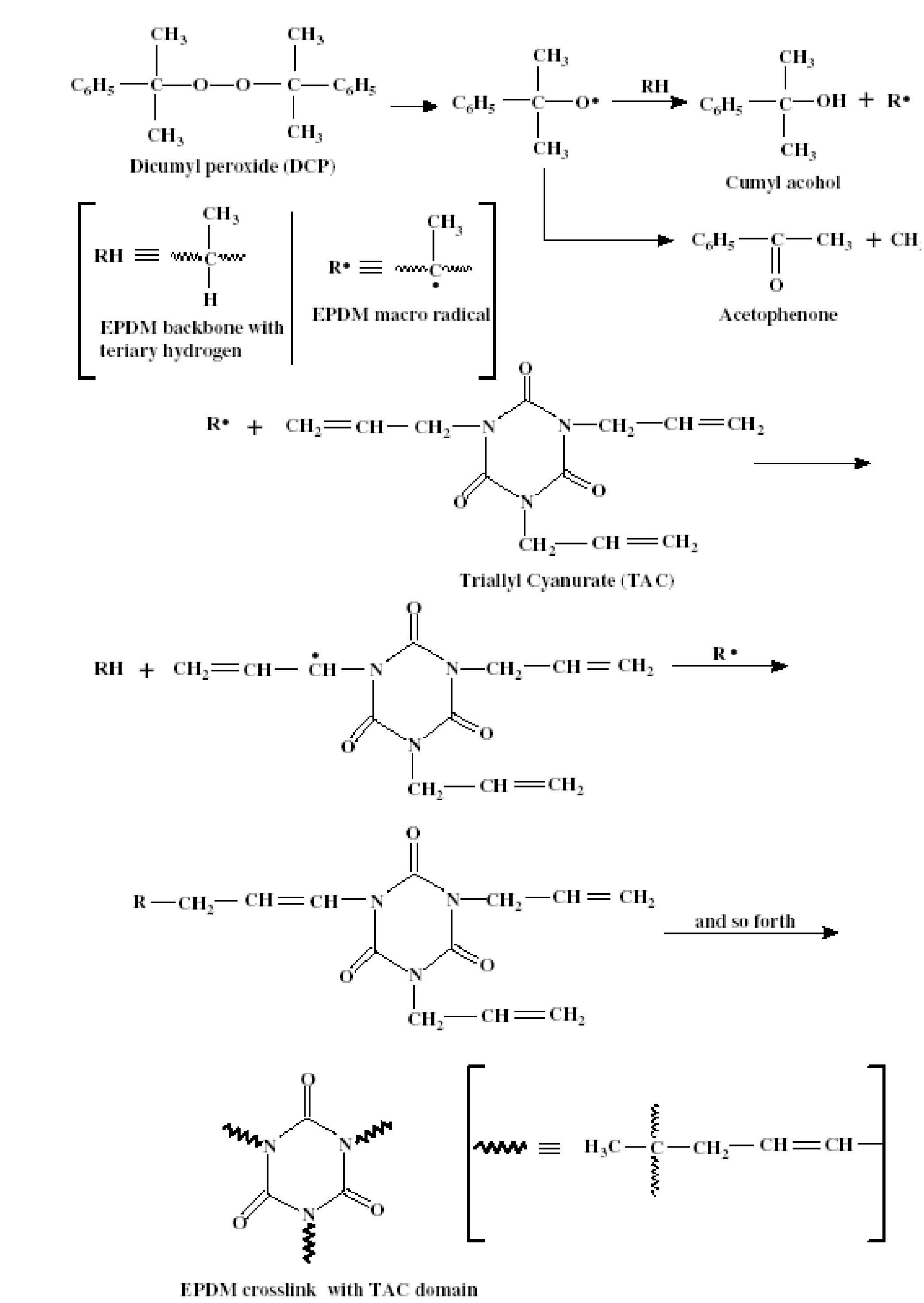


Figure 1.9 Crosslinking reaction of EPDM with dicumyl peroxide in the presence of coagent triallyl cyanurate

Peroxides create strong carbon-carbon type crosslinks whose bond dissociation enthalpy is about 350 kJ/mole. Table 1.4 outlines the bond dissociation energies of various crosslinks.[3]

Table 1.4 Bond dissociation energies of typical crosslinks

Bond Type	Dissociation Energy (kJ/mole)
C-C	335
C-S-C	314
C-S-S-S-C	230
C-Sx-C	147
C-O-Zn^{2+}-O-C	293

1.7 AIM OF THIS STUDY

EPDM polymer, like all other raw rubbers, is compounded via several types and amounts of ingredients. EPDM polymer is differentiated from all other rubbers by its property of including three different monomers whose relative ratio can be altered in production stage. It is clear that there are plenty of combinations of monomers and ingredients and also it is clear that these combinations will yield many of final products with different mechanical and rheological properties.

Aim of this study is to investigate mechanical and rheological properties of EPDM polymer compounded to different formulas whose certain ingredients varied gradually. Firstly a base formula was selected; stress-strain behavior, cure properties, deflection under compression and shore A hardness were measured for the changing amount of its filler, process oil and activator. Additionally DMA investigation was made both for changing amount of filler and vulcanizing agent, TGA investigation was made for changing amount of vulcanizing agent. Second, the effect of 5-ethylidenebicyclo(2.2.1)-hept-2-ene ratio on the cure properties, stress-strain behavior, shore A hardness and compression set of EPDM rubber was investigated. Compounding was achieved by using two different amounts of cure agents and coagents (diene suppliers) for four different EPDM type.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 EPDM Polymer

Trade names, brands, and compositions of EPDM polymers used in this study are given in Table 2.1

Table 2.1 Trade names, brands and compositions of EPDM polymer

Trade Name	Brand	Ethylene Content (%)	Diene (ENB) Content (%)
DUTRAL TER 4038 EP	POLIMERI EUROPA / ITALY	68,5	4,4
BUNA EP G 6850	LANXESS / GERMANY	51,2	7,5
KELTAN 27	DSM ELASTOMERS / HOLLAND	54,0	5,0
KELTAN 8340A	DSM ELASTOMERS / HOLLAND	54,9	5,6
KELTAN 4903	DSM ELASTOMERS / HOLLAND	48,5	8,9

2.1.2 Rubber Ingredients

Trade names, brands, compositions and functions of rubber ingredients used in this study are given in Table 2.2

Table 2.2 Trade names, brands, compositions and functions of rubber ingredients used in this study

Trade Name	Brand	Composition	Function
ROBAC SULFUR PM 80%	ROBINSON BROTHERS	80% elemental sulfur in EP binding system	Vulcanizing agent
PERKADOX 14/40 MB-gr	AKZO NOBEL	40% Bis(t-butylperoxy isopropyl)benzene in whiting and silica	Vulcanizing agent
LUPEROX 101XL45	ARKEMA	45% 2,5-Dimethyl-2,5-di(t-butylperoxy)hexane in carrier system	Vulcanizing agent
STEARIC ACID 101	CRC	Stearic acid	Activator
ZnO	METAL OKSİT KİMYA SANAYİİ A.Ş.	Zinc Oxide (min 99.7%)	Activator
FEF N 550	ALEXANDRA CARBON BLACK CO.S.A.E	Carbon Black (Surface area 42 m^2/g)	Filler
RHENOFIT TAC/S	RHEIN CHEMIE	70% Triallylcyanurate, 30% Silica	Coagent
SARTOMER SR 350	SARTOMER	Trimethylolpropane trimethacrylate	Coagent
TUDALEN 3909	HANSEN& ROSENTHAL	High refined saturated mineral oil	Plasticiser
FLECTOL TMQ	FLEXYSIS	2,2,4-Trimethyl-1,2-dihydroquinoline (polymerized)	Antioxidant
MIXLAND+MMBI 70	MLPC	Methyl-mercaptobenzimidazole (min 96%)	Antioxidant

2.2 INSTRUMENTATION

2.2.1 Two Roll Mill

The two roll mill with friction ratio of 2:1 was used for mixing.

2.2.2 Moving Die Rheometer (MDR)

The MDR 2000 Moving Die Rheometer was used to measure cure characteristics of compounds.

2.2.3 Tensometer

Hounsfield tensometer was used to measure ultimate tensile strength and ultimate elongation of vulcanized rubbers.

2.2.4 Type A Durometer

Zwick Roell Type A Durometer was used to measure the Shore A Hardness of vulcanized rubbers.

2.2.5 E Type Universal Testing Machine

Zwick Roell E Type Universal Testing machine was used to measure the Load Deflection of samples.

2.2.6 Dynamic Mechanic Analyser (DMA)

983 Dynamic Mechanical Analyzer Dupont Series was used to take DMA curves of samples. The temperature range for measurement was -100 and 200 ^{o}C.

2.2.7 Thermal Gravimetric Analysis (TGA-FT-IR)

The thermal gravimetric analyses (TGA) were carried out on Perkin Elmer Pyris 1 TGA which was connected to Perkin Elmer Spectrum 1 FTIR Spectrometer. TGA studies were carried out under N_2 atmosphere with the heating rate of 10 ^{o}C/min.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Compounding

Each compound were produced as 1 kg by first mixing all ingredients but vulcanizing agents and coagents for 30 minutes. After this, crosslinking agents were added and mixed for 15 minutes additionally.

2.3.2 Measurement of Vulcanization Characteristics

About 5 grams of uncured samples were placed in the rheometer cavity. They were cured 3 minutes at 190^{o}C. The moving die frequency and oscillation amplitude were 1.66 Hz and ±0.5^{o}, respectively. The print outs of resulting crosslinking isoterms includes t_{s1}, t_{s2}, t_{10}, t_{50}, t_{90}, M_L, M_H, $S^{II}@M_L$, $S^{II}@M_H$, $tg@M_L$, and $tg@M_H$ values.

2.3.3 Measurement of Ultimate Tensile Strength and Ultimate Elongation

Standart procedure detailed in ASTM D 412 (Test Method A) was used to measure ultimate tensile strength and ultimate elongation. Dumbbell shaped test specimens were cut from flat sheets of cured polymer which were vulcanized 10 minutes and at 180^{o}C. Die C (see ASTM D 412) was used for cutting flat sheets so that the final thicknesses of specimen were about 2 mm. They were placed in the grips of testing machine and ruptured at a speed of 500 mm/min. Ultimate tensile strength (maximum stress at break) and ultimate elongation (applied strain at break) were recorded from the machine readings. Although graphs are given in Force vs. Extension from this type of a machine one can directly obtain average ultimate tensile strength and ultimate elongation.

2.3.4 Measurement of Hardness

Durometer Hardness Method, described in ASTM D 2240 was used. Hardness was measured in Shore A unit from the test specimens which are 29 mm in diameter and 6 mm in thickness. The vulcanization conditions for samples were 180^{o}C and 5 minutes. Hardness of specimen was recorded as the average of readings from three different points.

2.3.5 Compression Test at a Specified Force

Compression tests were achieved according to standart test procedure described in ASTM D575-91 (Test Method B). Cylindrical test specimens (35 mm in diameter and 18 mm in thickness) were used for measurement of compression under constant force. Test specimen, vulcanized 15 minutes and at 155^{o}C, were first subjected to pre-load of 0.01 kN. Test speed and test load were 10 mm/min and 2 kN, respectively.

2.3.6 Measurement of Compression Set

Compression set tests were achieved according to standard test procedure described in ASTM D 395. According to Test Method A (Compression Set Under Constant Force), Type 1^A test specimens (vulcanized rubber cylinders 12,5 mm in thickness and 29.0 mm diameter) were prepared. They were compressed to 25% of their initial thickness by standard compression set device. The test period was 22 hours and test temperature was 70^{o}C.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 EFFECT OF AMOUNT OF INGREDIENTS ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPDM RUBBER

3.1.1 Effect of Filler

Compounding for different amounts of filler, i.e., carbon black FEF N 550 was achieved and named in Table 3.1.

Table 3.1 Compounding for different amount of filler

Ingredient	**Amount (phr)**			
	EC1	EC2	EC3	EC4
EPDM rubber (4.4% ENB)	100	100	100	100
Carbon black FEF N 550	**35**	**70**	**87.5**	**105**
Saturated mineral oil	30	30	30	30
ZnO	6	6	6	6
Stearic acid	1	1	1	1
Sulfur (80%)	0.25	0.25	0.25	0.25
Di (t-butylperoxy) diisopropyl benzene	5	5	5	5

For each compound crosslinking isotherms (Figure 3.1) were taken at 190°C for 3 minutes. The resulting scorch time, t_{S2}, cure time, t_{90}, minimum rheometer torque, M_L and maximum rheometer torque, M_H are given in Figure 3.2 for comparison.

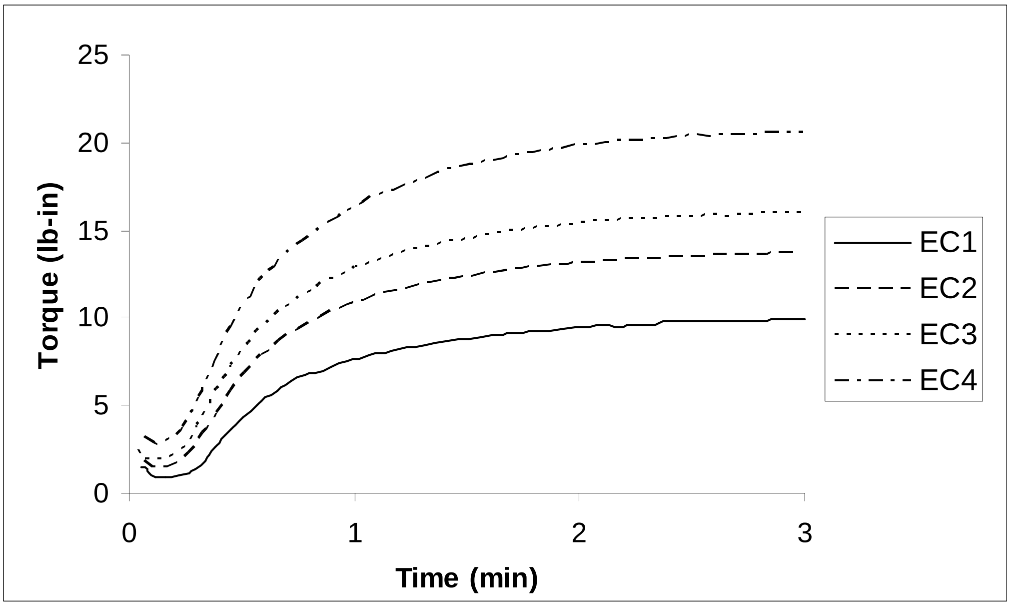


Figure 3.1 Crosslinking isotherms for the compounds with increasing amount of filler

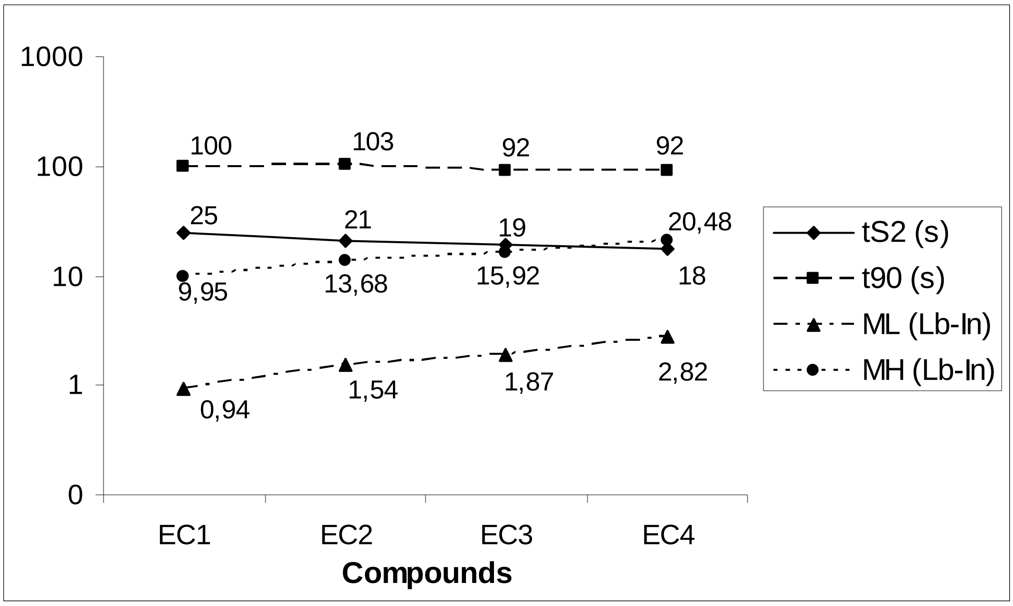


Figure 3.2 Rheometer readings for the compounds with increasing amount of filler

From the rheometer readings, torque value at any time t (M_t) and conversion time for any conversion (x) can be calculated as follows:

$$x = \frac{M_t - M_L}{M_H - M_L} \qquad (3.1.1.1)$$

Time required for any conversion can be calculated in this way. Also t_{s2}, t_{50}, t_{90}, M_L and M_H values can be directly be obtained from the rheometer output and these data can be used for interpreting cure behavior of compounds.

The reinforcement effect of a filler shows up especially in its ability to change the viscosity of a compound and also the vulcanizate properties with increasing amount of filler. In rheometer readings of EC1, EC2, EC3 and EC4 it is clearly observed that M_L values, which is directly related with the viscosity of compound, increases as the increasing amount of filler. M_H

value, from which one can interpret about the strength of vulcanizate, also increases directly proportional with increasing amount of filler.[1]

Interpretation for contribution of filler to the rate of cure was made by calculating the vulcanization reaction rate constant, k_T, of each compound by making use of rheometer data at 190^{o}C. For calculation of individual k_T values, torque values at approximately 30, 60, 90, and 120 seconds were selected for each compound. Table 3.2 gives vulcanization reaction rate constants as well as torque values at selected times, ratio of torques and -ln(1-Y) values at 190^{o}C.

Table 3.2 Rate constants of the compounds with increasing amount of filler for vulcanization reaction at 190^{o}C

	Time (s)	**Torque (lb-in)**	**Y (ratio of torque values)**	**- ln (1-Y)**	**k_T x 10^{-2} (s^{-1})**
EC1	30,6	4,35	0,44	0,57	2,70
	61,2	7,70	0,77	1,49	
	90,6	8,81	0,89	2,16	
	119,0	9,45	0,95	3,00	
EC2	30,6	6,90	0,50	0,701	2,74
	60,0	10,86	0,79	1,58	
	90,0	12,36	0,90	2,33	
	120,0	13,11	0,96	3,17	
EC3	30,0	8,09	0,51	0,709	3,01
	60,6	12,87	0,81	1,65	
	90,6	14,54	0,91	2,442	
	120,6	15,43	0,97	3,474	
EC4	30,6	10,72	0,52	0,74	3,02
	59,4	16,22	0,79	1,57	
	90,6	18,69	0,91	2,43	
	119,0	19,82	0,97	3,442	

As it can be seen from the table, rate constants tend to increase slightly. The active centers of filler surface can polarize double bonds of rubber molecule and can thus influence reactions. On carbon black surfaces phenolic, hydroxyl, quinone, carboxyl, lactone groups and reactive hydrogen bonds and others as well as free radicals have been formed which can react chemically with rubber molecules.[1]

The force vs. extension graphs for changing amount of filler in EPDM compounds are given in Appendix A. From the machine readings ultimate tensile stress and strain were obtained as average of three samples. They are tabulated in Figure 3.3 together with hardness values for comparison.

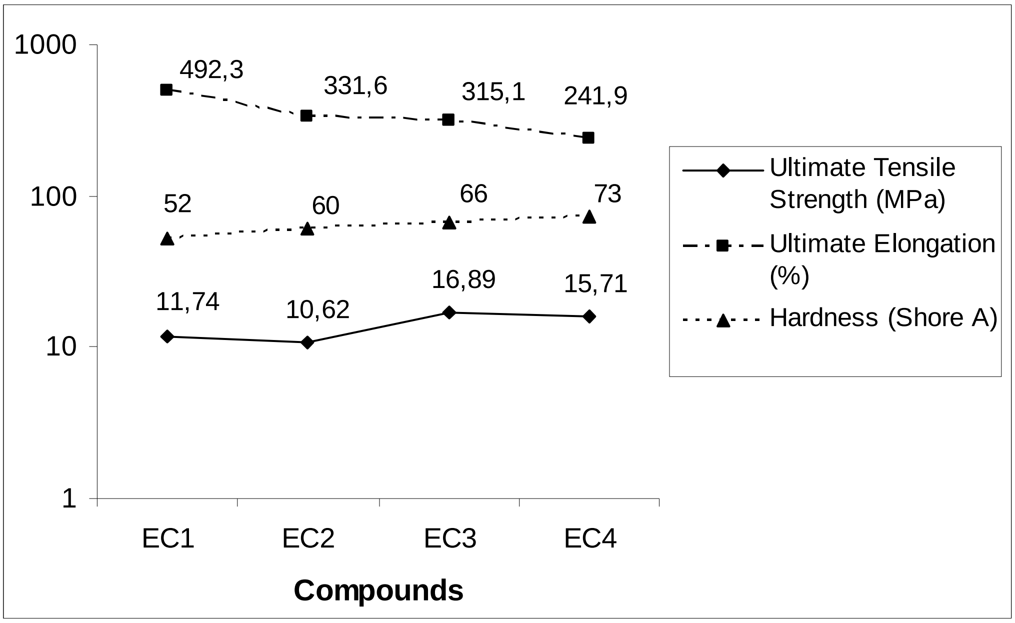
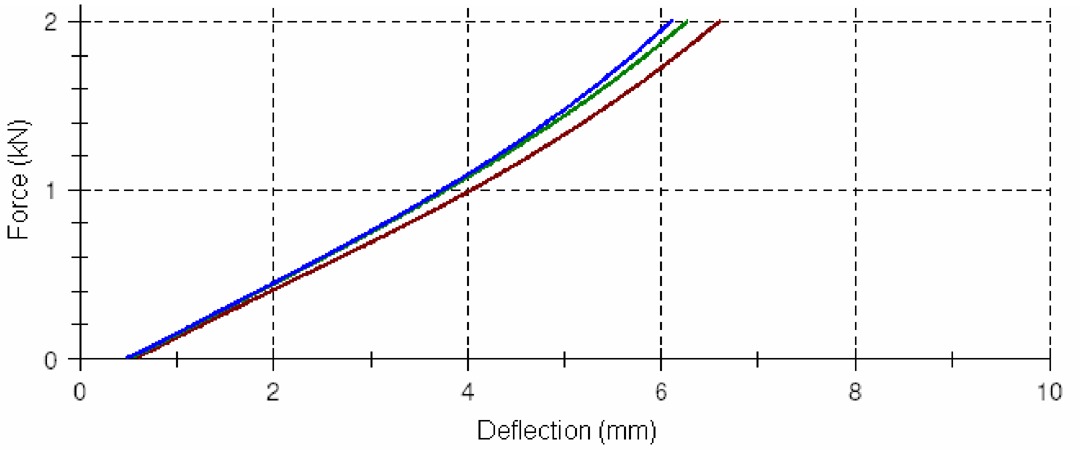


Figure 3.3 Ultimate tensile strength, ultimate elongation and hardness values for compounds EC1, EC2, EC3, and EC4

Stress-strain curves show no (or a very limited) linear portion. Therefore it is usually not practical to calculate Young's modulus, which would be the slope of a straight line drawn tangent to the curve and passing through the origin. Instead, stress at selected elongation is usually reported. These stress values for different elongations are reported by rubber technologists as 100% modulus, 300% modulus, etc. However these measures are not actually modulus values.[3] For that reason, in this study rather than comparing Young Modulus of compounds, ultimate tensile strength and ultimate elongation values are preferred to compare.

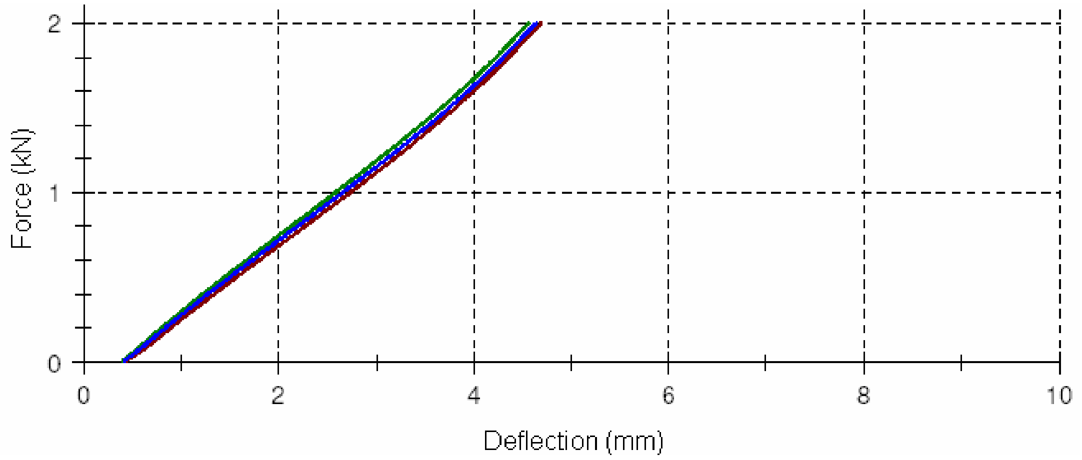
Reinforcement effect can be explained using stress-strain diagrams. Filler reinforcement increases the stiffness of vulcanizate compounds and improve variety of vulcanizate property, like tensile strength. The tensile stress-strain curve of a filler reinforced vulcanizate is steeper up to a higher stress at break compared to an unfilled vulcanizate. At the same time the stress values and the hardness are generally increased and as a rule other properties such as elongation at break and other properties depending on these lowered.[1] For the compounds EC1, EC2, EC3 and EC4 it can be observed that ultimate tensile strength and hardness tend to increase and ultimate elongation tends to decrease as filler loading increases.

Compression-deflection graphs for compounds EC1, EC2, EC3, and EC4 were obtained as average of three samples and recorded in kN/mm from the machine reading. The graphs are given in Figure 3.4 and the results are given in Figure 3.5 for comparison.



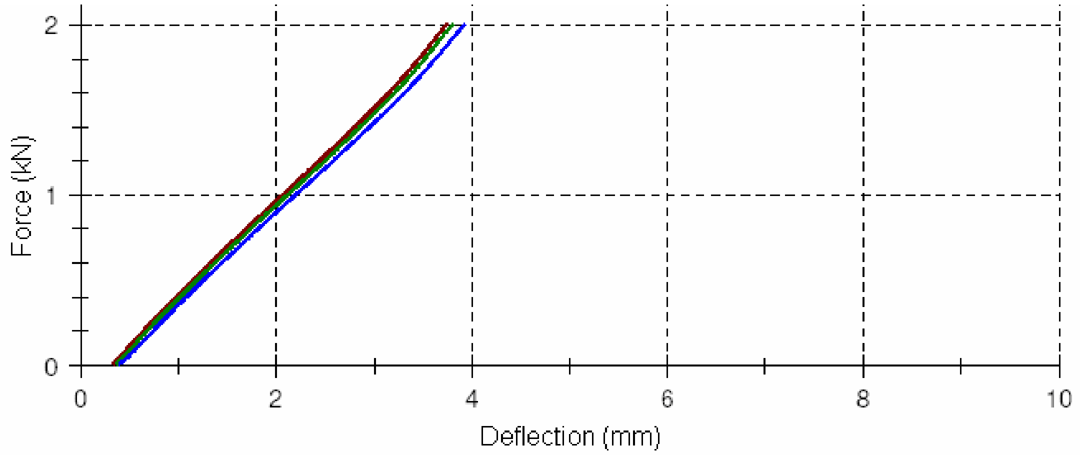
Force (kN)
0
1
2
0
2
4
6
8
10
Deflection (mm)

(a)



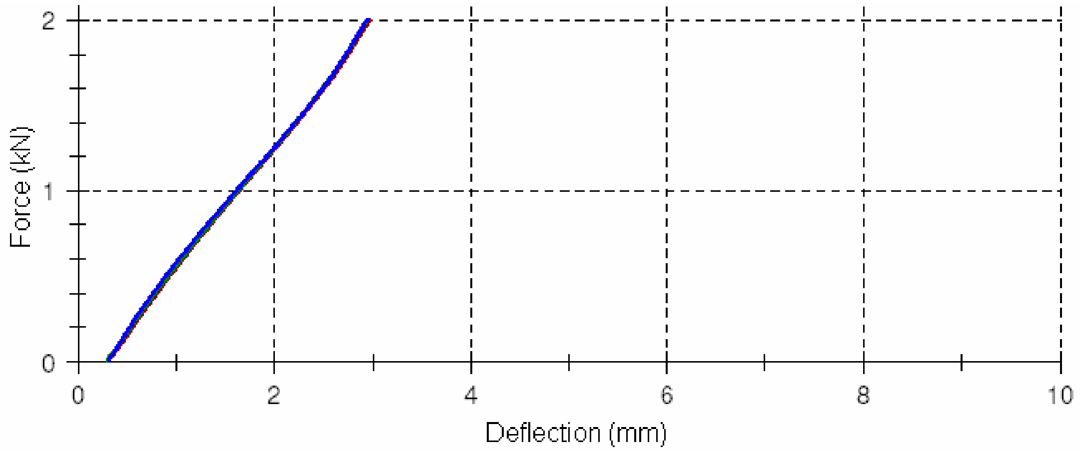
Force (kN)
0
1
2
0
2
4
6
8
10
Deflection (mm)

(b)



Force (kN)
0
1
2
0
2
4
6
8
10
Deflection (mm)

(c)



(d)

Figure 3.4 Force vs deflection graphs for EC1 (a), EC2 (b), EC3 (c), and EC4 (d)

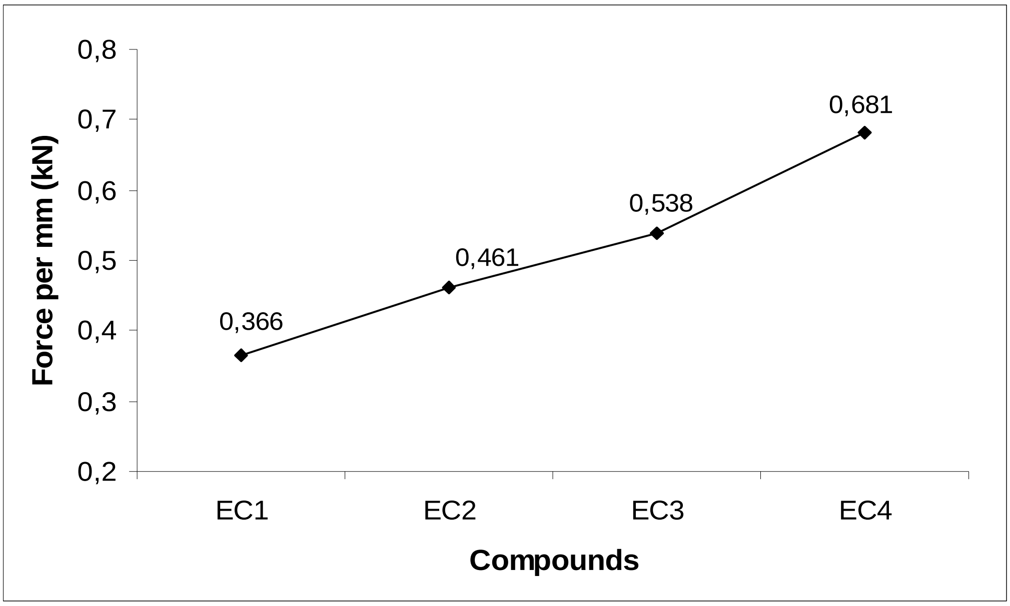


Figure 3.5 Force to deflect EC1, EC2, EC3 and EC4 samples 1 mm

For the compounds EC1, EC2, EC3 and EC4, deflection (change in thickness of the specimen upon application of a compressive force) increases as the filler load is increased. In other words; the force required to deflect the sample for 1 mm increases. It can be seen that the deflection is directly proportional with stiffness of vulcanizate.

DMA (Figure 3.6) for the filler effect showed that damping peak was decreased with the increase of the filler that is the viscoelasticity of the EPDM was decreased and it becomes more rigid. Tg increased with the increase of the filler content from 70 phr to 105 phr.

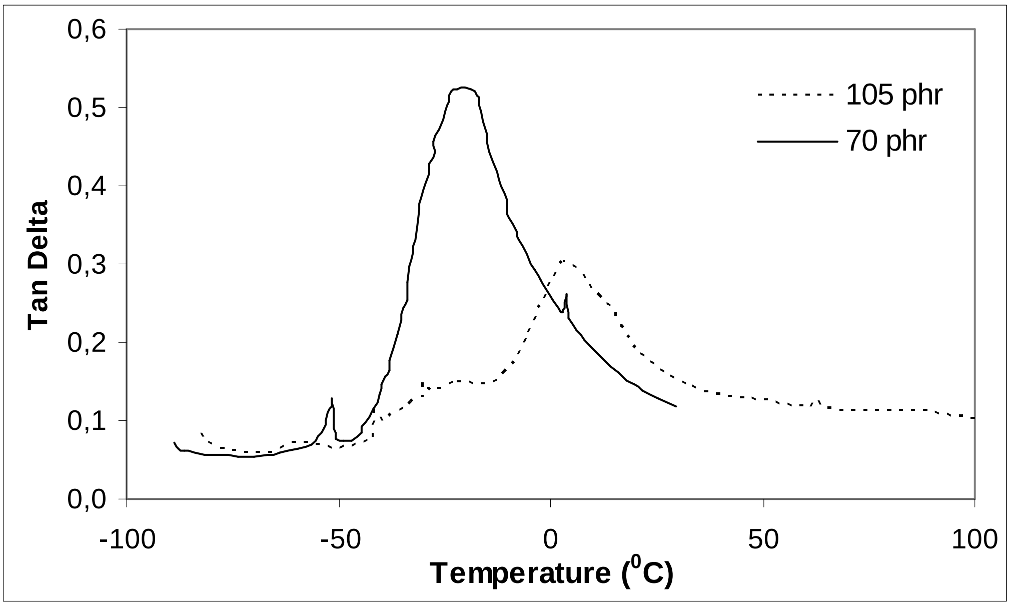


Figure 3.6 Damping for EC2 (70 phr carbon black) and EC4 (105 phr carbon black)

3.1.2 Effect of Process Oil

Compounding for different amounts of process oil, i.e., Tudalen 3909, was achieved and named as in Table 3.3.

Table 3.3 Compounding for different amount of process oil

Ingredient	**Amount (phr)**		
	EY1	EC2	EY2
EPDM rubber (4.4% ENB)	100	100	100
Carbon black FEF N 550	70	70	70
Saturated mineral oil	**15**	**30**	**45**
ZnO	6	6	6
Stearic acid	1	1	1
Sulfur (80%)	0.25	0.25	0.25
Di (t-butylperoxy) diisopropyl benzene (40%)	5	5	5

For each compound crosslinking isotherms (Figure 3.7) were taken at 190°C for 3 minutes. The resulting scorch time, t_{S2}, cure time, t_{90}, minimum rheometer torque, M_L and maximum rheometer torque, M_H are given in Figure 3.8 for comparison.

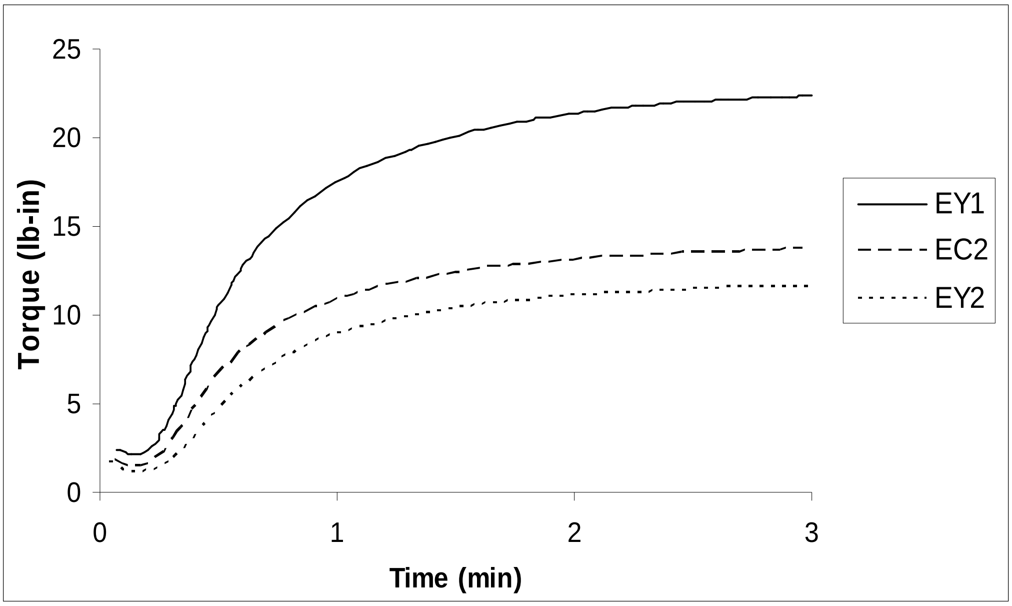


Figure 3.7 Crosslinking isotherms for the compounds with increasing amount of process oil

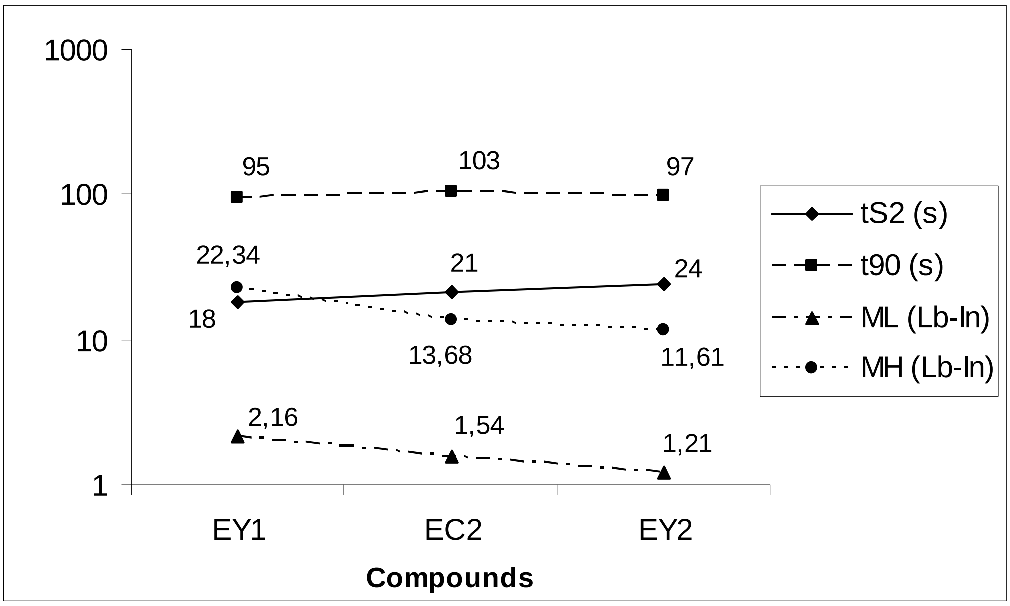


Figure 3.8 Rheometer readings for the compounds with increasing amount of process oil

One can differentiate between two groups of plasticizers based on their interaction with rubber, the primary and secondary plasticizers. Primary plasticizers assist micro- and macro Brownian motion of the polymer chains and thereby also the viscous flow. Since the plasticizers swell rubber, they reduce the viscosity of the unvulcanized rubber compound considerably. Plasticizers that solubilize very little or not at all are secondary plasticizers; they act as lubricants between the rubber chain molecules, improve formability without any appreciable effect on the viscosity of the compounds. Between these groups of plasticizers there are many transitions possible and it is impossible to draw a sharp line between them because for different rubbers, different plasticizers can function as primary and secondary plasticizers.[1] In the The M_L values, which are proportional to viscosity of compounds, a constant decrease is seen from EY1 to EY2. From this information one can interpret that TUDALEN 3909 is a primary plasticizer for EPDM rubber.

Plasticizers can accelerate or decelerate the vulcanization reaction. Unsaturated compounds react chemically with the sulfur that is needed to vulcanization. t_{s2}, t_{90} and k_T values (Table 3.4) are slightly affected by increasing amount of plasticizer because TUDALEN 3909 is saturated mineral oil; theoretically it is not expected to affect vulcanization reaction.

Table 3.4 Rate constants of the compounds with increasing amount of process oil for vulcanization reaction at 190°C

	Time (s)	**Torque (lb-in)**	**Y (ratio of torque values)**	**- ln (1-Y)**	**k_T x 10^{-2} (s^{-1})**
EY1	30,0	10,55	0,47	0,64	2,77
	59,4	17,45	0,78	1,52	
	91,2	20,15	0,90	2,32	
	121,2	21,42	0,96	3,19	
EC2	30,6	6,90	0,50	0,70	2,74
	60,0	10,86	0,79	1,58	
	90,0	12,36	0,90	2,33	
	120,0	13,11	0,96	3,17	
EY2	30,0	4,57	0,39	0,501	2,91
	59,4	8,85	0,76	1,435	
	88,8	10,35	0,89	2,216	
	120,0	11,11	0,96	3,146	

The force vs. extension graphs for changing amount of process oil in EPDM compounds are given in Appendix B. From the machine readings ultimate tensile stress and strain were obtained as average of three samples. They are tabulated in Figure 3.9 together with hardness values for comparison.

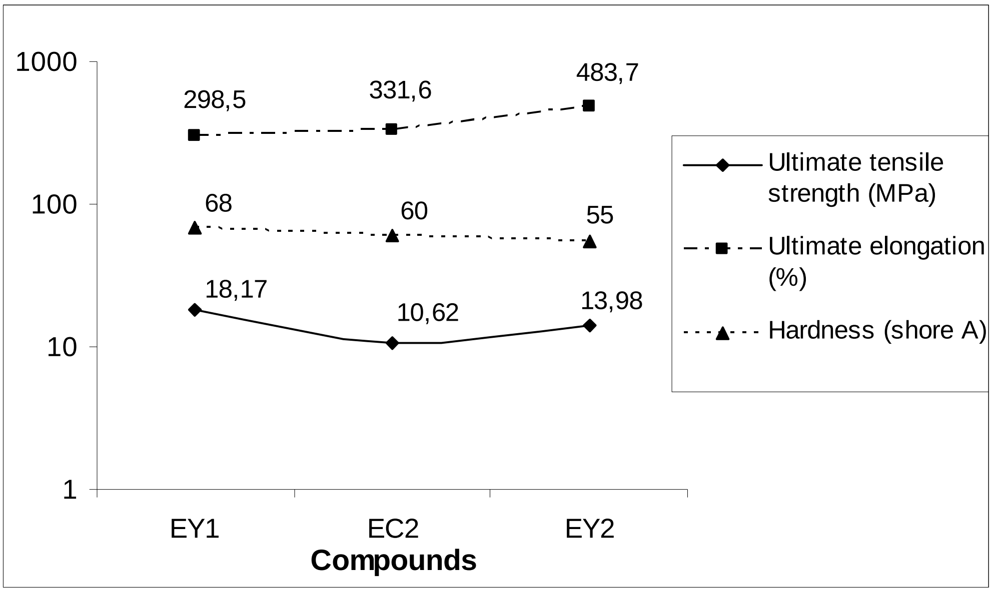
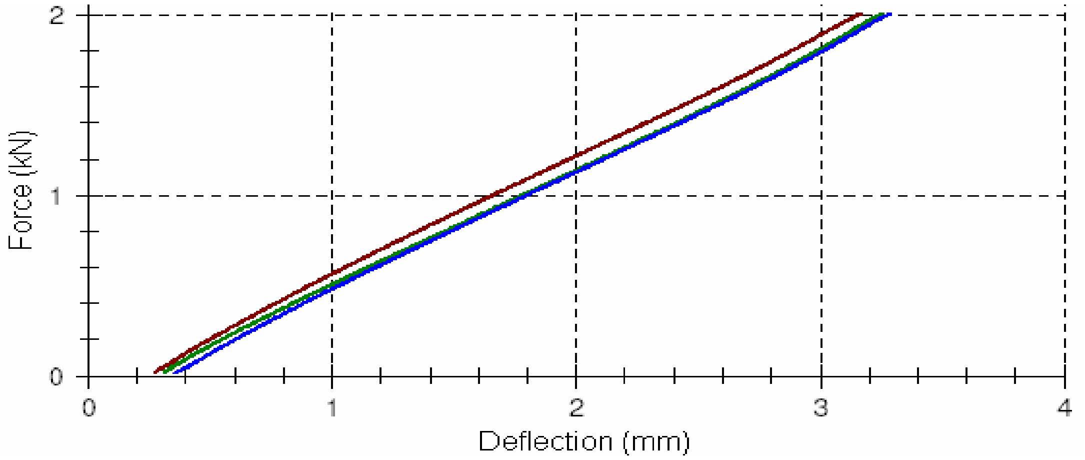


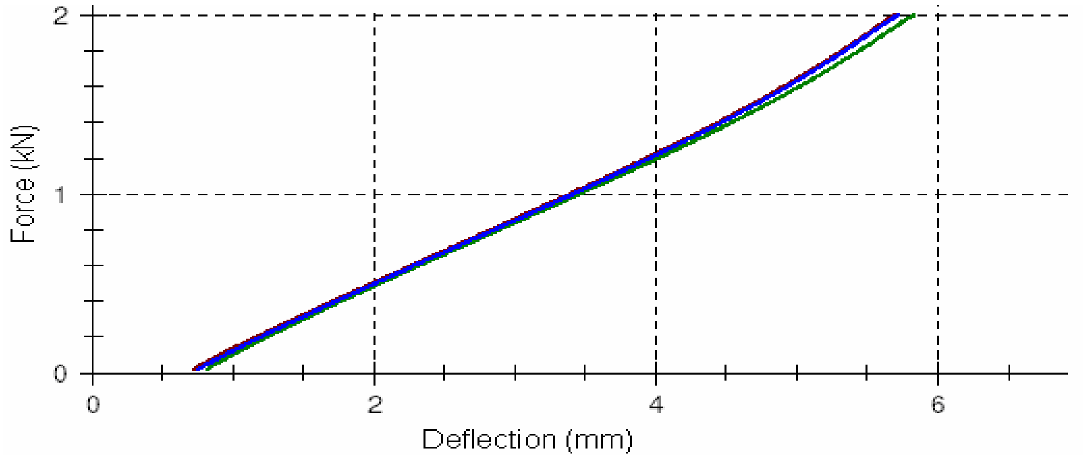
Figure 3.9 Ultimate tensile strength, ultimate elongation and hardness values for compounds EY1, EC2 and EY2

Process oils are added to the polymer or to rubber compounds primarily to lower viscosity and to reduce both stress-strain resistance and the hardness of the finished article. Carbon black and process oil tend to affect such properties as viscosity, hardness, modulus, and elongation in opposite directions, for example, more carbon black increases viscosity, whereas more oil reduces it.[3] As it can be seen from the Figure 3.9 increasing amount of process oil considerably increase the elongation and decrease the hardness. Tensile strength is minimum for EC2 however this result is not expected. In rubbery, i.e. solid state, the oil is generally believed to be absorbed by the EPDM.[13] In this case oil may not be absorbed by the EPDM totally because of the mixing conditions and the result (10.62 MPa) may taken less than expected.

Force vs. deflection graphs for compounds EY1, EC2 and EY2 were obtained as average of three samples and recorded in kN/mm. Graphs are given in Figure 3.10 and results are given in Figure 3.11



(a)



(b)

Figure 3.10 Force vs. deflection graphs for EY1 (a) and EY2 (b)

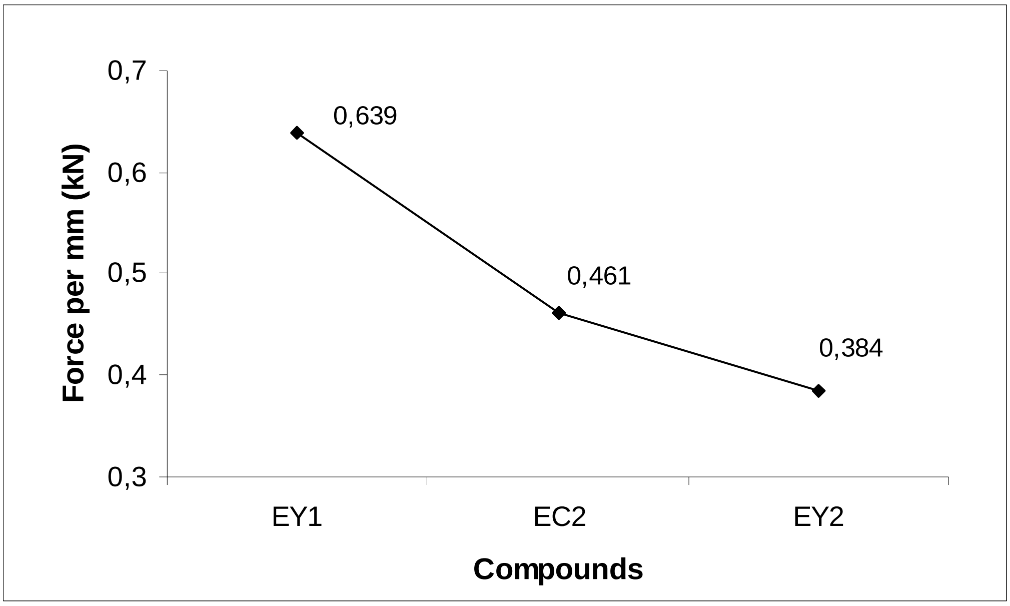


Figure 3.11 Force to deflect EY1, EC2 and EY2 samples by 1 mm

For the compounds EY1, EC2 and EY2 deflection decreases as the process oil load is increased. Force required deflecting the sample 1 mm decreases. This result is expected because the softer the compound, less force for deflection is required.

3.1.3 Effect of Vulcanizing Agent

Compounding for different amounts of vulcanizing agent, i.e. BBPIB, was achieved and named in Table 3.5.

Table 3.5 Compounding for different amount of vulcanizing agent

Ingredient	**Amount (phr)**			
	EV1	EC2	EV2	EV3
EPDM rubber (4.4% ENB)	100	100	100	100
Carbon black FEF N 550	70	70	70	70
Saturated mineral oil	30	30	30	30
ZnO	6	6	6	6
Stearic Acid	1	1	1	1
Sulfur (80%)	0.25	0.25	0.25	0.25
Di (t-butylperoxy) diisopropyl benzene (40%)	**2.5**	**5**	**7.5**	**10**

For each compound crosslinking isotherms (Figure 3.12) were taken at 190^{o}C for 3 minutes. The resulting scorch time, t_{S2}, cure time, t_{90}, minimum rheometer torque, M_L and maximum rheometer torque, M_H values are given in Figure 3.13 for comparison:

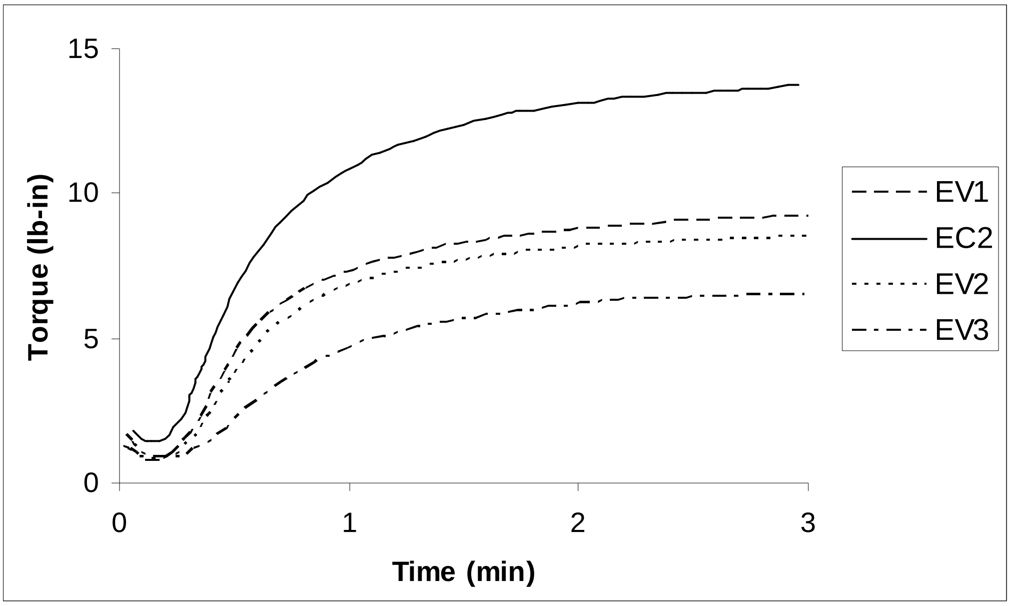


Figure 3.12 Crosslinking isotherms for the compounds with increasing amount of vulcanizing agent

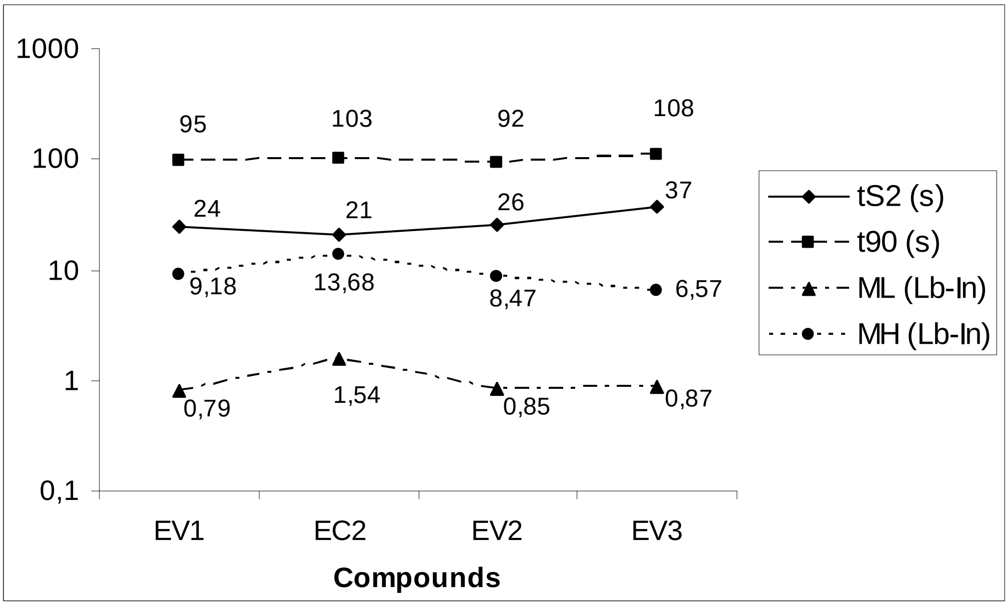


Figure 3.13 Rheometer readings for the compounds with increasing amount of vulcanizing agent.

It can be seen from the Figure 3.15 that scorch time, t_{s2}, is minimum for EC2. Cure time, $t_{90,}$ is maximum for EV3. Also M_H is maximum for EC2 then it tends to decrease. This figure exhibits that increasing amount of peroxide cure agent does not increase the properties direct proportional with its amount.

Figure 3.14 shows the relationship between M_H-M_L (maximum rheometer torque – minimum rheometer torque) and peroxide increment. From theory it is shown that the torque difference is a measure of the shear dynamic modulus which indirectly relates to the crosslink density of vulcanizates.[11] Since the M_H-M_L correlates crosslink density of vulcanized rubbers it can be said that from EV1 to EV3 compounds increasing amount of peroxide gives better crosslink density to some extent.

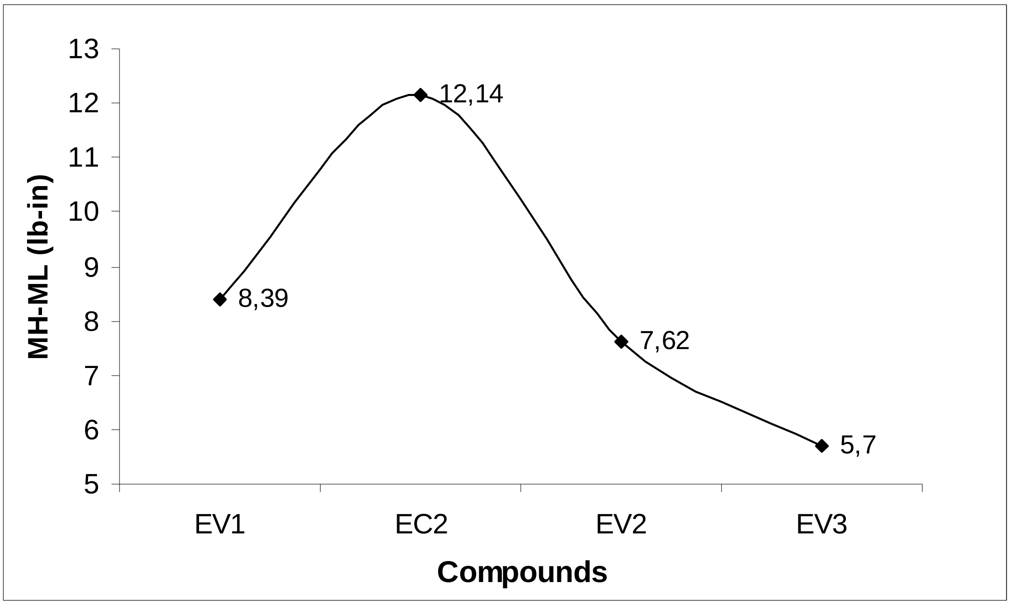


Figure 3.14 M_H-M_L for the compounds EV1, EC2, EV2, and EV3

The similar trend is also seen for rate constants. As it can be seen from the Table 3.6 it increases until 7.5 phr and then again decreases probably due to the decomposition of excess curing agent.

Table 3.6 Rate constants of the compounds with increasing amount of vulcanizing agent for vulcanization reaction at 190°C

	Time (s)	**Torque (lb-in)**	**Y (ratio of torque values)**	**- ln (1-Y)**	**k_T x 10^{-2} (s^{-1})**
EV1	30,6	4,60	0,50	0,70	2,64
	59,4	7,25	0,79	1,56	
	90,6	8,30	0,90	2,34	
	122,0	8,78	0,95	3,12	
EC2	30,6	6,90	0,50	0,70	2,74
	60,0	10,86	0,79	1,58	
	90,0	12,36	0,90	2,33	
	120,0	13,11	0,96	3,17	
EV2	30,6	3,82	0,45	0,60	3,35
	59,4	6,76	0,80	1,60	
	89,4	7,66	0,90	2,34	
	120,6	8,15	0,96	3,70	
EV3	30,0	2,22	0,34	0,41	2,70
	59,4	4,63	0,71	1,22	
	91,2	5,69	0,87	2,01	
	120,6	6,20	0,94	2,88	

The force vs. extension graphs for changing amount of vulcanizing agent in EPDM compounds are given in Appendix C. From the machine readings ultimate tensile stress and strain were obtained as average of three samples. They are tabulated in Figure 3.15 together with hardness values for comparison.

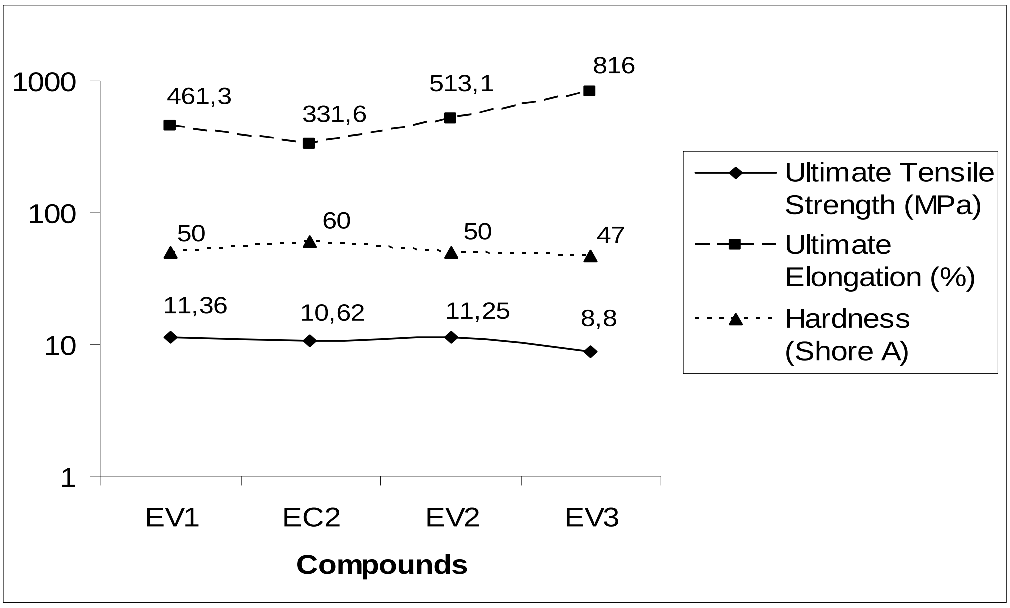
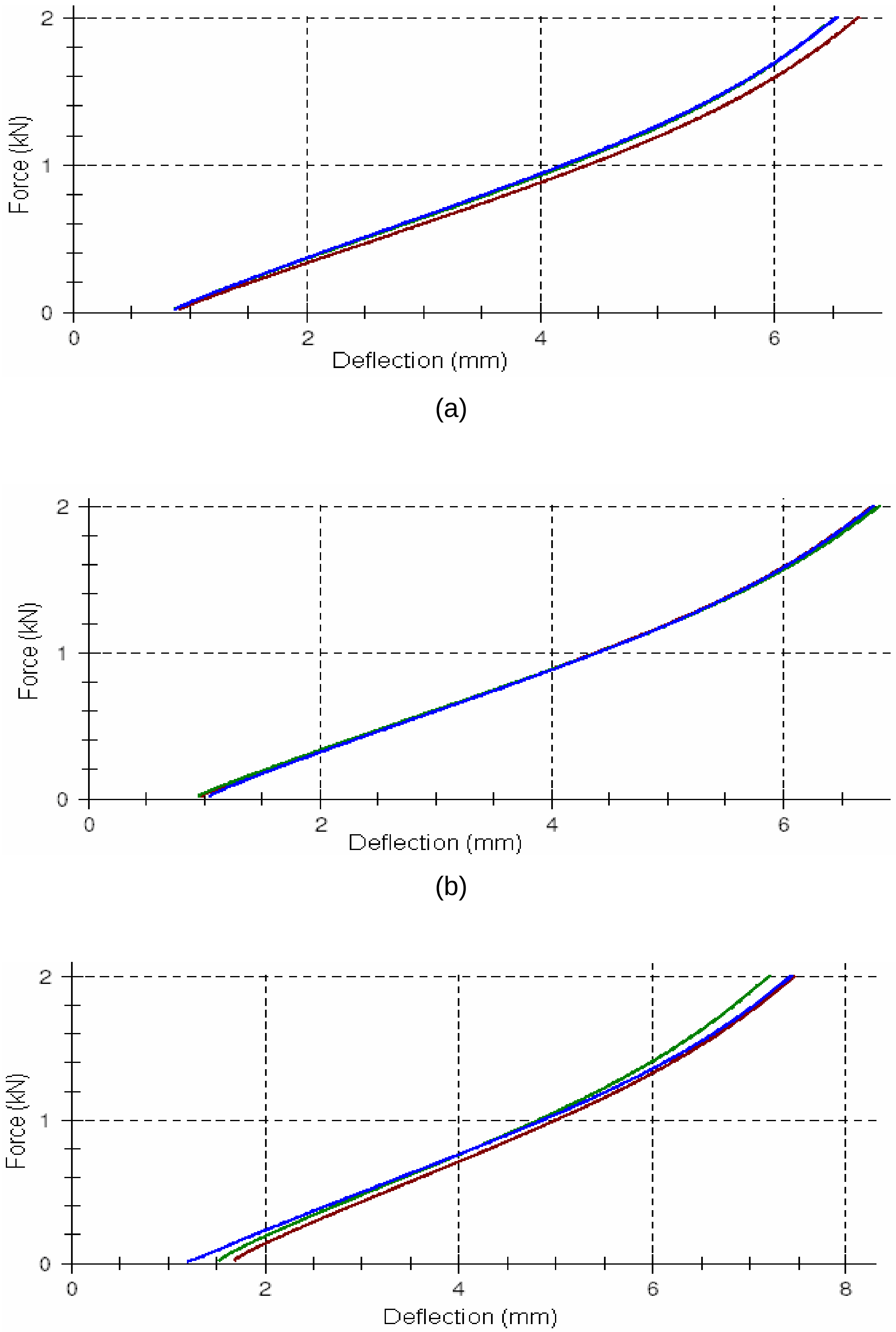


Figure 3.15 Ultimate tensile strength, ultimate elongation and hardness values for compounds EV1, EC2, EV2 and EV3

Ultimate tensile strength tends to decrease and ultimate elongation tends to increase probably because of decreasing crosslinking efficiency. Curing by using peroxide alone often leads to unwanted chain scission due to the presence of tertiary hydrogen in the main backbone (propylene unit) and competes with the desired crosslinking resulting poor crosslinking efficiency.[8] It is also noted that hardness, which is maximum for compound EC2 and then tends to decrease correlates maximum rheometer torque, M_H.

Force vs. deflection graphs for compounds EY1, EC2 and EY2 were obtained as average of three samples and recorded in kN/mm from the machine reading. The graphs are given in Figure 3.16 and the results are given in Figure 3.17



(a)

(b)

(c)

Figure 3.16 Force vs. deflection graphs for EV1 (a), EV2 (b), EV3 (c)

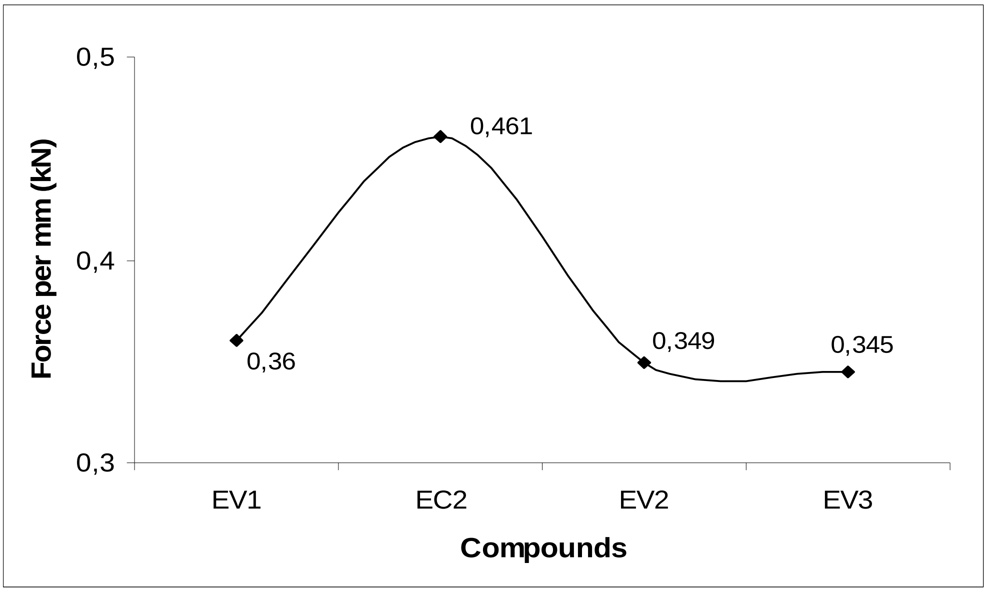


Figure 3.17 Force to deflect EV1, EC2, EV2 and EV3 samples by 1 mm

For the compounds EV1, EC2, EV2 and EV3 deflection increases until 5 phr peroxide content and then decreases with 7.5 and 10 phr peroxide content relatively. This result is very similar to that of carbon black compounds and process oil compounds in that the compression-deflection graph shows similar trend with hardness of related compounds.

Change of dynamic mechanical properties with the vulcanizing agent content was also studied. Two glass transitions were observed from the DMA spectrum of the EPDM (Figure 3.18). Both of the glass transition temperatures were decreased with the increase of the vulcanizing agent content from 2.5 phr to 10 phr and this was consistent with the decrease of mechanical properties at 10 phr vulcanizing agent content. Damping peak widened that is the molecular weight distribution and the heterogeneity index was increased with the increase of the vulcanizing agent from 5 phr to 10 phr and this confirms the decrease of the mechanical properties and also confirms decrease of the relative degree of crosslinking at 10 phr vulcanizing agent content.

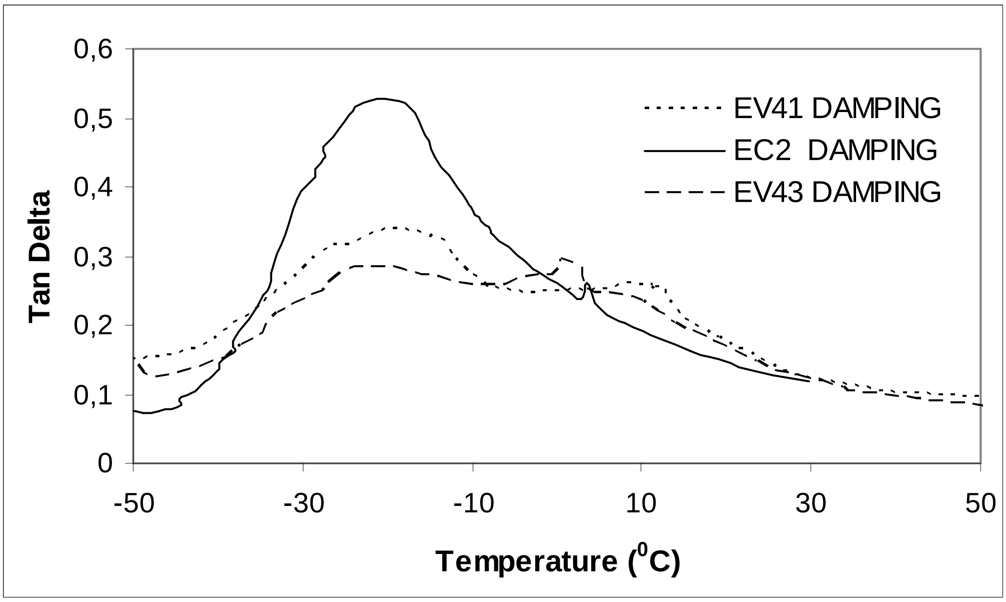


Figure 3.18 DMA spectrum of EV1, EC2 and EV2

Thermal Gravimetric Analysis was also studied for the compounds EV1 and EC2. Figure 3.19 show the TGA graphs of EV1 and EC2 in which contain 2.5 and 5 phr vulcanizing agent, relatively. These two graphs are so similar that one can not easily interpret about EV1 and EC2 compounds since the increment of vulcanizing agent is only 2.5 phr. This method is useful for investigation of different amount of carbon black in a rubber mixture.

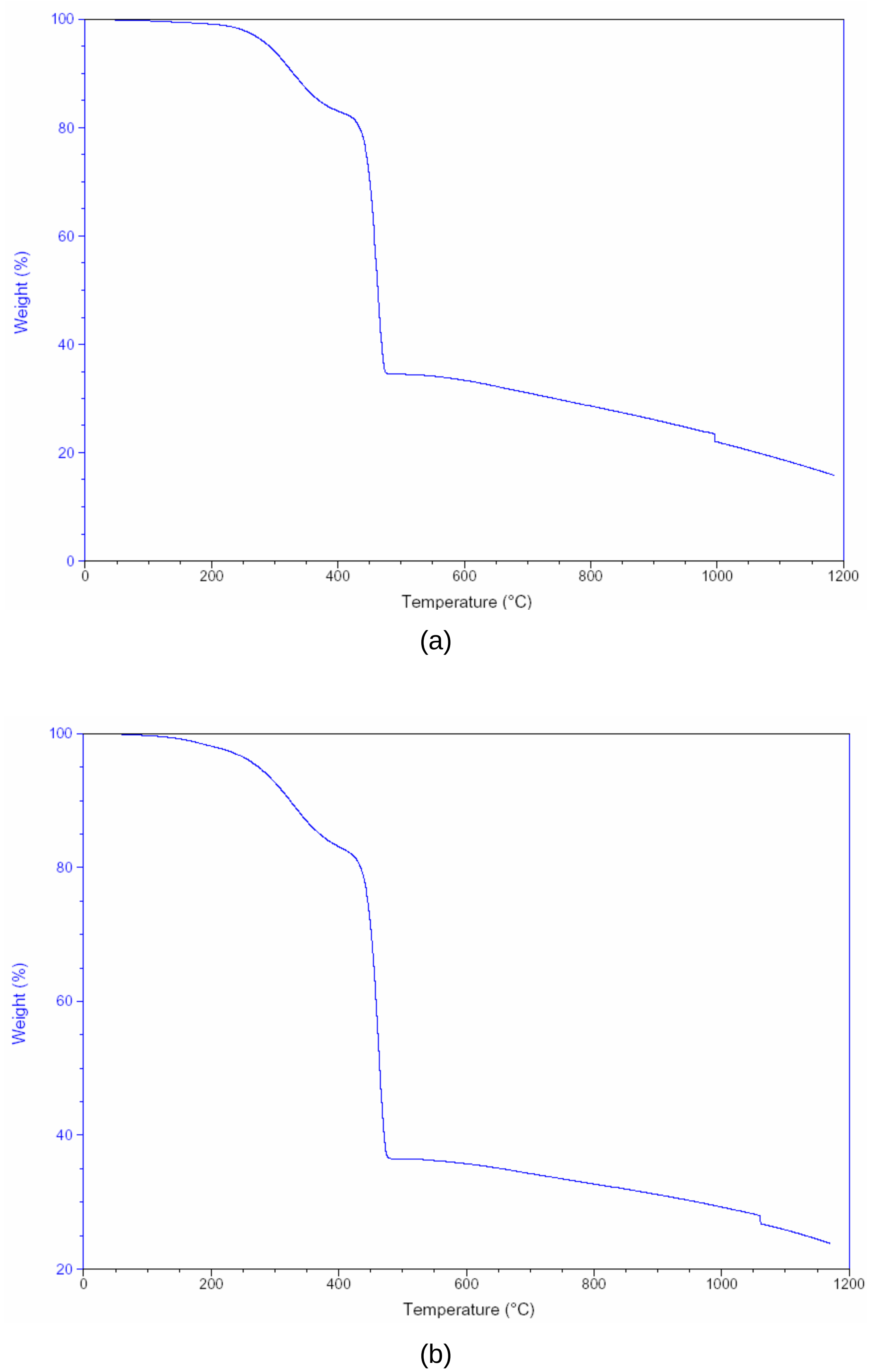


Figure 3.19 Thermal Gravimetric Analysis of EV1 (a) and EC2 (b)

3.2 EFFECT OF ENB RATIO ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPDM RUBBER

EPDM with ENB [5-ethylidenebicyclo(2.2.1)-hept-2-ene] ratio of 5.0% (Keltan 27), 5.6% (Keltan 8340 A), 7.5% (Buna EPG 6850), and 8.9 % (Keltan 4903) were used for compounding. Table 3.7 shows details for compounding and naming. Here investigation was made for two different amount of curing agent [45% 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (Luperox 101XL45)] and coagent [trimethylolpropane trimethacrylate (SR 350)]. 45% 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and trimethylolpropane trimethacrylate were used 3 and 2 phr in cure system 1, 5 and 3 phr in cure system 2, respectively.

Table 3.7 Compounding for different amount of ENB ratio

Ingredient	Amount (phr)							
	A1	**A2**	**B1**	**B2**	**C1**	**C2**	**D1**	**D2**
EPDM rubber (5% ENB)	100	100						
EPDM rubber (5.6% ENB)			100	100				
EPDM rubber (7.5% ENB)					100	100		
EPDM rubber (8.9% ENB)							100	100
FEF N 550 Carbon Black	90	90	90	90	90	90	90	90
Saturated Mineral Oil	30	30	30	30	30	30	30	30
TMQ	1	1	1	1	1	1	1	1
MMBI	1	1	1	1	1	1	1	1
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
2,5-Dimethyl-2,5-di(t-butylperoxy) hexane (45%)	3	5	3	5	3	5	3	5
Trimethylolpropane trimethacrylate	2	3	2	3	2	3	2	3

For two cure systems crosslinking isotherms, given in Figure 3.20 and Figure 3.21, were taken at 190°C for 3 minutes. The resulting scorch time, t_{S2}, cure time, t_{90}, minimum rheometer torque, M_L and maximum rheometer torque, M_H are given in Figure 3.22 for cure system 1 and Figure 3.23 for cure system 2 for comparison.

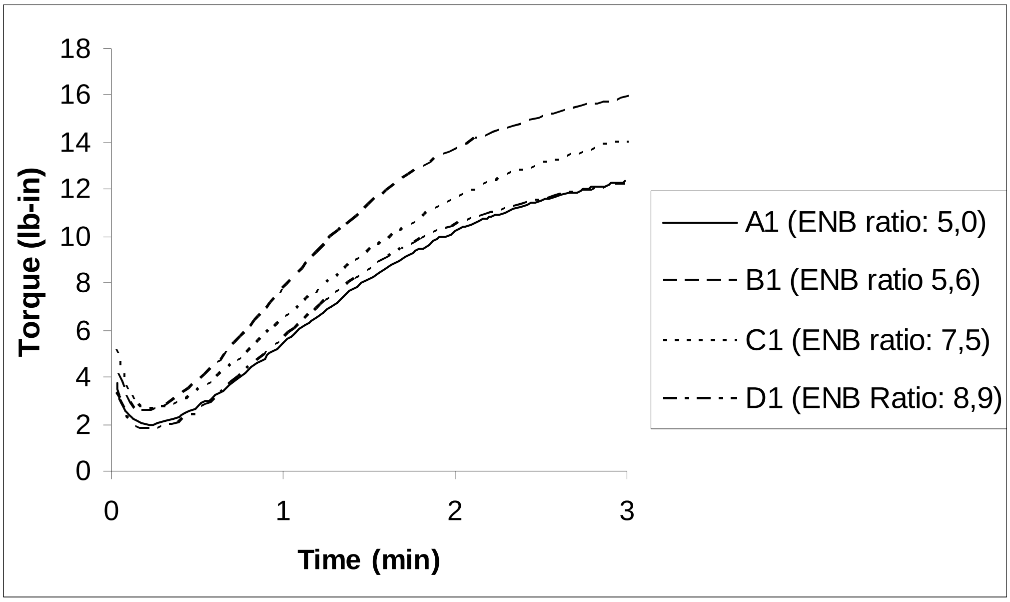


Figure 3.20 Crosslinking isotherms for compounds with increasing ENB ratio for cure system 1

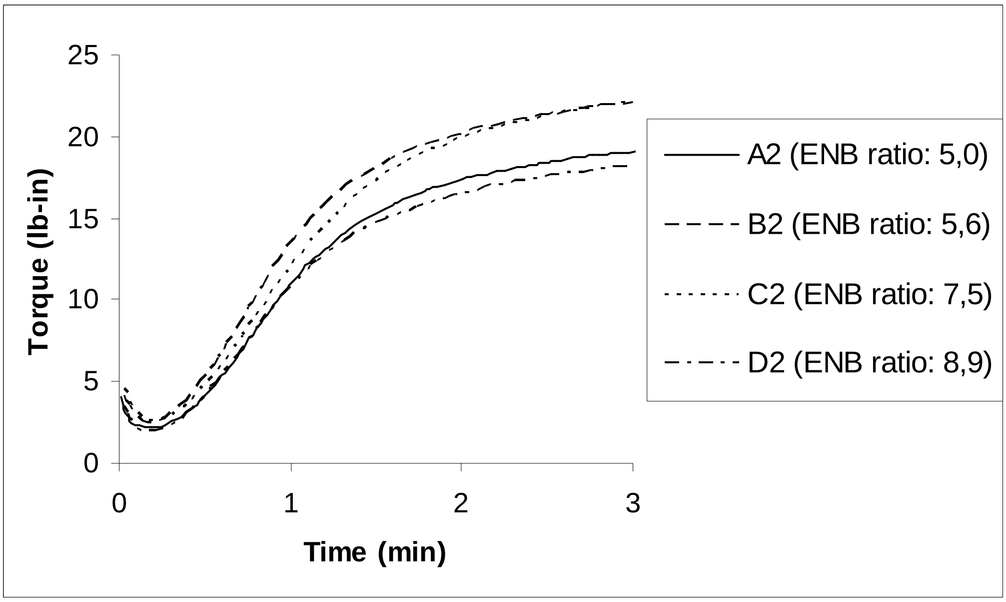


Figure 3.21 Crosslinking isotherms for compounds with increasing ENB ratio for cure system 2

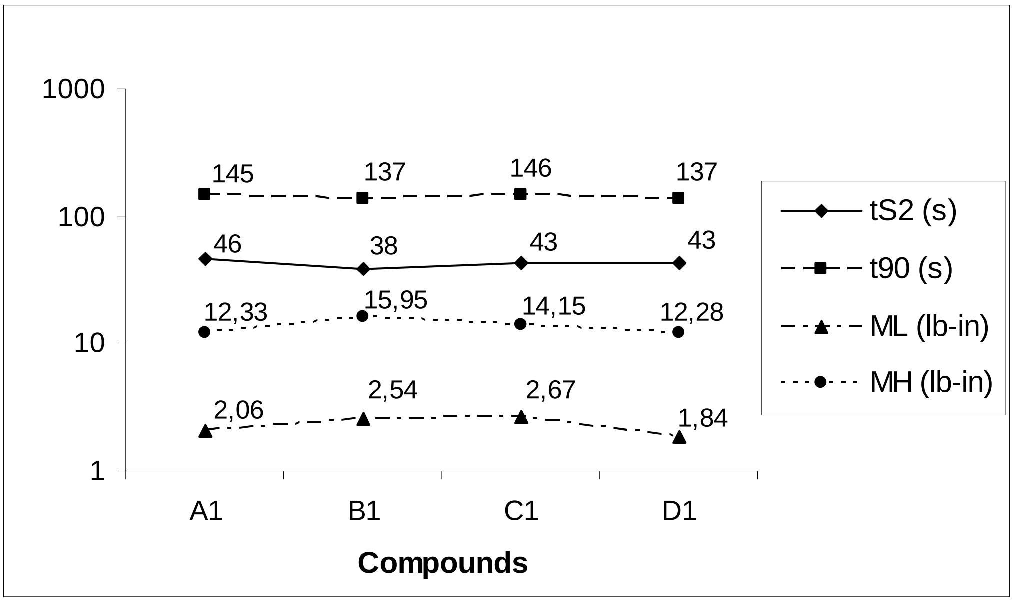


Figure 3.22 Rheometer readings for the compounds with increasing ENB ratio (cure system 1)

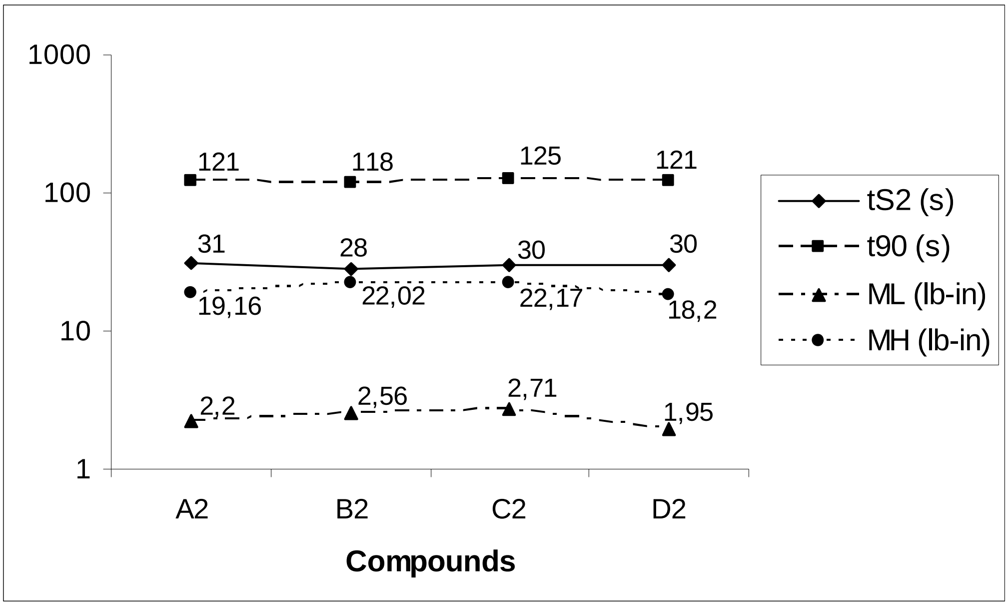


Figure 3.23 Rheometer readings for the compounds with increasing ENB ratio (cure system 2)

For both cure systems, similar trends of rheometer readings are observed; scorch time, t_{s2}, minimum for B1 and B2. Cure time, t_{90} values show no regular trend. Minimum rheometer torque, M_L, which is related to viscosity of uncured compound, is relatively high for compounds with 5.6% and 7.5% ENB ratios. Maximum rheometer torque, M_H, which is related to stiffness of cured compound is maximum for the compounds with 7.5% ENB ratio. As double bonds are introduced to the system constant increase in properties are not observed since they can activate the reactions and improve strength of cured rubber to some extent but after curing agent saturate double bonds remaining excess amount of them may hinder the course of reactions as well. This results are supported with M_H-M_L vs. ENB ratio graphs in Figure 3.24 and 3.25.

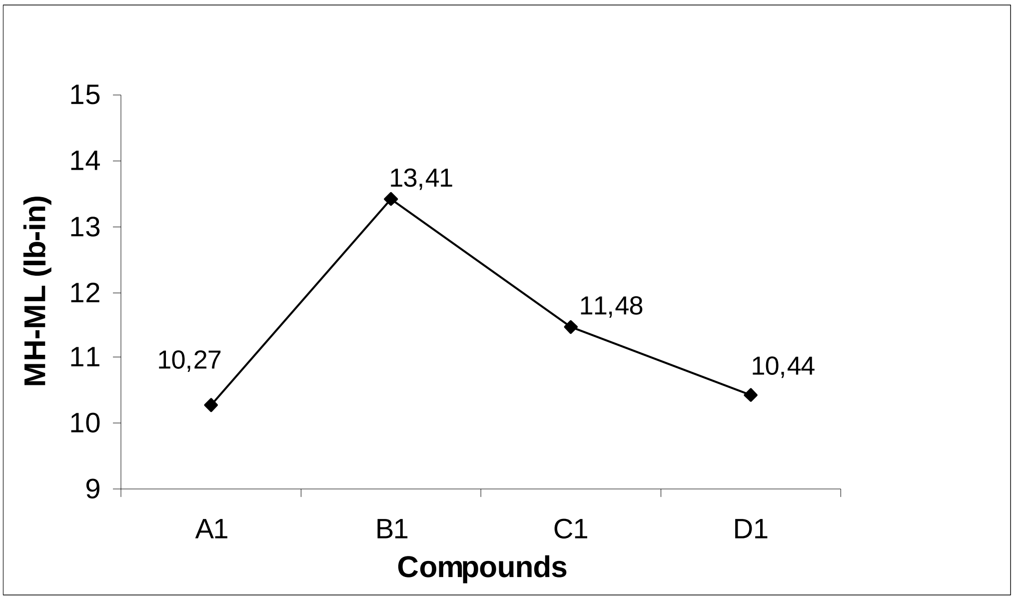


Figure 3.24 M_H-M_L for compounds with increasing ENB ratio for cure system 1

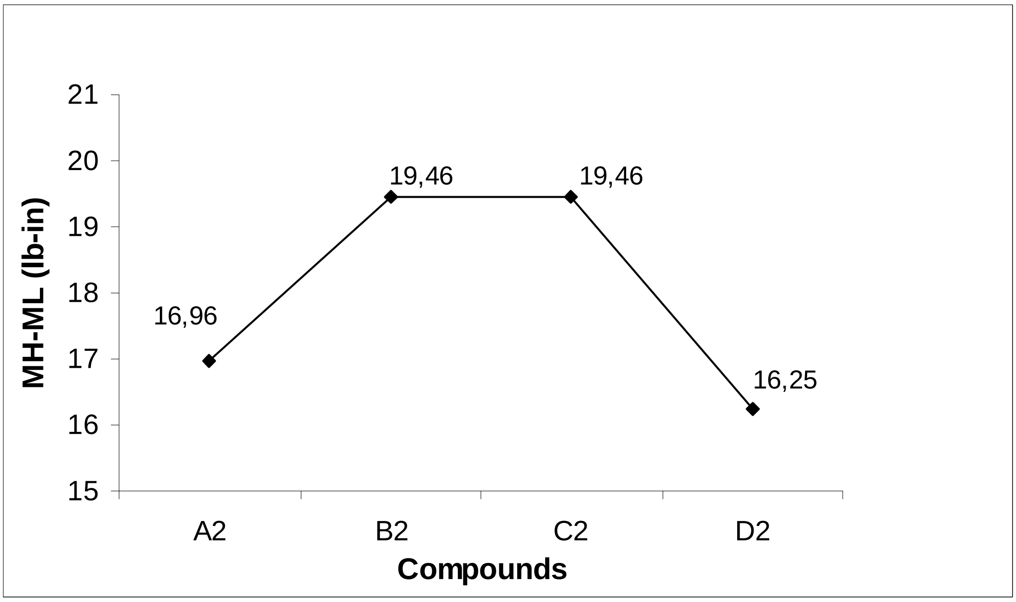


Figure 3.25 M_H-M_L for compounds with increasing ENB ratio for cure system 2

As the ENB ratio is increased for both cure systems, crosslink density does not tend to increase although more double bonds are introduced to the system. If the croslinking efficiency is not directly related to the variation of C=C bonds, it is not directly to the amount of double bonds initially present, because the increasing diene content does not help to increase the number of crosslinks.[9]

Table 3.8 and Table 3.9 show the rate constants for vulcanization reaction of compounds for two different cure systems.

Table 3.8 k_T values for compounds with increasing ENB ratio at 190°C (cure system 1)

	Time (s)	**Torque (lb-in)**	**Y (ratio of torque values)**	**- ln (1-Y)**	**k_T x 10^{-2} (s^{-1})**
A1	29,4	2,65	0,22	0,24	1,63
	60,0	5,47	0,44	0,59	
	91,2	8,24	0,67	1,10	
	118,8	10,08	0,82	1,70	
B1	30,0	3,81	0,24	0,27	1,89
	60,0	7,72	0,48	0,66	
	90,0	11,33	0,71	1,24	
	120,6	13,75	0,86	1,98	
C1	31,2	3,47	0,25	0,28	1,59
	61,2	6,55	0,46	0,62	
	89,4	9,32	0,66	1,08	
	118,8	11,50	0,81	1,68	
D1	30,6	2,60	0,21	0,24	1,87
	59,4	5,58	0,45	0,61	
	89,4	8,53	0,70	1,19	
	119,4	10,43	0,85	1,89	

Table 3.9 k_T values for compounds with increasing ENB ratios at 190°C (cure system 2)

	Time (s)	**Torque (Lb-In)**	**Y (ratio of torque values)**	**- ln (1-Y)**	**k_T x 10^{-2} (s^{-1})**
A2	29,4	4,00	0,21	0,23	2,35
	60,6	11,15	0,58	0,87	
	90,6	15,33	0,80	1,61	
	120,6	17,36	0,91	2,36	
B2	30,0	5,31	0,24	0,28	2,46
	61,2	13,71	0,62	0,98	
	90,0	18,01	0,82	1,70	
	118,8	20,13	0,91	2,45	
C2	30,0	4,72	0,21	0,24	2,26
	60,0	12,04	0,54	0,78	
	90,6	17,33	0,78	1,52	
	119,4	19,83	0,89	2,24	
D2	30,6	4,18	0,23	0,26	2,36
	60,6	10,85	0,60	0,91	
	90,0	14,66	0,81	1,64	
	120,0	16,49	0,91	2,36	

They both show similar trends; rate constants are not decreasing or increasing regularly. Probably the diene contents in these compounds cause reactions proceed in different ways.

The force vs. extension graphs for changing amount of ENB content in EPDM compounds for two cure systems are given in Appendix D. From the machine readings ultimate tensile stress and elongation for two cure systems were obtained as average of three samples. They are given in Figure 3.26 and Figure 3.27 for comparison. Hardness values are given in Figure 3.28.

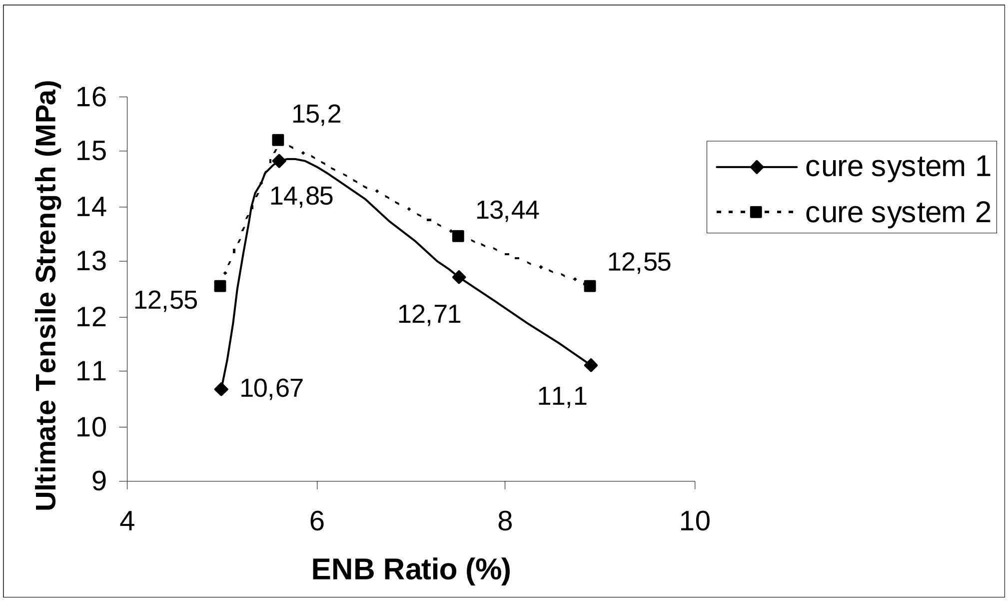


Figure 3.26 Tensile strength for the compounds with increasing ENB ratio for cure system 1 and cure system 2

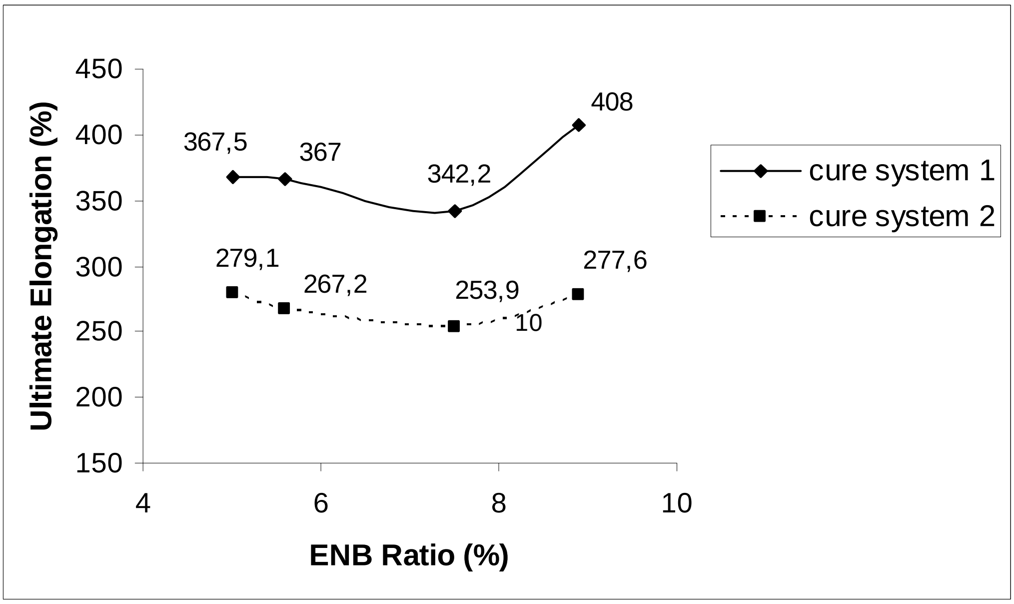


Figure 3.27 Ultimate elongation for the compounds with increasing ENB ratio for cure system 1 and cure system 2

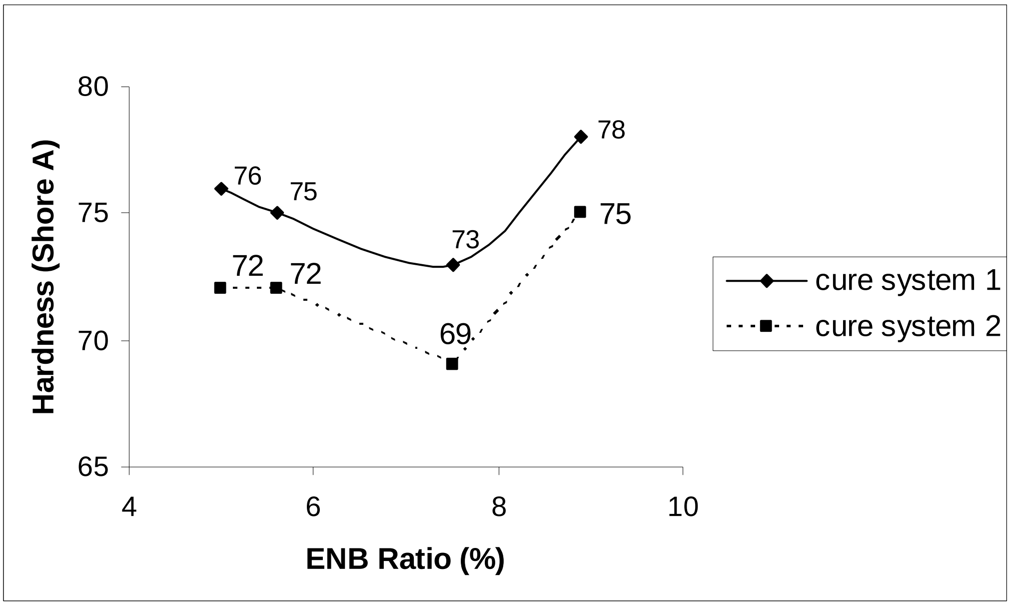


Figure 3.28 Hardness for the compounds with increasing ENB ratio for cure system 1 and cure system 2

For both cure systems, ultimate tensile strength is maximum for the compounds B1 and B2 which contain EPDM with 5.6% ENB. Ultimate elongation and hardness are at minimum for the compounds with 7.5% ENB ratio. The more double bonds are introduced to the system, the strength and hardness are improved and elongation is decreased to some extend. In each case the results for D1 and D2 compounds are worst due to the hindrance by double bonds. After curing agent and coagent are consumed by the double bonds, excess diene remains unreacted and may lead to weakening of properties.

Compression set vs. ENB content graphs for two cure systems are given in Figure 3.29.

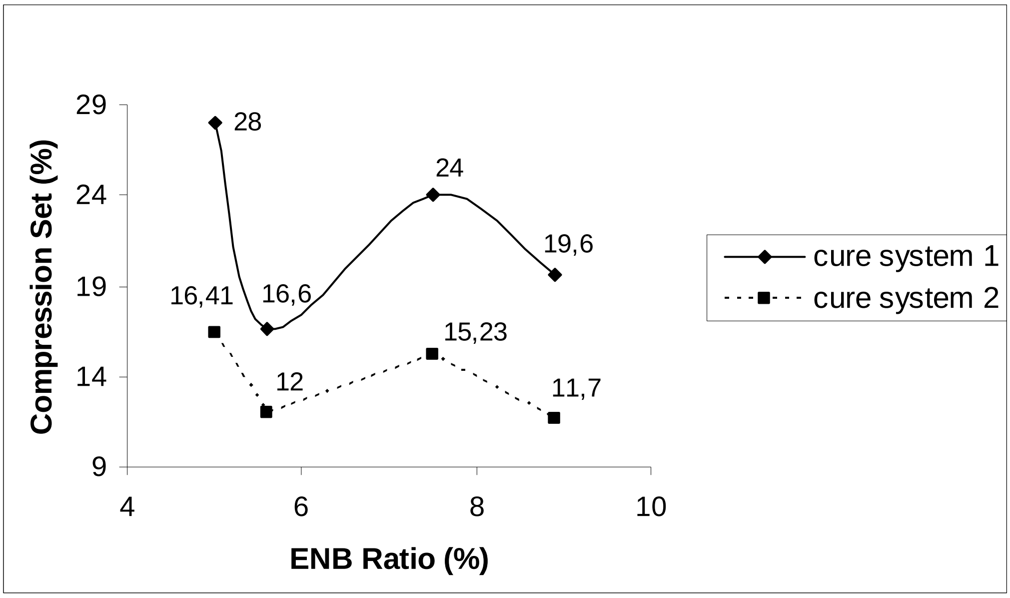


Figure 3.29 Compression set for the compounds with increasing ENB ratio for cure system 1 and cure system 2

Compression set tests are intended to measure the ability of rubber compounds to retain elastic properties after prolonged action of compressive stress[10]. Elastic properties of compounds do not show a regular trend after compressive stress is removed; compression set is not increasing or decreasing with increasing ENB ratio. Different diene ratio may affect the course of reactions in different way and consequently elastic properties of cured rubber may not show a regular trend as in the case of cure time and rate constant.

CHAPTER 4

CONCLUSIONS

From the results of this experimental investigation, the following conclusions can be mentioned:

1. Increasing amount of semi-active filler FEF N 550 in an EPDM compound increases viscosity, rate constant of vulcanization reaction, strength, hardness and deflection under compression.

2. Damping of EPDM compound with 70 phr filler is higher than that of with 105 phr.

3. Increasing amount of filler decreases elongation.

4. Saturated mineral oil in EPDM compound decreases viscosity, strength, deflection under compression, increases elongation, while it does not affect rate constant of vulcanization considerably.

5. Increasing amount of vulcanizing agent in an EPDM compound affects viscosity, strength, rate constant of vulcanization reaction, hardness, elongation, and compression-deflection properties but not in a regular way. In general the properties give a maximum or minimum at 5 phr vulcanizing agent.

6. Relative crosslink density is maximum for the compound with 5 phr peroxide vulcanizing agent.

7. TGA analysis gives no useful data for investigation of properties for peroxide amount change.

8. Although the double bonds are introduced to the system by increasing ENB ratio in EPDM rubber, it does not improve properties of vulcanizate regularly.

9. Relative crosslink density is maximum for the compound with ENB ratio of 5.6%.

10. The results from two cure system showed that cure time, rate constants and compression set change in irregular way with increase in ENB ratio.

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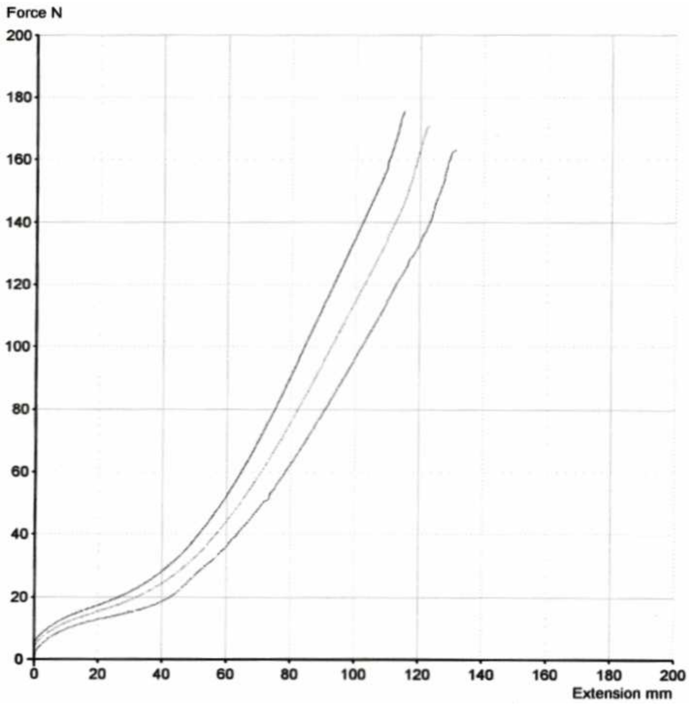
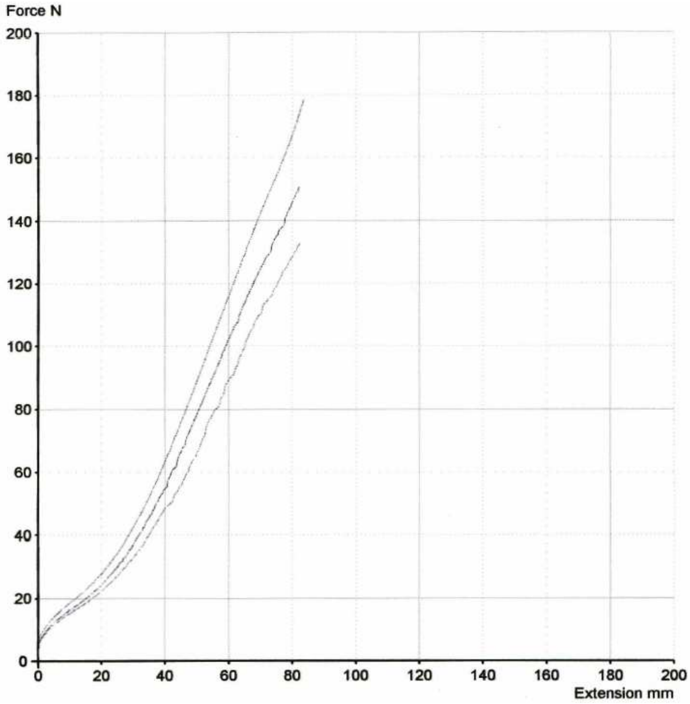
APPENDICES

APPENDIX A

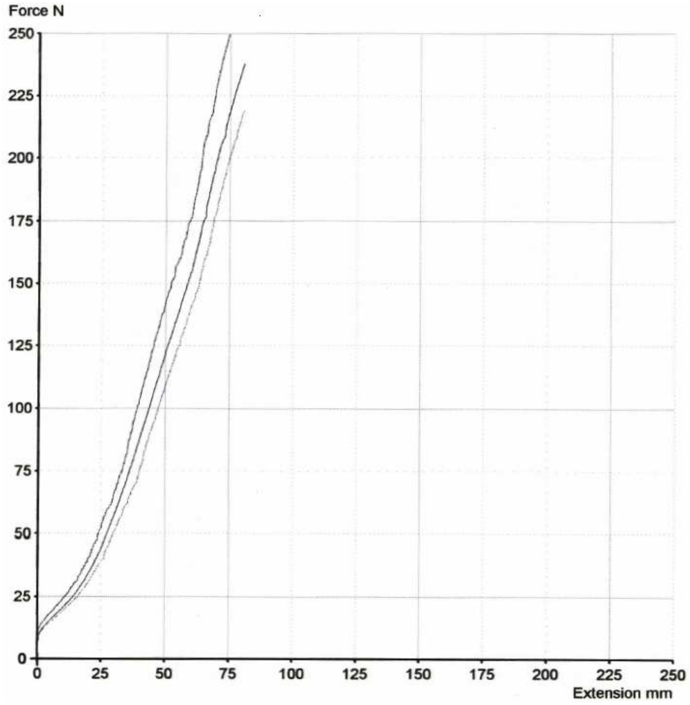
FORCE vs. EXTENSION GRAPHS FOR THE COMPOUNDS EC1, EC2, EC3, AND EC4



(EC1)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
200
Extension mm

(EC2)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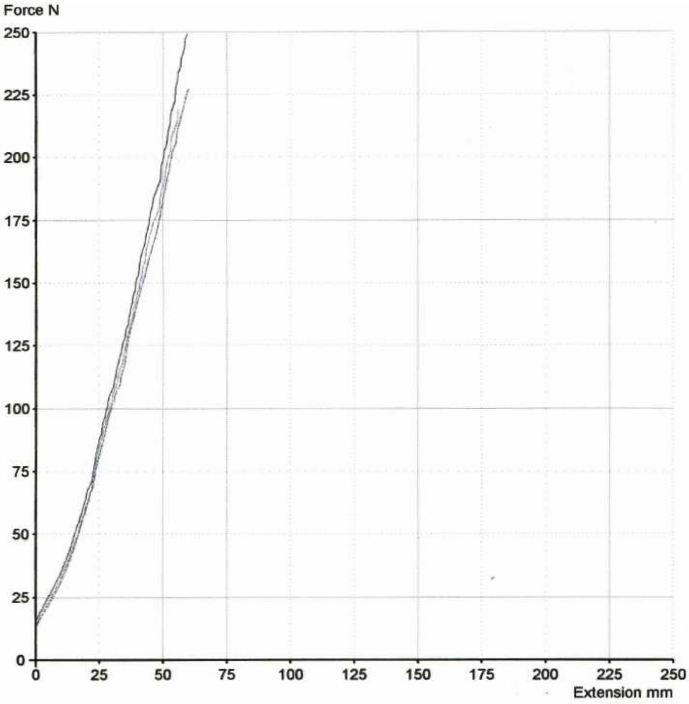
225
200
175
150
125
100
75
50
25
0
0
25
50
75
100
125
150
175
200
225
250
Extension mm

(EC3)


Force N
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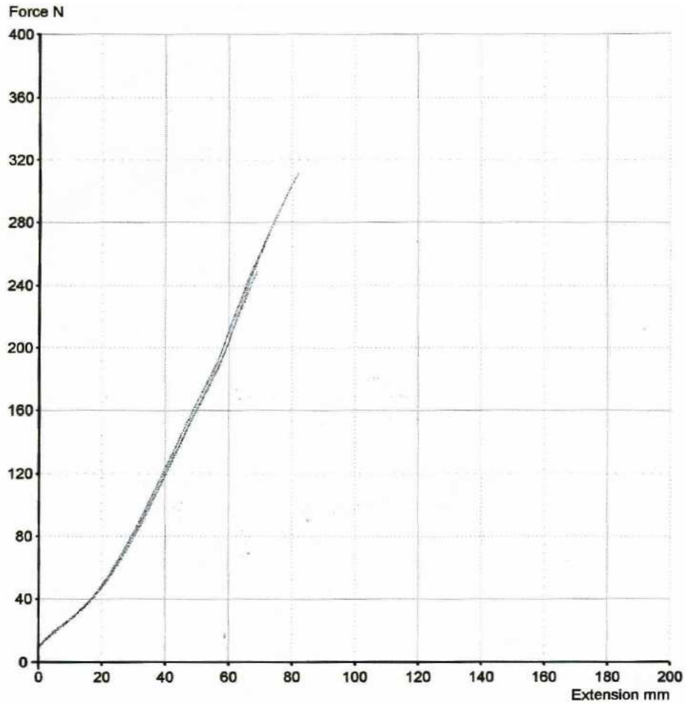
225
200
175
150
125
100
75
50
25
0
0
25
50
75
100
125
150
175
200
225
250
Extension mm

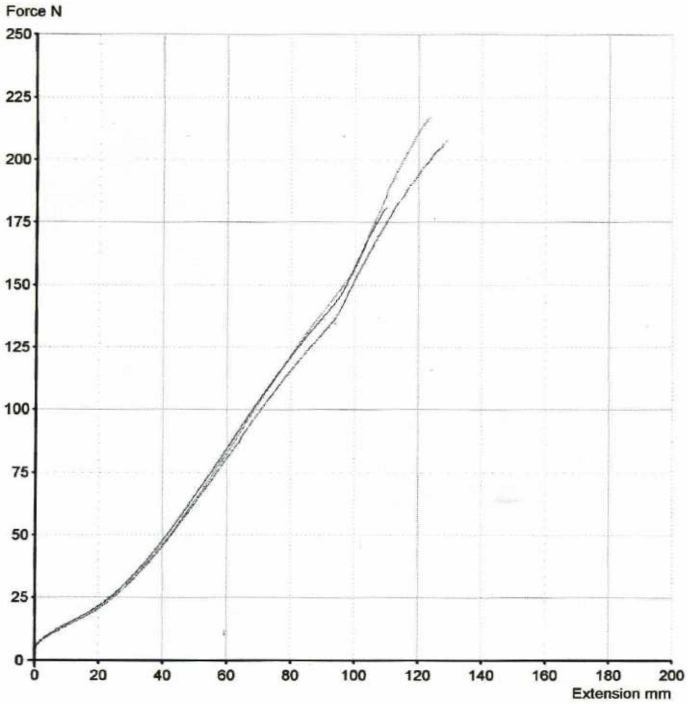
(EC4)

APPENDIX B

FORCE vs. EXTENSION GRAPHS FOR THE COMPOUNDS EY1 AND EY2



(EY1)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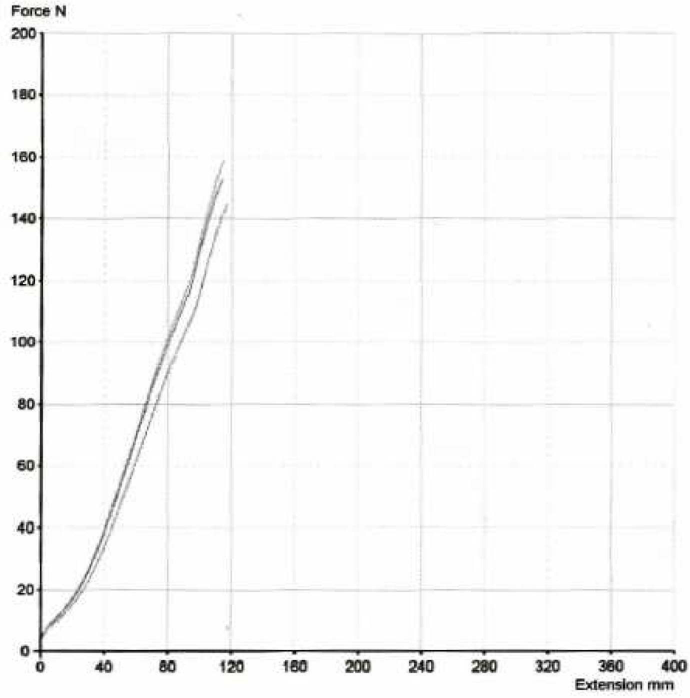
225
200
175
150
125
100
75
50
25
0
0
20
40
60
80
100
120
140
160
180
200
Extension mm

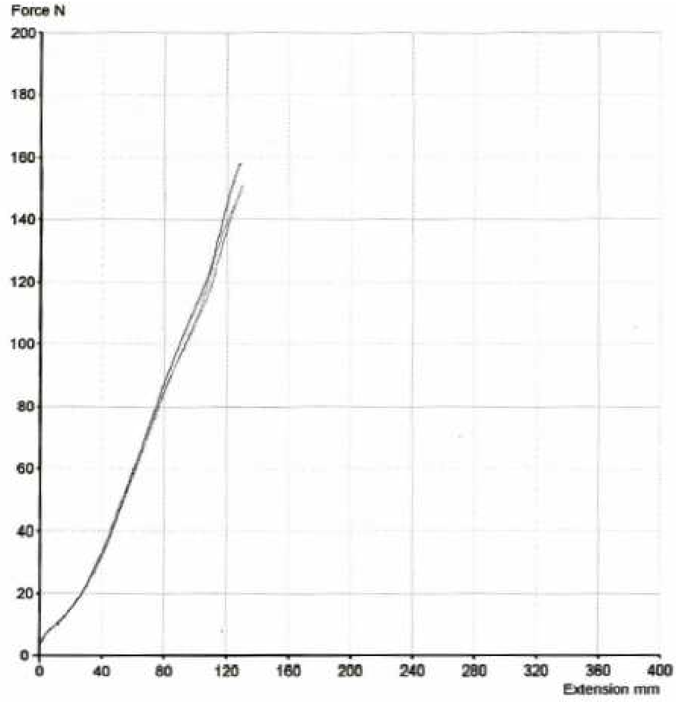
(EY2)

APPENDIX C

FORCE vs. EXTENSION GRAPHS FOR THE COMPOUNDS EV1, EV2, AND EV3



(EV1)


Force N
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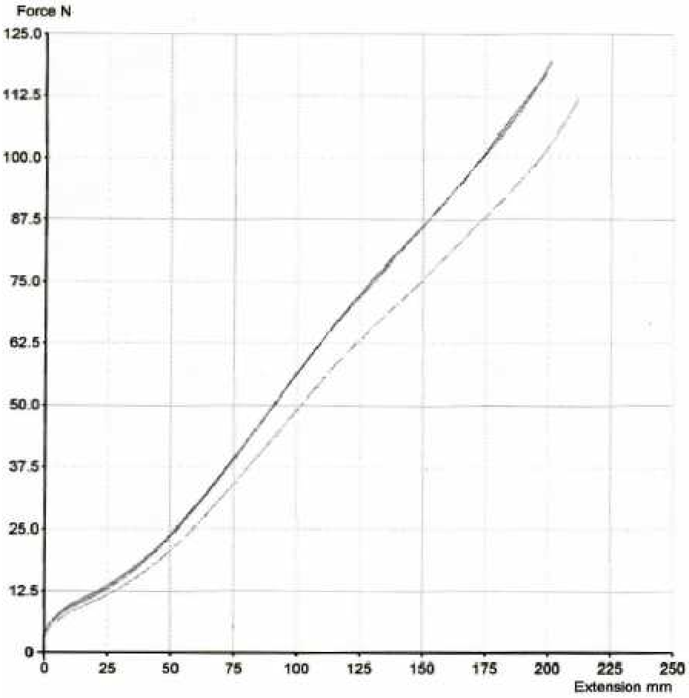
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
280
320
360
400
Extension mm

(EV2)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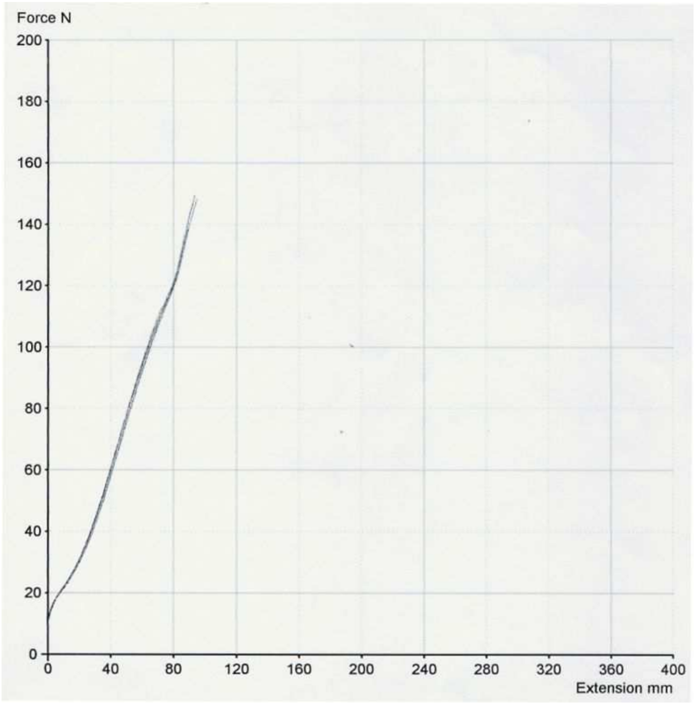
100.0
87.5
75.0
62.5
50.0
37.5
25.0
12.5
0
0
25
50
75
100
125
150
175
200
225
250
Extension mm

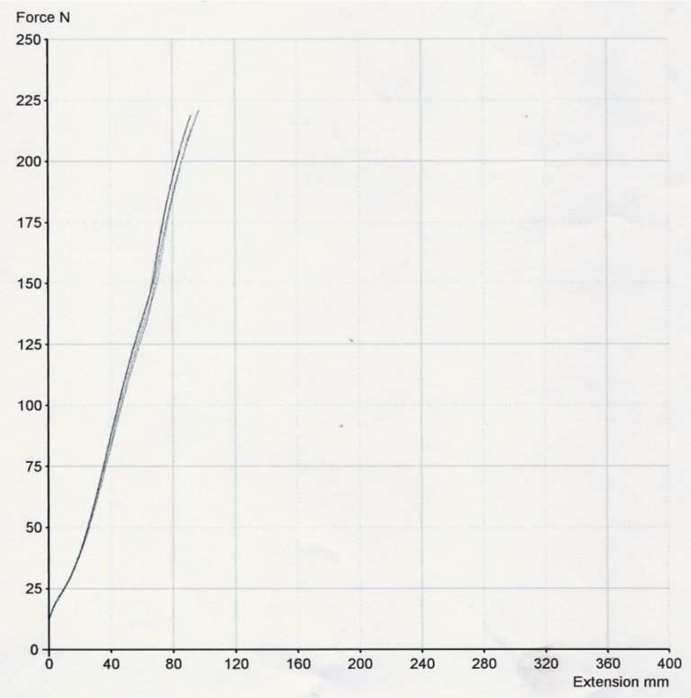
(EV3)

APPENDIX D

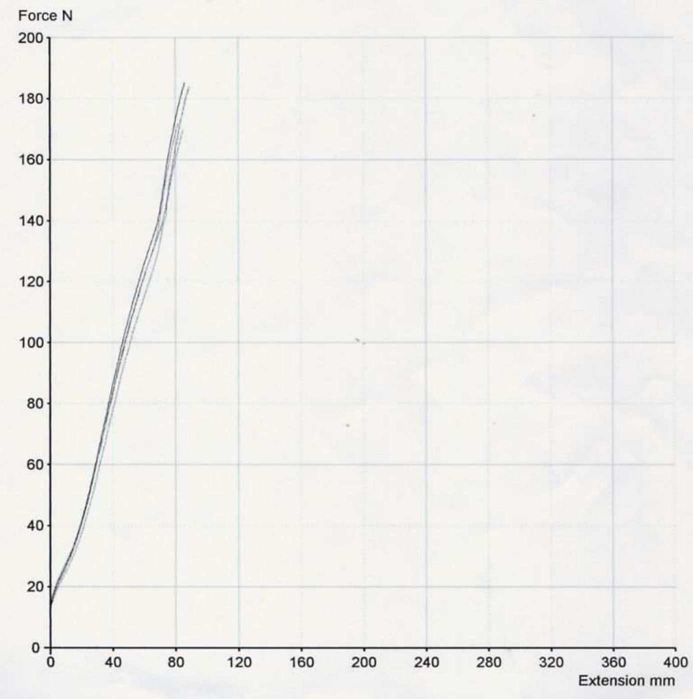
FORCE vs. EXTENSION GRAPHS FOR THE COMPOUNDS A1, A2, B1, B2, C1, C2, D1 AND D2



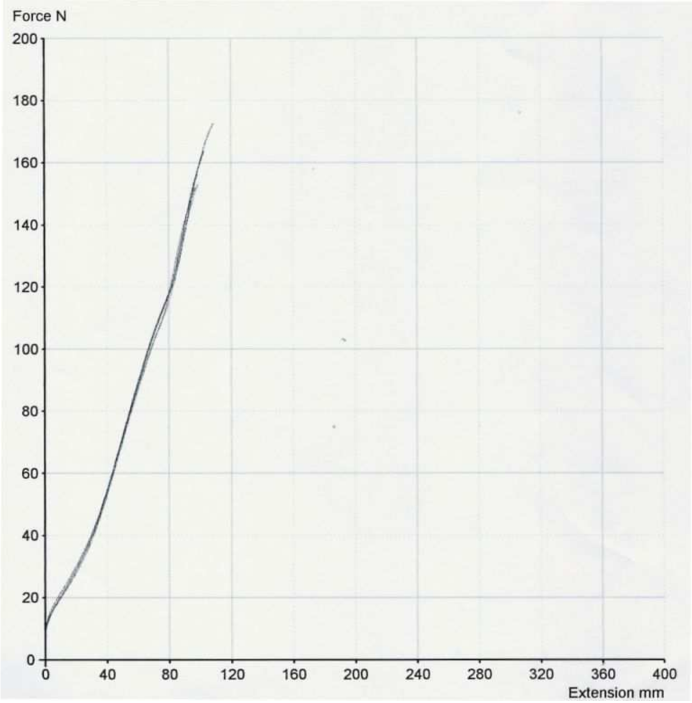
(A1)


Force N
250
225
200
175
150
125
100
75
50
25
0
0
40
80
120
160
200
240
280
320
360
400
Extension mm

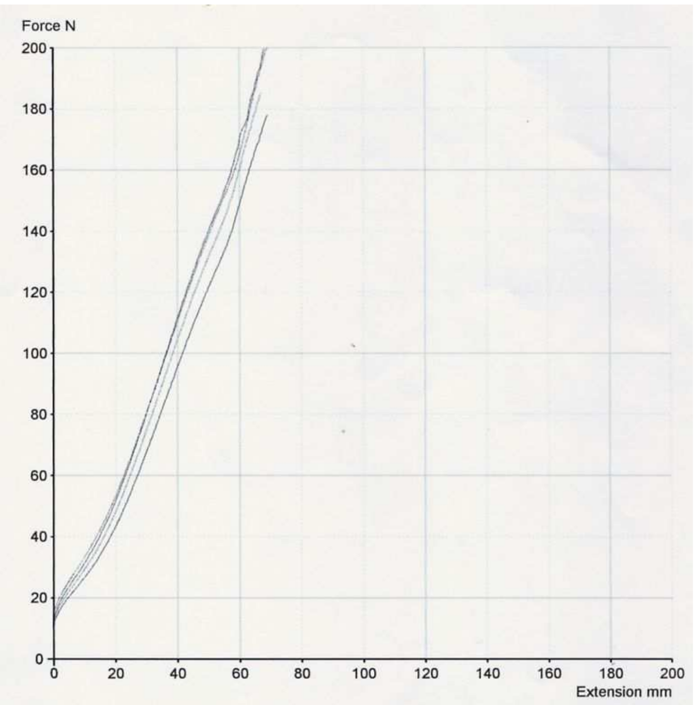
(B1)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
280
320
360
400
Extension mm

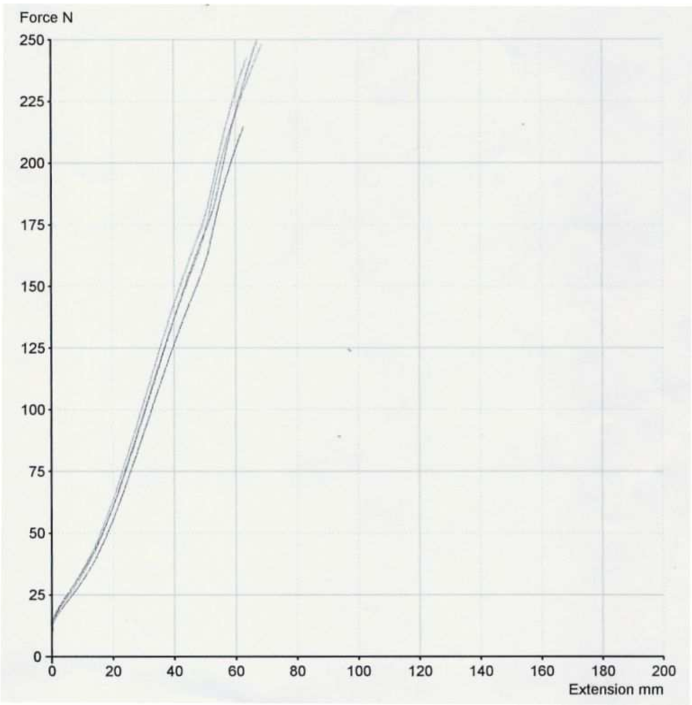
(C1)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
280
320
360
400
Extension mm

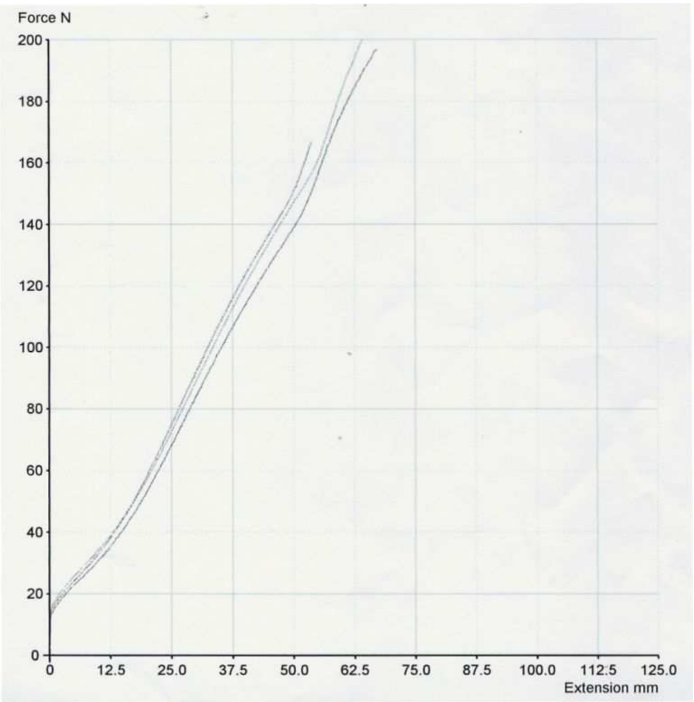
(D1)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
200
Extension mm

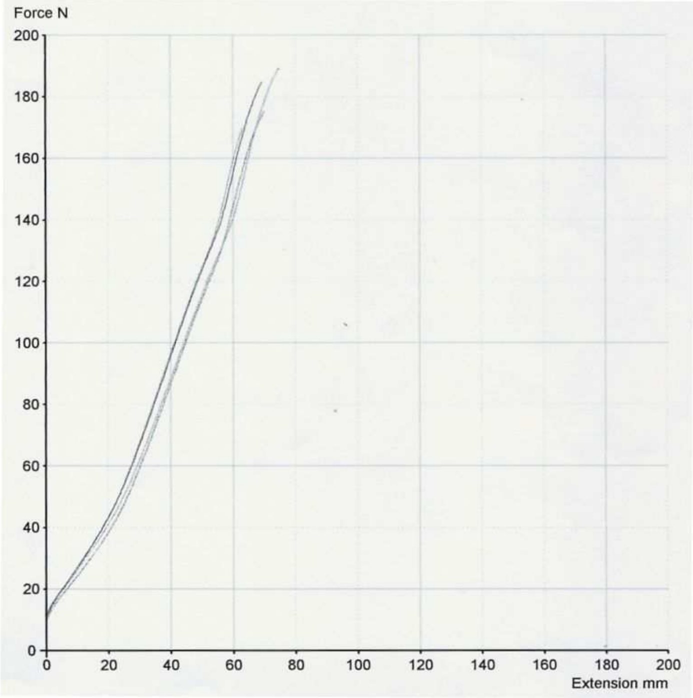
(A2)


Force N
250
225
200
175
150
125
100
75
50
25
0
0
20
40
60
80
100
120
140
160
180
200
Extension mm

(B2)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
12.5
25.0
37.5
50.0
62.5
75.0
87.5
100.0
112.5
125.0
Extension mm

(C2)


Force N
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
200
Extension mm

(D2)