EFFECTS OF FILLERS ON MECHANICAL, PHYSICAL, SWELLING AND THERMAL PROPERTIES OF HYDROGENATED ACRYLONITRILE BUTADIENE RUBBER (HNBR)

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<u>Dedication</u>

At first I dedicate this thesis to Allah, the Almighty, who has created me as a human being and has written a good fate in my favor. Then I would like to dedicate to my parents who make me a grown up person from a child with love and care so that I can be able to do useful work from a stage when I was unable to do any thing by myself, in the childhood.

At the last I would like to dedicate this thesis to my wife, so that without her support, love and care it might be difficult to accomplish this task with convenience.

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Abstract

HNBR in pure form has low mechanical and physical properties and therefore not suitable for some special applications. Moreover under some typical environmental condition in industries and aerospace high thermal stability of rubber components are required. Furthermore HNBR has resistance to oil, fuels and other solvent, therefore it can be used for different o-rings and gasket, but under special requirements, pure HNBR cannot serve the purpose due to their high swelling ratio.

Compression strength is an important parameter, because most of the products are subjected to compressive loads like tires of automobiles, footwear, oil seals, engine mounting and rubber bearings for bridges and brake linings.

In order to overcome these problems and enhance physical, mechanical, thermal and swelling properties for using of rubber components for proper industrial applications, some ingredients are added to the pure HNBR called additives. This process of addition of ingredients/additives is called rubber compounding/mixing. In ingredients mainly filler, cross linker, accelerator and activator are used. In filler carbon black, silica and clay is use for reinforcement, cross linker like sulphur is used for cross linking whereas accelerator and activator are used to shorten the curing time, because curing is a very tedious process and required a lot of time.

In this experimental work rubber compounding is carried out by using two roll-mill machine and eleven recipes have been prepared having different ratio of carbon black and silica loading keeping the remaining ingredients constant. Curing has been carried out by using compression molding machine, testing for physical, mechanical, thermal and swelling properties have been carried out accordingly and finally test results are shown in tabulated form as well as graphical form for analysis.

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LIST Of ABBREVATION

CB	Carbon Black
HNBR	Hydrogenated Acrylonitrile Butadiene Rubber
S	Sulphur
ZnO	Zinc Oxide
SA	Stearic Acid
PBN	Phenyl Naphtylamine
MBTS	Dibenzothiazyle Disulphide
TMTD	Tetramethyl Thiuram Disulphide
DOP	Dioctyl Phthalate
SR	Swelling Ratio
TGA	Thermo gravimetric Analyzer
HSP	Hansen Solubility Parameter

CHAPTER 1

Introduction

1.1   Background

1.1.1 Elastomer

The word elastomer is a combination of two words elastic (ability of a material to retain its dimensions/shape on removing the applied force) and mer (The basic molecular unit that combines in long chains to form polymers). Hence elastomer is defined as "A formation of a thermoplastic or thermoset that can stretch and then return back to its original shape without permanent deformation. In elastomer significant segmental movements is available, therefore a long range reversible elasticity is found in these materials and so it reconfigure after removal of applied stress. The elastomer is often named as rubber.

In rubber the common chemical elements are Hydrogen (H) and carbon (C). Natural rubber polymers are mainly built of these elements; however in synthetic rubber these elements are the products of petrochemical industry. Rubber is mainly divided into two categories:

* Natural Rubber
* Synthetic Rubber

1.1.2   Natural Rubber

In many countries the rubber trees are cultivated for the production of natural rubber. Thailand Malaysia and Indonesia are the biggest producers of rubbers and these countries collectively fulfill the 80% of the world consumption. Plantation in South America and Africa can also be found. In order to take latex from the tree a cut is made through the bark, so that latex drips into the cup as shown in the fig. Finally the contents of the cup is stored into a big container and transported to a rubber factory. To promote coagulation acetic acid is added to the latex.

1.1.3   Limitations of Natural Rubber

The limitation of natural rubber is, its poor resistance to oil, fuels and ozone, and hence swelling of the same degrades its properties.

1.1.4   Synthetic Rubber

Synthetic rubber can be produced by the polymerization of different petroleum-based precursors called monomers. Styrene-butadiene rubber (SBR) a most prevalent synthetic rubber made from copolymerization of styrene and 1, 3-butadiene. Similarly other synthetic rubbers are made from chloroprene (2-chloro-1, 3-butadiene), isoprene (2-methyl-1,3-butadiene), and isobutylene (methyl propene) with a small percentage of isoprene for cross-linking. In order to achieve the desired physical, mechanical and chemical properties these and other monomers are mixed together for copolymerization. The addition of additive can be also carried out in order to achieve the optimal properties; this phenomenon is called rubber compounding.

Synthetic rubber further divided into many sub categories; however our interest is in the HNBR (Hydrogenated Acrylonitrile Butadiene Rubber). After long-term exposure to oil, chemical and heat, HNBR still retain physical strength and other properties. However pure HNBR also has some limitations discussed below.

1.1.5   Limitation of HNBR

Pure HNBR has low physical and mechanical properties, therefore from applications point of view, physical and mechanical properties of HNBR can be enhanced by loading of different fillers. HNBR tensile strength can be increased to the desired value depending on the loading quantity and type of fillers. Similarly hardness, modulus and density etc can be enhanced according to the requirement.

1.1.6 Chemistry of HNBR

$$CH_2=CH-CH=CH_2 \ + \ CH_2=CH-C\equiv N$$

1,3-Butadiene   **Acrylonitrile**

$$\left(CH_2-CH=CH-CH_2\right)_n\left(CH_2-CH\atop \ \ C\equiv N\right)_m$$

Acrylonitrile butadiene rubber

Catalyst $\vert$ H_2

$$\left(CH_2-CH_2-CH_2-CH_2\right)_n\left(CH_2-CH\atop \ \ C\equiv N\right)_m$$

Hydrogenated acrylonitrile butadiene rubber
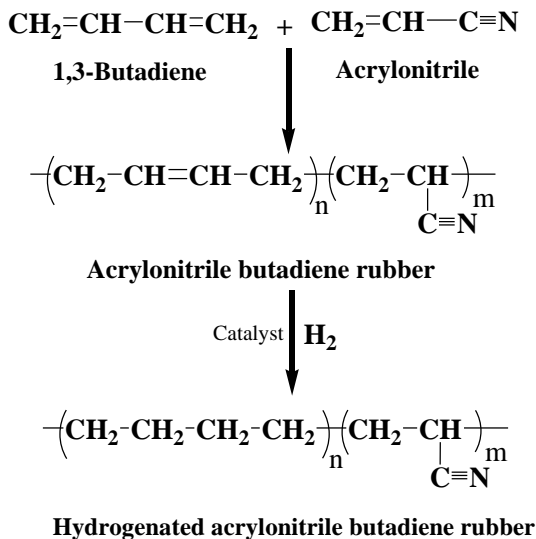
1.1.7 Application of HNBR

Due to the unique nature of HNBR it has been used widely in industrial, automotive and other high demanding applications. The largest consumer is the automotive market, using HNBR for a host of dynamic and static seals, hoses, and belts. In industries HNBR has also been widely employed in sealing for oil field exploration and processing, as well as rolls for steel and paper mills.

1.2 Statement of the problem

HNBR in pure form have low physical and mechanical properties. Due to this limitation pure HNBR cannot be used where high physical and mechanical strength is required. Carbon black and Silica serve as good reinforcing fillers and have a capacity to impart enhance physical and mechanical properties to HNBR.

Moreover HNBR in pure form is not thermally stable, whereas at some special applications high thermally stability is required, which can be achieved by the addition of different fillers.

Additionally in some applications swelling properties are concerned, therefore swelling properties of HNBR can also be changed by using different fillers.

1.3   Definition of Terms

Terms	Definition
Additive	In order to improve/change the properties some substance is added to a rubber/plastic called additive.
Cross-linking	It is the development of primary bonds that form between polymer molecules.
Filler	Filler is an additive which is normally used in rubber for reinforcement.
Monomer	Monomer is a basic unit that combines in long chains to form polymers.
Natural Polymer	It is a polymer which is obtained from raw materials found in nature.
Natural Rubber	It is a natural elastomer which is obtained as a sap from tropical trees.
Plasticizer	Plasticizer is an additive which gives flexibility and softness to rubber/plastic in order to facilitate the manufacturing process.
Polymer	Polymer is a technical term which is used for plastic. It contains large molecules and generally does not have crystalline structure.
Primary Bond	Primary bond is formed between atoms and it involves the transfer/sharing of electrons. .
Secondary bond	Secondary bond is the attraction between molecules. It does not involve the exchange of electrons.
Synthetic Polymer	Synthetic polymer is manufactured chemically from separate materials.
Thermoplastic	It is a type of plastic which is hardened by cooling and softened by heat then hardened by cooling and softened by heating over and over again. Thermoplastics are not cross-linked.
Thermoset	It is a type of plastic which is hardened by cooling permanently. Thermosets are heavily cross-linked.
Vulcanization	It is a manufacturing process in which the number of crosslinked bonds increases due to the addition of chemicals and additives under proper condition of heat and pressure.
coagulation	Coagulation is a process in which a latex change from liquid state to some more viscous or jelly like state.

1.4   Purpose of the study

As discussed in problem statement that HNBR in pure form have low Physical and Mechanical properties and cannot be used where high physical and mechanical properties are required. Therefore compounding of HNBR has been carried out by using different fillers and other additives like vulcanizing agent, activator, accelerator, antioxidant, and plasticizer.

Hence the purpose of this study is the compounding of HNBR having enhanced physical and mechanical properties by using different Carbon Black and Silica loading keeping the remaining additives constant.

Moreover HNBR in pure form is not thermally stable and hence decompose on increasing of the outside temperature. In order to increase the thermal stability different fillers are added to the HNBR. Furthermore swelling behaviors of HNBR can also be changed by changing the loading quantity of different fillers.

1.5   Contributions of the study

This study will give the broad ideas that how the physical, mechanical, swelling and thermal properties of HNBR can be changed by using different filler loading quantities keeping the remaining additives constant. Because for special application improved properties of HNBR are required, which are not fulfilled by unfilled HNBR, therefore some ingredients are added to achieve that properties.

1.6   Organization of the study

The rest of the thesis is organized as follows:

- In chapter no. 1, **Introduction,** brief background of rubber has been discussed.
- In chapter no. 2, **Literature Review**, the related work already done by different peoples has been discussed.
- In chapter no. 3, **Experimental Wor**k, methodology and different characterization have been discussed.
- In chapter no. 4, **Results and Discussion**, analysis of results has been carried out and same are discussed.
- In chapter no. 5, **Conclusions,** conclusive remarks obtained from the experimental work has been discussed and finally references have been noted.

CHAPTER 2

Literature Review

2.1   Introduction

When Goodyear developed the first useful rubber compound: natural rubber + Sulphur , it was the start of rubber industry. The concept of mixing rubber to enhance the properties is still of primary importance. Rubber good without compounding would be of any commercial value. In tire manufacturing the curing is the final step whereby the desired shape of the green rubber is formed in the press. Heat is transferred from the surface to the tire in the curing press, which are maintained at high temperatures, inducing the rubber compounds curing reaction, thereby converting them to a strong elastic material. To achieve an optimal curing state for the rubber goods the vulcanization process is optimized, which ensure the mechanical properties required for each component. A rheometer is used for the prediction of curing state, in which by the torque variation during curing the kinetics is described [1-3]. The role of fillers networking in the elastic properties of elastomer composites have been investigated by different authors [4-7]. Especially at higher loading, filler-filler interactions are primary mechanism in reinforcement. Filler-filler interactions depend on physical interactions, chemical interaction between the filler particle surfaces (filler-filler, filler-rubber) and morphology of the filler volume fraction and filler network. . In different investigations the reinforcement of elastomers by fillers has been studied [8] and it has been accepted that this phenomenon is mainly depend on filler properties, elastomer properties and processing [9-10].

Changing the loading qty of fillers can enhanced the tensile strength and it is important because the elastomers may be subjected to different tension loads.

For rubber application in industry, compression strength is an important parameter, because most of the products are subjected to compressive loads like tires of automobiles, footwear, oil seals, engine mounting and rubber bearings for bridges and brake linings. In order to overcome the applied stress without significant change the rubber vulcanizates must be designed accordingly.

For product performance assessment, hardness measurement is an important parameter and it is used for, identification, classification and quality control of products [11~13].

The mechanical properties of the polymer matrix can be enhanced by the addition of fillers to polymeric materials. The reinforcement effect is directly related to properties of interphase and this effect depends on the nature of the specific interactions between the reinforcing fillers and polymer [14]. The filler incorporation into elastomers imparts many useful and interesting properties. It has been investigated that these properties depends on the filler particles dispersion condition as well as the on filler particles principle properties like particle size , aggregate structure , surface area, surface activity and on the rubber-filler interactions [15]. Vulcanization behavior of filled compounds depends on the surface chemistry of carbon black. If the filler is well dispersed in the rubber matrix optimal reinforcement power can be achieved. In reinforcing effect the physical and chemical interaction between the rubber-filler is another important factor [16]. The filler-polymer interaction is mainly of physical nature in the case of carbon black [17].

Due to the excellent resistance of HNBR to oil, grease and fuel etc, it is generally used for o-rings and gasket. HNBR/NBR grade depends on the acrylonitrile content.Crosslinked density of cured rubber can be measured by using swelling phenomena, because crosslinked rubber are swellon with a good solvent [18~21]. Crosslinked rubber swelling behavior is a diffusion process. The degree of compatibility between rubber and solvent is a main factor for the amount of solvent to diffuse into rubber until it reaches equilibrium. If a hydrophilic water absorbent resin is available in rubber composite it can swell water [22~25].Silica and Carbon Black are the important reinforcing fillers used in rubber compounds [26-30].

The dependency of physical, mechanical, thermal and electrical properties of filler loaded rubber compounds on the filler size, type of filler and type of host rubber attracts the interest of investigators [31-40].

To produce new composites suitable for typical technological application the choice of filler-rubber combination is an important factor [41–45].

The aim of this research work is to determine the effect of Carbon Black as well as Silica filler on physical, mechanical swelling and thermal properties of HNBR.

2.2   <u>Rubber Compounding</u>

Elastomers have low elasticity as well as strength with high molecular weight; therefore it can easily flow when any stress is applied. Due to lack of mechanical strength the polymeric matrix in its original form is not much usable. In order to improve the mechanical and physical properties, some ingredients called additives are added to the polymeric matrix. This process of addition of additives is called rubber compounding. Table 2.1 gives the detail of some additives.

Table 2.1 list of some important additives used in this research work.

Class	Function	Examples
Vulcanizing agents/ Curatives	forms chemical crosslinks between rubber chains	sulphur, metal oxides, peroxides, amines, phenolic resins, irradiations
Accelerators	controls the onset, rate and extent of crosslinking	amines, sulfenamides, xanthates, thioureas, thiurams
Activators	improve the efficiency of accelerators	zinc oxide, stearic acid, litharge, amines
Fillers	improve the physical and mechanical properties of the rubber compounds	carbon black, silica, aluminium silicate, clays
Antidegradants	retards the ageing process by ozone and oxygen present in air	alkylated bis-phenols, phenylenediamine derivatives
Plasticizer	Impart softness and flexibility to a plastic in order to facilitate the manufacturing process.	

2.3   Vulcanization / Cross linking

The conversion of elastomer to a plastomer is called vulcanization or cross linking. In this phenomenon covalent, hydrogen or other bonds are established. This technique is used for formation of crosslinks which ultimately change the polymeric properties. In the rubbery material cross linking can be achieved by any of the following methods:

- sulphur sources
- peroxides
- metal oxides
- amines
- phenolic resins
- γ-radiations

In sulphur cross linking , sulphur can be used in different forms in polymer , however curing process is very slow therefore some accelerators and activators are used to shorten the the curing time and reduce the unwanted reactions.

2.4   Additives

As already discussed that additive is a substance that added to the rubber to improve its properties. Following are some additives which are normally added during rubber compounding.

2.4.1   Fillers

A filler is an additive use for a polymer composition. It is usually use in large amount and normally use for reinforcement in rubbers. It modifies the physical and mechanical properties of HNBR.

The choice of filler is most important and its selection depends upon the intended use of rubber composite. The filler is not only use for reinforcement but some time it may be used as an extender. In reinforcement filler carbon black use as black filler whereas Silica and clay are non black filler. In extender calcium carbonate, talc etc are used.

For industrial purpose normally carbon black is the choice of filler. For white and colored compound normally silica and clay are the choice of fillers. Reinforcement in the elastomer means the increase in tensile strength, hardness and tear resistance.

Filler may have high surface area, low particle size but still it will offer low reinforcement if it has low specific surface activity. The polar filler has good surface activity with polar elastomer whereas non polar filler has good surface activity with non polar elastomer. This is a chemical compatibility between the filler and elastomer. Furthermore the filler having high surface area have more contact area available and therefore having the higher capability of reinforcement.

Filler particle shape is also one of the important factor in reinforcement. Planner shape particles have more surfaces available for contact than spherical particles with an average particle diameter, e.g. clay having planer shape gives more reinforcement than spherical shape of calcium carbonate having similar average particle size.

After mixing the fillers in the elastomer many properties are enhanced, e.g. tensile strength, hardness, density etc.

2.4.1.1 Carbon Black as reinforcing filler

Carbon black is produced by the incomplete combustion of coal tar, wood etc. Carbon black has high surface area to volume ratio. Carbon black is mainly used as reinforcing filler in rubber industries. In plastic, inks, paints etc carbon black is used as a color pigment.

2.4.1.2 Silica as reinforcing filler

There is no doubt that carbon black is a good reinforcing filler, but there are some problems with this filler one of which is that it render the whole article black , moreover sometime it is also required to produce color components, therefore non black like silica is used. Therefore the trend for using the white filler in industries is due to production of color products.

2.4.2 Accelerators

An accelerator is an additive to accelerate the cross linking/curing process. Addition of accelerator in the recipe not only increases the rate of curing but it also gives some other beneficial effects like decrease of unwanted reactions leading to cyclization reactions and polysulphide linkage. Another most important effect of accelerator is to shorten the curing processes which ultimately reduce the energy consumption and making the process cost-effective.

2.4.3 <u>Activators</u>

Activator is an additive to increase the vulcanization of rubber by activating the accelerator. Mostly two activator components are used in vulcanization systems. A metal oxide (usually zinc oxide) and a fatty acid (usually stearic acid) are normally used. These activators forming zinc stearate which forms rubber soluble complexes with the accelerator.

2.4.4 <u>Antioxidant</u>

An antioxidant is a molecule which reduces the oxidation of HNBR and hence increases the life of rubber composite. Antioxidant decreases the ratio of double bond available in HNBR, which as a result the free oxygen from atmosphere does not affect the rubber composite.

2.4.5 <u>Plasticizer</u>

Plasticizer is an additive which imparts the softness and flexibility to the rubber composites in order to ease the manufacturing process.

CHAPTER 3

Experimental work

3.1 Introduction

In this chapter the experimental work has been discussed in detail. In experimental work first of all the material has been arranged, then compounding and curing has been carried out and finally testing for different properties have been performed and results obtained presented in tabulated form.

3.2 Process Flow of the experimental work

The process flow of experimental work has been shown in fig 3.1.

3.3 Materials/Ingredients

The several HNBR samples were prepared with different loading of Carbon Black (particle size-mean value: 7.2 µm) and Silica (SiO_2) (particle size-mean value: 46.78 µm).Zinc Oxide (ZnO) and Stearic Acid (SA) were used as vulcanization activators. Sulphur (S) was used as cross linker/vulcanizing agent. Antioxidant was Phenyl Naphtylamine (PBN). Curing accelerators were Dibenzothiazyle Disulphide/ Dibenzothiazyle (MBTS/MBT) & Tetramethyl Thiuram Disulphide (TMTD). The Plasticizer/Softner was Dioctyl Phthalate (DOP). Further details of materials are given in table 3.1 & 3.2.

Table 3.1- Detail of ingredients for rubber compounds with Carbon Black loading.

Ser No.	Name	A/U	C-0	C-1	C-2	C-3	C-4	C-5
1	HNBR		100	100	100	100	100	100
2	S		1.5	1.5	1.5	1.5	1.5	1.5
3	ZnO		5	5	5	5	5	5
4	SA		1	1	1	1	1	1
5	CB	*Phr	0	8.3	16.7	33.3	50	66.7
6	PBN		1	1	1	1	1	1
7	MBTS		1	1	1	1	1	1
8	TMTD		0.5	0.5	0.5	0.5	0.5	0.5
9	DOP		2.5	2.5	2.5	2.5	2.5	2.5
* Phr = Parts per hundred rubber.								

Table3.2- Detail of ingredients for rubber compounds with Silica loading.

Ser No.	Name	A/U	Si-0	Si-1	Si-2	Si-3	Si-4	Si-5
1	HNBR		100	100	100	100	100	100
2	S		1.5	1.5	1.5	1.5	1.5	1.5
3	ZnO		5	5	5	5	5	5
4	SA		1	1	1	1	1	1
5	SiO_2	*Phr	0	8.3	16.7	33.3	50	66.7
6	PBN		1	0	0	0	0	0
7	MBT		1	1	1	1	1	1
8	TMTD		0.5	0.5	0.5	0.5	0.5	0.5
9	DOP		2.5	2.5	2.5	2.5	2.5	2.5
* Phr = Parts per hundred rubber.								

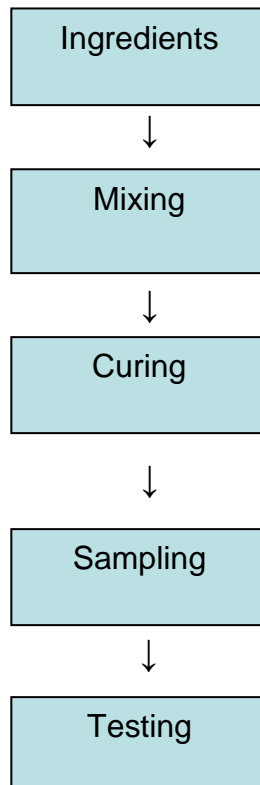Ingredients

↓

Mixing

↓

Curing

↓

Sampling

↓

Testing

Fig 3.1   Process Flow of the experimental work.

3.4 Mixing/Compounding

The rubber compounds were prepared by mixing all ingredients in a two-roll mixing mill. First of all the HNBR was masticated and then other ingredients were added one after the other as summarized in table 3.1 and 3.2.

3.5 Curing

The vulcanized HNBR was prepared by curing at temperature (165 ^{0}C) and pressure (10 MPa) for 40 minutes in a compression molding machine. And finally sheets of thickness 2 mm and 6mm were prepared.

3.6 Sampling and Testing

After curing and preparation of rubber sheets, sampling and testing has been carried out. In this experimental work testing of mechanical, physical, swelling and thermal properties has been carried out.

3.6.1 Measurement of Mechanical & Physical properties

Following physical and mechanical properties of rubber composite have been measured.

3.6.1.1 Tensile Strength

Tensile strength is the maximum stress applied for the stretching of the sample until failure of the sample occurs. Tensile test is the most important characterization parameter used in rubber industries.   The tensile-elongation curve is quantitatively described as

$$\sigma \quad = \quad E_0/3 \, (\lambda - \lambda^{-2}) \, \ldots\ldots\ldots\ldots. \, (1)$$

Where σ is the stress (tensile) value, Eo is the young's modulus and λ is the extension ratio.

For the tensile strength a dumbbell shape sample as shown in fig 3.2 has been cut from the sheet of thickness 2mm. Tensile strength, elongation at break, modulus were measured on an electric tensile testing machine (Ingstron 4465), the speed of machine was kept 100mm/minute. Moreover the density of the samples also measured.

Fig 3.2 Tensile test sample

3.6.1.2 Elongation at break

Elongation is ratio of the change in length to the original length. Elongation is measured along with tensile strength simultaneously. It is measured in % (% of elongation vs. initial size when break occurs).

3.6.1.3 Modulus

Modulus is the slope of stress-strain curve in the elastic deformation region. It is also measured alongwith tensile strength simultaneously. The modulus unit is MPa. All type of moduli i.e. young, bulk and shear describe the stiffness of the material.

3.6.1.4 Hardness

Hardness is the measurement of resistance to the indentation of a material under defined condition. For hardness 6 mm sheet is used. It is to be noted that penetration depth depends on the type of loading, penetrating body and young's modulus. For measurement of this property different methods are available which mainly depends upon the strength of the material. Shore A has the universal appreciation for measurement of rubber hardness.

3.6.1.5 Density

Density of a material is a mass per unit volume. It is measured in kg/m^3 or g/cm^3. For measurement of density normally 2mm thickness sheet is used.

3.6.1.6 Compression set

For compression set a sample in circular disc form as shown in fig 3.3 has been used. The initial thickness of the sample "h_1" is measured. To get 25% compression set, particular spacer is used between the compression plates. Then the sample is compressed in compression plates for 24 hrs at 70 ^{0}C and after completing the desired time and temperature then again thickness "h_2" is measured. Finally the following formula is used to find the compression set. Where h_3 is the spacer thickness.

$$\text{Compression Set (\%)} = [(h_1-h_2)/(h_1-h_3)] \times 100 .... (2)$$

Fig 3.3 Compression set samples

Table- 3.3 Different parameters measured values.

Ser#	Parameters	Blank sample C-0/Si-0	Carbon black filled					Silica filled				
			C-1	C-2	C-3	C-4	C-5	Si-1	Si-2	Si-3	Si-4	Si-5
1	Tensile Strength (MPa)	1.65	3.19	6.88	12.36	21.99	23.44	2.13	4.57	17.86	27.54	24.01
2	Elongation at break (%)	374	427	598	514	617	434	441	788	1502	1418	1174
3	Modulus (MPa)	1.07	1.67	2.11	3.81	5.89	10.60	1.45	1. 91	3.41	11.26	26.66
4	Density(g/cm^3)	1.034	1.066	1.095	1.146	1.194	1.232	1.065	1.107	1.156	1.207	1.258
5	Hardness (at 20 ^{0}C)	51	55	60	69	76	83	55	60	70	85	87
6	Compression Set (%)	8	10	9	9	9	10	14	17	27	43	52

3.6.2 <u>Measurement of Swelling Properties</u>

The swelling behavior of blank (without filler) and filled HNBR was studied using small rectangular disks (of dimension 1 cm x 1 cm). Initial weight "W_u" was noted for each sample before dipping into three solvents (toluene, ethanol and water). Then samples were dipped into solvents and swelled weight "W_s" was noted at different intervals. It is pertinent to mention that all measurements were done at room temperature following the ASTM D471 method using a sensitive balance with an accuracy of 0.0001 gm. Moreover the elastomer was immediately placed back in the solvent and the time was recorded for each set of measurements. Finally the Swelling Ratio (SR) was calculated by using the equation (3).

$$SR (\%) = 100 \text{ x } [(W_s\text{-}W_u)/W_u] \text{ ……………. (3)}$$

Table 3.4- Swelling Ratio in ethanol for different carbon black loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
C-0	3.314917	6.077348	7.479813	13.59966	13.81215	13.08967	11.38972
C-1	3.924491	5.762543	6.110283	12.3696	13.06508	11.87283	9.985097
C-2	3.162651	4.932229	5.986446	11.63404	13.10241	12.23645	9.713855
C-3	3.216123	4.202401	5.060034	9.691252	9.862779	9.862779	7.975986
C-4	3.290043	3.549784	4.718615	8.484848	8.831169	8.831169	7.012987
C-5	2.632583	3.586417	4.654712	7.668829	9.347577	9.385731	7.783289

Table 3.5- Swelling Ratio in toluene for different carbon black loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
C-0	136.3353	170.1739	178.7784	181.6763	180.0267	178.9568	181.2305
C-1	122.601	148.569	153.7879	156.8182	155.0084	155.0084	156.3973
C-2	108.9299	132.525	142.1093	146.2664	142.6482	142.2248	142.0708
C-3	89.06314	109.3686	115.2291	116.4259	117.7466	114.6925	115.3116
C-4	76.52968	92.19178	98.3105	96.84932	98.03653	96.0274	95.93607
C-5	59.2233	75.6922	81.30169	84.28623	83.60302	81.19382	80.87019

Table 3.6- Swelling Ratio in Water for different carbon black loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
C-0	0.18412	0.460299	0.782509	1.173763	2.094361	1.703107	1.910242
C-1	0.23107	0.515464	0.959829	0.675435	0.995379	1.333096	1.38642
C-2	0.083668	0.217537	0.41834	0.819946	1.204819	1.271754	1.589692
C-3	0.101816	0.23757	0.390294	0.916341	1.289666	1.136942	1.153911
C-4	0.350183	0.639464	0.761267	0.974421	1.278928	1.431181	1.035323
C-5	0.064516	0.306452	0.435484	1.967742	1.096774	1.322581	1.322581

Table 3.7- Swelling Ratio in ethanol for different silica loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
Si-0	3.314917	6.077348	7.479813	13.59966	13.81215	13.08967	11.38972
Si-1	2.269983	4.443371	6.302825	11.37406	13.81309	13.30596	11.92949
Si-2	2.753165	5.253165	7.310127	12.53165	13.29114	12.37342	11.13924
Si-3	2.004773	4.176611	5.656325	10.47733	10.47733	9.427208	9.594272
Si-4	2.03547	3.587263	4.877066	8.847239	9.774285	9.532447	10.39903
Si-5	2.154882	3.569024	4.938272	9.337823	10.99888	10.41526	9.943883

Table 3.8- Swelling Ratio in toluene for different silica loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
Si-0	136.3353	170.1739	178.7784	181.6763	180.0276	178.9568	181.2305
Si-1	62.92135	115.222	143.2049	180.9256	177.9294	179.3472	181.2199
Si-2	77.64178	128.519	161.4443	180.049	174.949	176.377	178.1722
Si-3	63.06533	112.7024	140.2848	162.3674	156.8677	159.129	158.6544
Si-4	40.41137	97.27768	123.0188	137.4168	136.6001	136.2371	134.755
Si-5	41.59686	75.54974	99.08377	120.6545	121.5969	120.5497	119.6859

Table 3.9- Swelling Ratio in water for different silica loading.

	1 hr	3 hrs	5 hrs	24 hrs	72 hrs	144 hrs	216 hrs
Si-0	0.18412	0.460299	0.782509	1.173763	2.094361	1.703107	1.910242
Si-1	0.218273	0.311818	0.576863	0.857499	1.294044	1.590271	1.824135
Si-2	0.387522	0.426274	0.736291	1.24007	2.286379	2.6739	3.545824
Si-3	0.300992	0.655099	1.097734	1.257082	2.478754	2.99221	4.320113
Si-4	0.459731	0.834327	1.498382	1.941086	4.086498	5.755151	7.628129
Si-5	0.568736	0.861228	1.251219	2.031199	4.062398	5.703607	7.848554

3.6.3 Measurement of Thermal properties

In rubber industry one of the prime objectives is to increase thermal properties of the rubbers pats according to the environmental requirements.

For thermal properties we normally use Thermo Gravimetric Analysis (TGA). In this method change in physical and chemical properties of materials are measured as a function of temperature. Physical properties include vaporization, absorption, adsorption and sublimation etc, whereas chemical properties include dehydration, oxidation, reduction decomposition etc. TGA is a useful technique for the characterization of polymeric materials like elastomers, thermoplastics, thermosets, composites, fibers and paints etc. TGA accuracy depends upon the precision of three parameters i.e. mass loss, temperature and temperature change. Therefore the basic requirements of TGA are precise balance with a pan for a sample and programmable furnace.

Table 3.10 Thermo gravimetric Analysis data.

Ser#	Sample Name	Wt. loss	Temp (C^0)/ Residue (%)	Remarks
1	C-0	10%	$367C^0$	
		50%	$439\ C^0$	
		Residue (at 550 C^0)	10.18%	
2	C-1	10%	$374.05\ C^0$	
		50%	$442.55\ C^0$	
		Residue (at 550 C^0)	15.77%	
3	C-2	10%	$381.04\ C^0$	
		50%	$442.28\ C^0$	
		Residue (at 550 C^0)	20.15%	
4	C-3	10%	$388.97\ C^0$	
		50%	$456.43\ C^0$	
		Residue (at 550 C^0)	34.09%	
5	C-4	10%	$399.32\ C^0$	
		50%	$458.04\ C^0$	
		Residue (at 550 C^0)	38.16%	
6	C-5	10%	$411.75\ C^0$	
		50%	$475.77\ C^0$	
		Residue (at 550 C^0)	46.08%	
7	Si-1	10%	$375.32\ C^0$	
		50%	$440.18\ C^0$	
		Residue (at 550 C^0)	15.01%	
8	Si-2	10%	$381.01\ C^0$	
		50%	$444.06\ C^0$	
		Residue (at 550 C^0)	22.71%	
9	Si-3	10%	$386.71\ C^0$	
		50%	$451.85\ C^0$	
		Residue (at 550 C^0)	28.53%	
10	Si-4	10%	$392.24\ C^0$	
		50%	$456.38\ C^0$	
		Residue (at 550 C^0)	35.94%	
11	Si-5	10%	$397.36\ C^0$	
		50%	$459.23\ C^0$	
		Residue (at 550 C^0)	42.12%	

CHAPTER 4

Results and Discussion

4.1   Introduction

In previous chapter different properties have been measured for different Carbon Black/Silica loading and results of same are shown in tabulated form. In this chapter same results are drawn in graphical form for further analysis and discussion.

4.2   Discussion on physical and mechanical properties

As testing for mechanical and physical properties like tensile strength, elongation at break, modulus, hardness, density and compression set have been carried out for different carbon black and silica loading. However to carry out further analysis and drawn some conclusions same are drawn in graphical form in this chapter.

4.2.1 Tensile strength

Tensile strength is defined as "the maximum stress that a material can withstand while being pulled or stretched before breaking or failing". For characterization of material this test is mostly used. For tensile strength mostly dumb-bell shape sample is held between the jaws of tensile strength machine and is stretched uni-axially until it fail or breaks. This test is not only use to measure tensile strength, but it also use to provide the value of elongation at break and modulus etc. From fig 4.1 it is clear that tensile strength increases with the increase of both fillers loading until it reaches some maximum/optimal value and then decreases. This decrease in value is due to the brittleness of the rubber compound with further loading after some optimal value of tensile strength. From fig 4.1 it is also clear that Silica filler gives more tensile strength to rubber compound than Carbon Black filler.
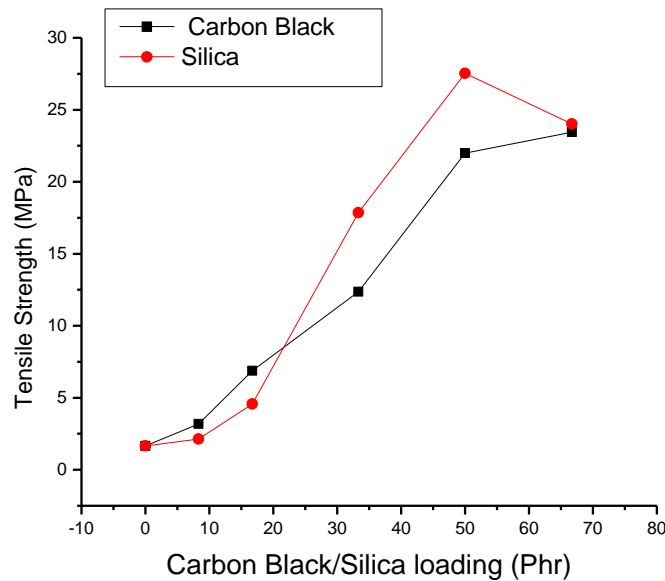
Fig 4.1   Tensile Strength versus different Carbon Black and Silica loading.

4.2.2 Elongation at break

It is the ratio between increased length and initial length after breakage of the tested specimen. Elongation is the property of material to resists changes in its shape without cracking. It is measured in % (% of elongation vs. initial size when break occurs).

From fig 4.2 it is clear that elongation at break increases with the increase of both fillers loading until it reaches some maximum/optimal value and then decreases. This decrease in value is due to the brittleness of the rubber compound. From fig 4.2 it is also clear that Silica filler gives higher value of elongation to rubber compound than Carbon Black filler.
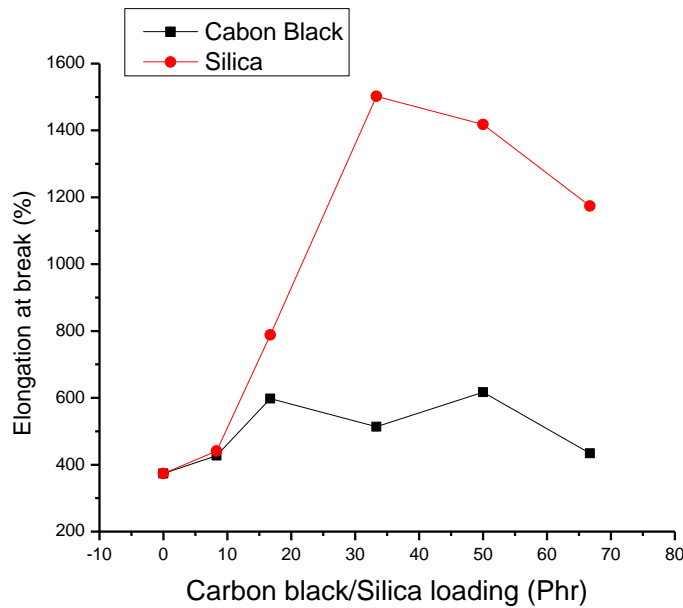
Fig 4.2   Elongation at break versus different Carbon Black and Silica loading.

4.2.3 Modulus

Modulus is defined as "the slope of its stress–strain curve in the elastic deformation region. Higher the modulus stiffer will be the material. As modulus is the ratio of stress and strain, therefore it is measured in MPa..

From fig 4.3 it is clear that modulus increases with the increase of both fillers loading. From fig 4.3 it is also clear that Silica filler gives higher value of modulus to rubber compound than Carbon Black filler.
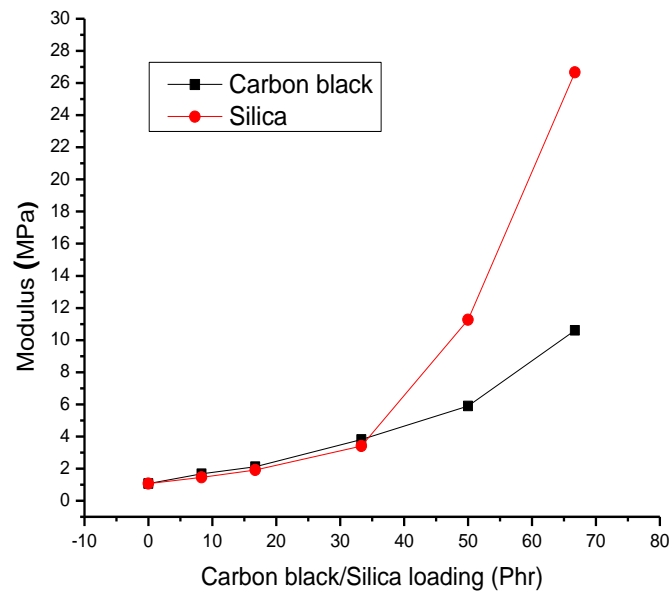
Fig 4.3   Modulus versus different Carbon Black and Silica loading.

4.2.4   **Hardness**

Hardness is defined as "the measurement of resistance to the indentation of a material under defined condition". For rubber normally shore hardness is used. Different methods are available for measuring of this property.

From fig 4.4 it is clear that hardness increases with the increase of both fillers loading.
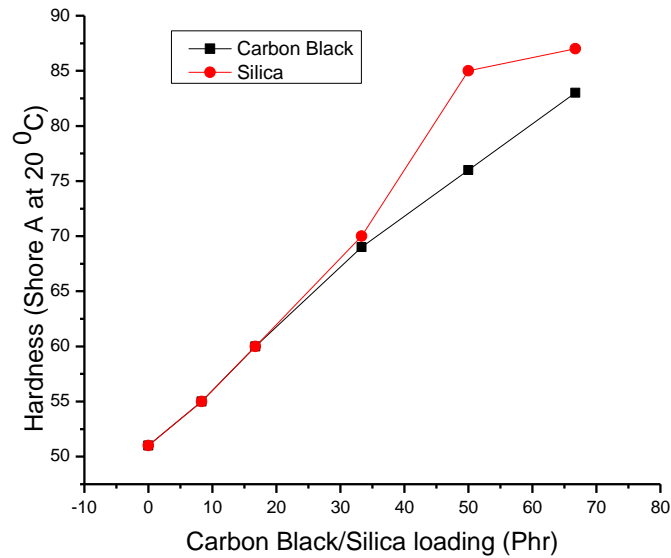
Fig 4.4   Hardness versus different Carbon Black and Silica loading.

4.2.5 Density

Density is defined as "Mass per unit volume". Density unit is normally kg/m^3 or g/cm^3. From fig 4.5 it is clear that density increases with the increase of both fillers loading, because when the loading quantity increases mass per unit volume increases. From fig 4.5 it is also clear that Carbon Black filler increases approximately same ratio to rubber compound as Silica filler.
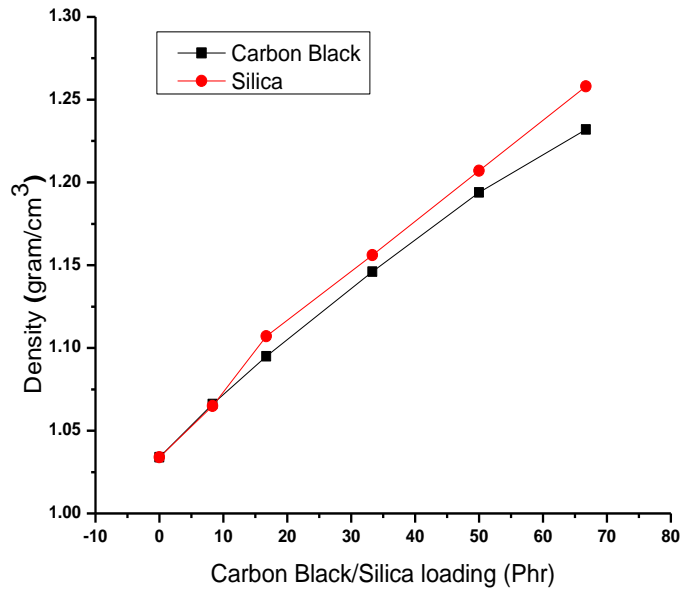
Fig 4.5   Density versus different Carbon Black and Silica loading.

4.2.6   Compression Set

It is permanent deformation which remains in the material when the applied force is removed. Compression Set is normally measured for soft materials. For compression set we generally use a cylindrical disk like a button as shown in fig 3.8.

From fig 4.6 it is clear that the compression set increase with the increase of the silica loading whereas in carbon black filler there is no significant change in the compression set. Because, SiO_2 has good compatibility with HNBR due to the hydrogen bond formed between nitrile groups of HNBR and a lot of hydroxyl groups on the surface of SiO_2. Under the external force action, HNBR molecular chains slip easily on the surface of SiO2particles and new hydrogen bond at the new seat are forms, so HNBR molecular chain could not recover its original state. Thereby, the compression set of HNBR filled with SiO_2 powder is very high [46].
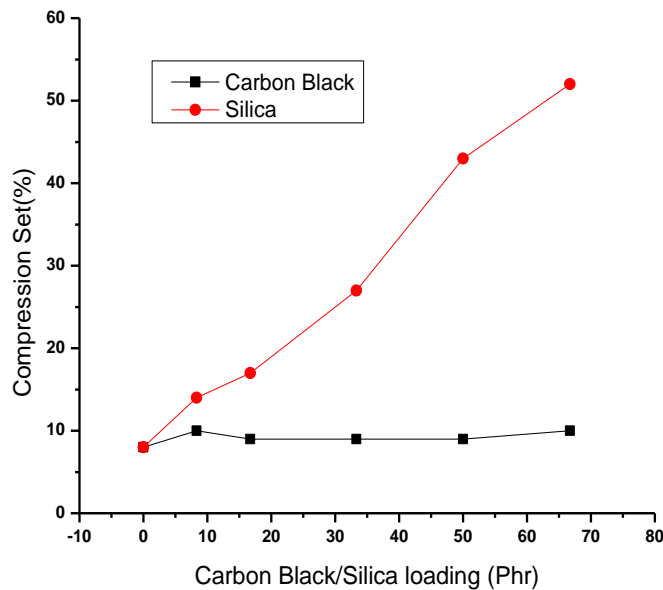
Fig 4.6   Compression set versus different carbon black/silica loading.

4.3   Discussion on swelling properties

The swelling may be defined as "it is the act of expansion due to diffusion of some solvent". The swelling is measured in percentage (%). The swelling experiment was carried out for different intervals of time in different solvents (i.e. toluene, ethanol and water). In a polymer matrix the diffusion of solvent molecules depends on the ease with which the polymer chain segments allow penetration of solvent molecules according to the free volume available. Following fig 4.7~4.12 gives the graphical representation of swelling ratio versus swelling time in different solvents (i.e. toluene, ethanol and water) for both fillers.
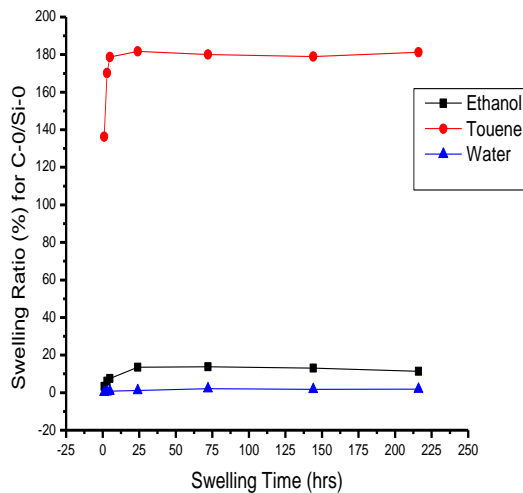
Fig 4.7- Swelling ratio versus Swelling time in different solvents for C-0/Si-0
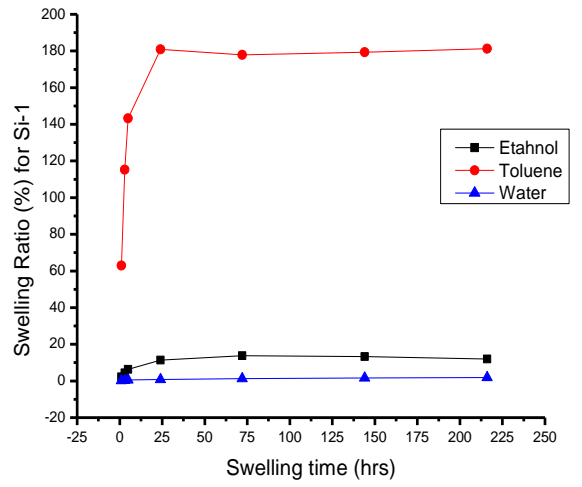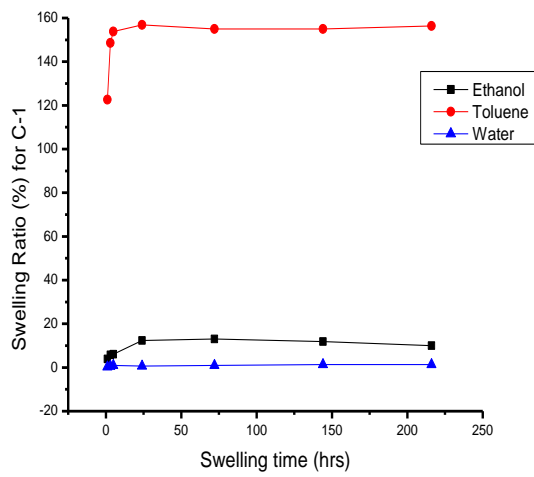
Fig 4.8- Swelling ratio versus Swelling time in different solvents for C-1 and Si-1
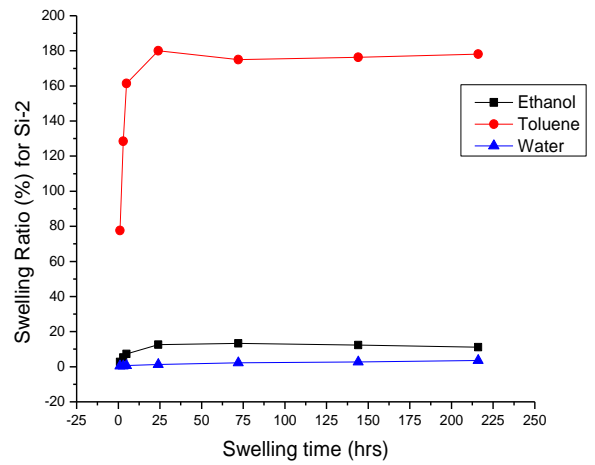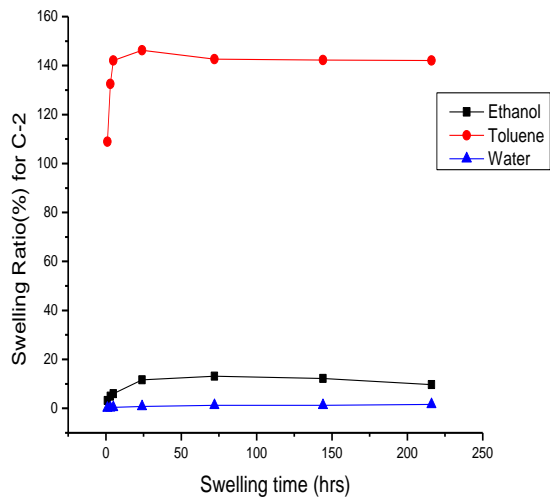
Fig 4.9- Swelling ratio versus Swelling time in different solvents for C-2 and Si-2
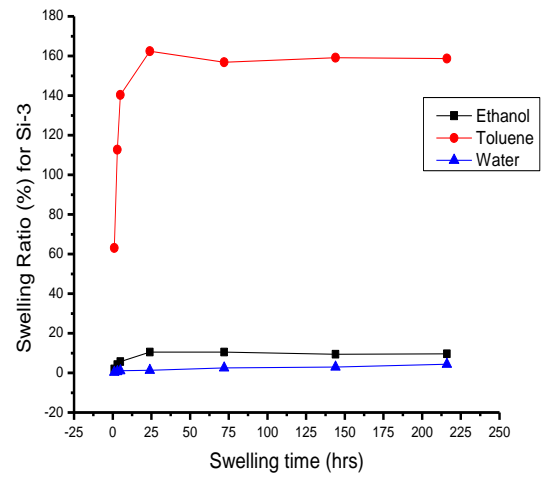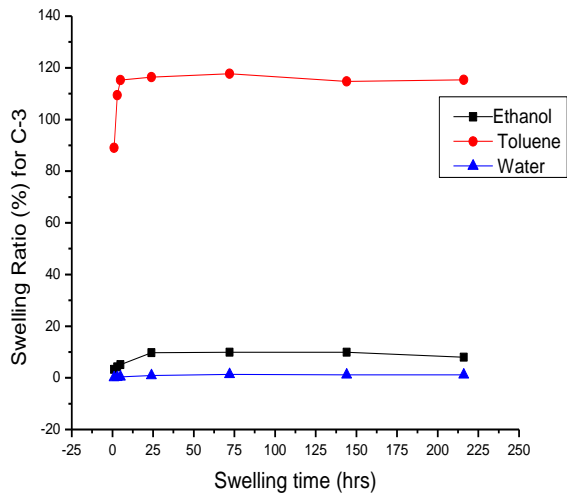
Fig 4.10- Swelling ratio versus Swelling time in different solvents for C-3 and Si-3
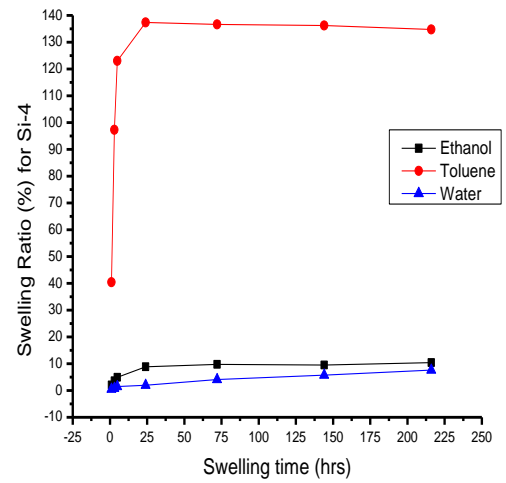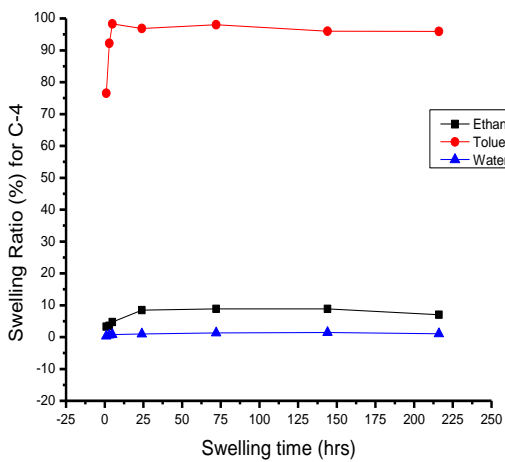

Fig 4.11- Swelling ratio versus Swelling time in different solvents for C-4 and Si-4
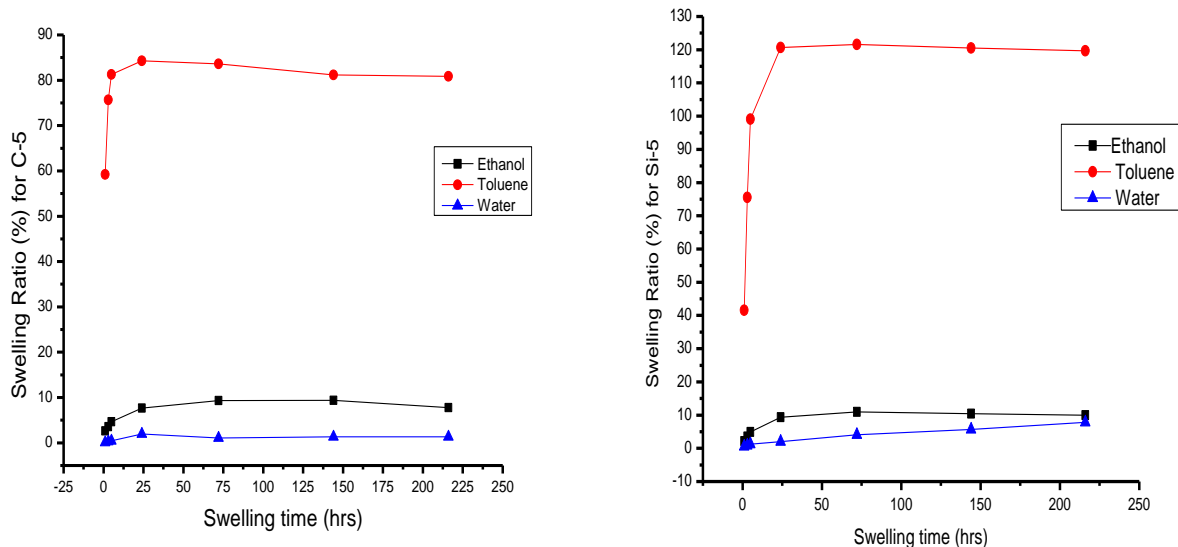
Fig 4.12- Swelling ratio versus Swelling time in different solvents for C-5 and Si-5

It has been reported that with the increase in loading quantity of fillers, swelling ratio decreases, this decrease in swelling ratio of rubber compounds with the increase in the loading quantity could be explained as a consequence of the existing pressure involved between the solvent and rubber network that act to expand the rubber network. In practice, the cross linking density in rubber compound increases with the increase in filler loading which results rise in network elasticity. These crosslinks restrict extensibility of the rubber chains induced by swelling and make it difficult for solvent to diffuse into the gaps between the rubber molecules and hence decrease the swelling ratio [47-49]. However it is not always true that with the increase of filler loading the swelling ratio will decreases. For example in case of silica filler, the swelling ratio in water increases with the increase silica loading quantity. It can be explained that water can be absorb by the silica, because silanol group (Si-OH) available in silica form hydrogen bond with water and hence higher the silica content higher will be the swelling ratio [50]. Thus in true sense it is more suitable to say that swelling ratio is affected by different fillers loadings.

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From fig 4.7~4.12 it is clear that for different solvents the swelling ratio of samples increases with the increase of swelling time until reach some optimal values and then fluctuate around the constant value and sometimes decreases very slowly. This decrease in mass with long-term exposure is likely due to extraction of some part of the fillers by the solvents as indicated in the studies by Graham [51].

Furthermore it is also clear from the fig 4.7~4.12 that swelling ratio of rubber compound in toluene for both fillers is very much higher than ethanol and water. This is due to the higher solubility and compatibility of toluene than ethanol and water. Because the swelling is diffusion process and if the solubility of any solvent in the rubber composite increases it will increase its swelling ratio accordingly.

In order to explain further the Hansen Solubility Parameters (HSPs) can be used, which are often applied for understanding the solubility of polymers/elastomers in solvent.

According to the HSPs

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ (3)$$

Where $\delta_t^2 = E/V$, $\delta_d^2 = E_d/V$, $\delta_p^2 = E_P/V$ and $\delta_h^2 = E_H/V$.

E is the measurable cohesive energy for a molar volume V of a fluid. From equation (3) it is clear that E comes from three separate components: atomic (dispersive) forces (E_d), molecular dipolar forces (E_P) and molecular hydrogen bonding (E_H).

In literature the HSPs standard values for different solvents as well as polymers/elastomers are available. The values of HSPs for solvents and elastomer used in this research work are given in table 4.1.

The HSPs values of elastomer and solvents can predict their solubility/diffusion and hence swelling behaviors. Closer the HSPs values of elastomer and solvent, higher will be the swelling. From table 4.1, For HNBR the HSP value $\delta_{t=}$ 21, which is very close to toluene than ethanol and water, therefore toluene is more soluble than ethanol and water and hence gives higher swelling ratio than ethanol and water.[52]

Table 4.1 − Hansen Solubility parameters values for solvents and Elastomers.

Sr. No.	Name	Type	Hansen Solubility Parameters (δ_t)
1	Toluene	Solvent	18.2
2	Ethanol	Solvent	26.5
3	water	Solvent	47.8
4	HNBR	Elastomer	19.3

4.4 Discussion on Thermal properties

In thermal properties, weight loss at different temperature of rubber composite has been determined. For discussion temperature at different weight loss i.e. at 10% weight loss and 50 % weight loss of initial samples have been considered. Moreover char yield (%) at 550 ^{0}C is also considered.

4.4.1 Temperature at 10 % wt. loss with different carbon black /silica loading

It is a temperature at which the 10 % weight loss of initial sample occurred. From fig 4.13 it is clear that sample C-5 is more stable than all remaining samples and hence gives highest value 411.75 ^{0}C.
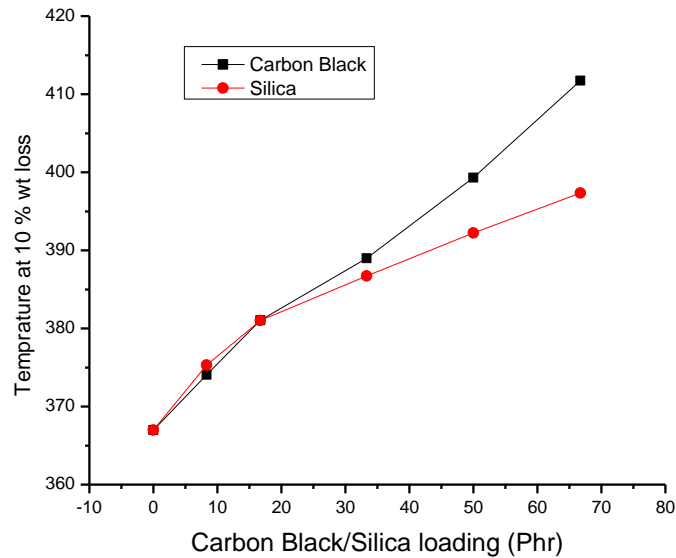
Fig 4.13   Temp at 10 % wt. loss versus different Carbon black/Silica loading.

4.4.2 <u>**Temperature at 50 % wt. loss with different carbon black /silica loading**</u>

      It is a temperature at which the 50 % weight loss of initial sample occurred. From fig 4.14 it is clear that sample C-5 is more stable than all remaining samples and hence gives highest value 475.77 ^{0}C at 50 % weight loss. From fig 4.14 it is also clear that temperature at 50% weight loss increases with the increase in loading quantity of both fillers.
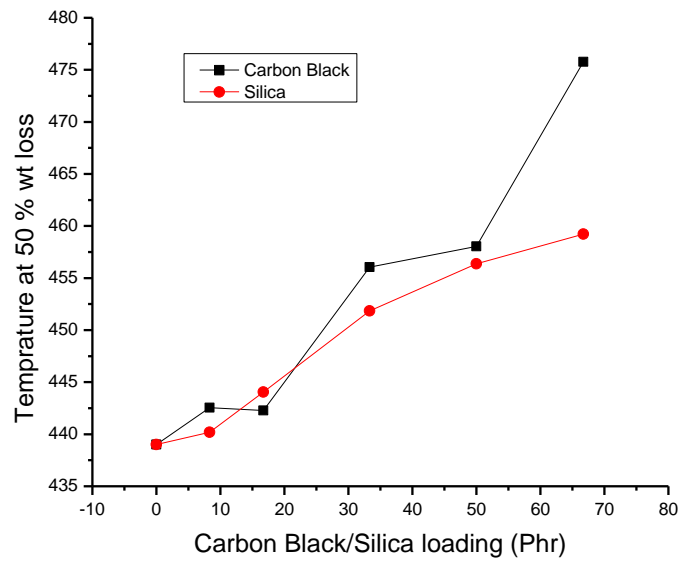

Fig 4.14   Temp at 50 % wt. loss versus different Carbon black/Silica loading

4.4.3   <u>Char Yield (residue) at 550 ^{0}C with different carbon black/silica loading</u>

Char yield is the residue which remains constant with the increase of temperature. From fig 4.15 it is clear that blank sample has the smallest char yield which is approximately 10 % of initial weight of the sample, whereas C-5 has the highest char yield which is 46.08 % of the initial weight of the sample. From fig 4.15 it is also clear that in both fillers the char yield increases with the increase of loading quantity. It is due to the ash content which increases with the increase of filler quantity, because at this temperature (i.e. 550 ^{0}C) both fillers are thermally stable.
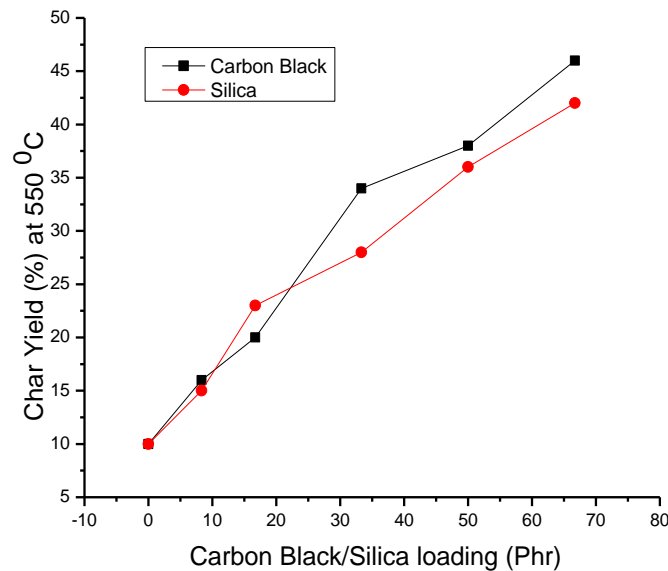
Fig 4.15   Char Yield at 550 ^{0}C versus different Carbon black/Silica loading

4.4.4   **Weight loss versus temperature for different carbon black/silica loading**

As fig 4.12~4.14 show the combine results for 10% wt. loss, 50 % wt. loss and char yield for blank sample, all carbon black and silica loading. However in order to show the results for blank sample and each type of loading separately, following fig 4.15~4.25 have been drawn. In these figs it is clear that char yield increases with the increase of loading quantity.
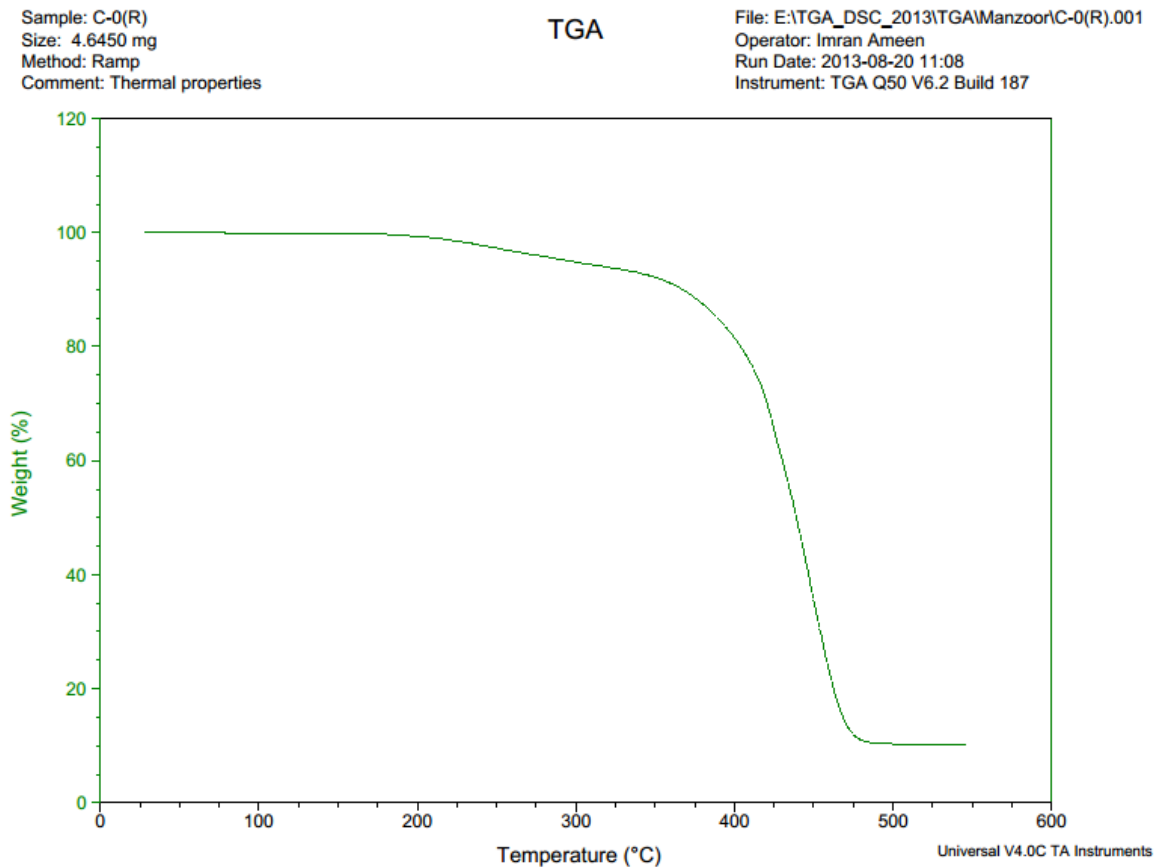

Fig 4.16   Wt. loss versus temperature for C-0/Si-0.

Sample: C-25
Size: 7.0560 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\C-25.001
Operator: Imran Ameen
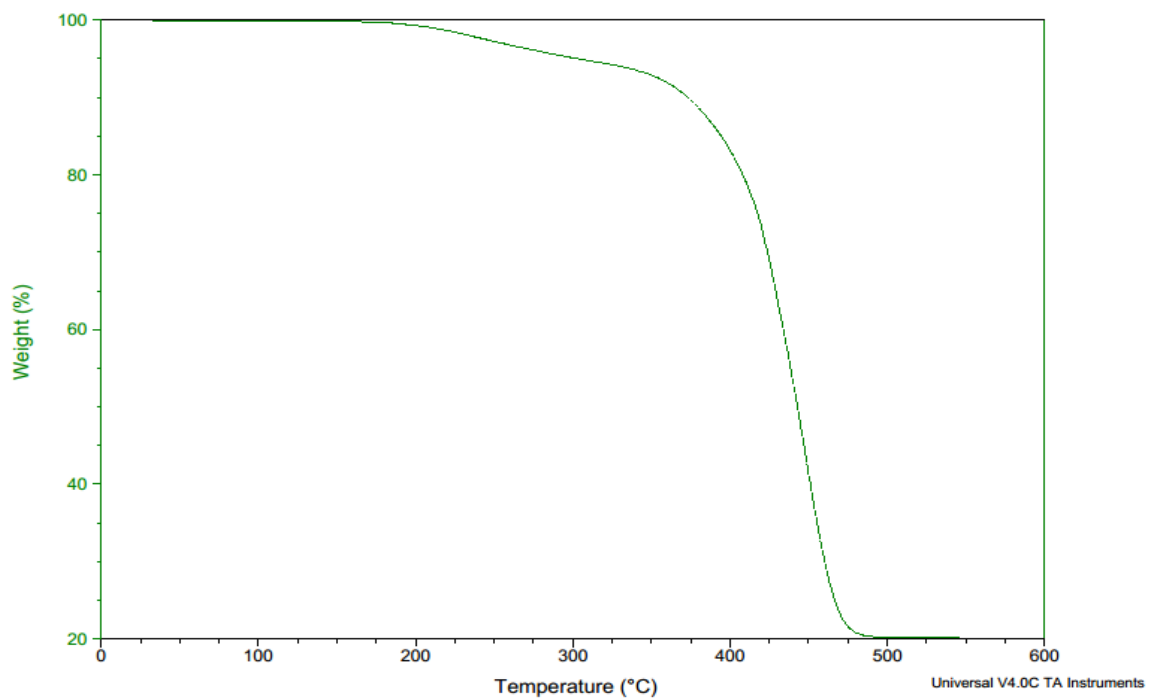Run Date: 2013-08-19 11:24
Instrument: TGA Q50 V6.2 Build 187
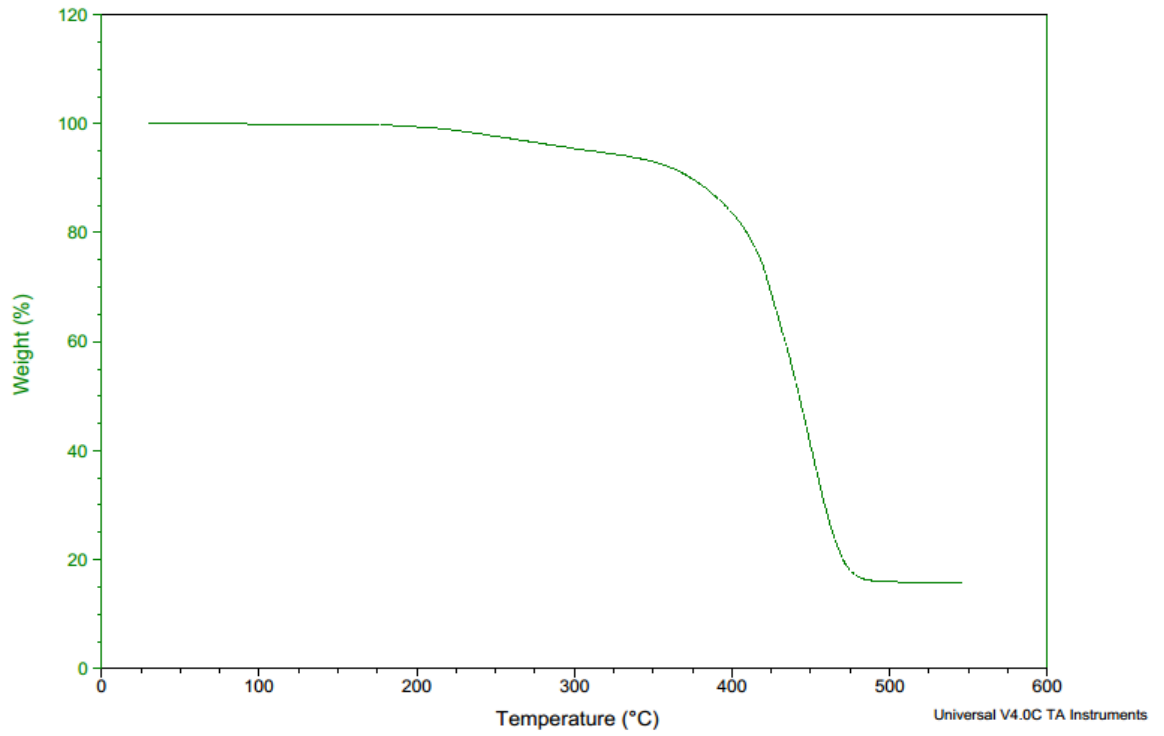
Fig 4.17 Wt. loss versus temperature for C-1.

Sample: C-50
Size: 3.5060 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\C-50.001
Operator: Imran Ameen
Run Date: 2013-08-19 13:26
Instrument: TGA Q50 V6.2 Build 187

Fig 4.18 Wt. loss versus temperature for C-2.

Sample: C-100
Size: 3.2470 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\C-100.001
Operator: Imran Ameen
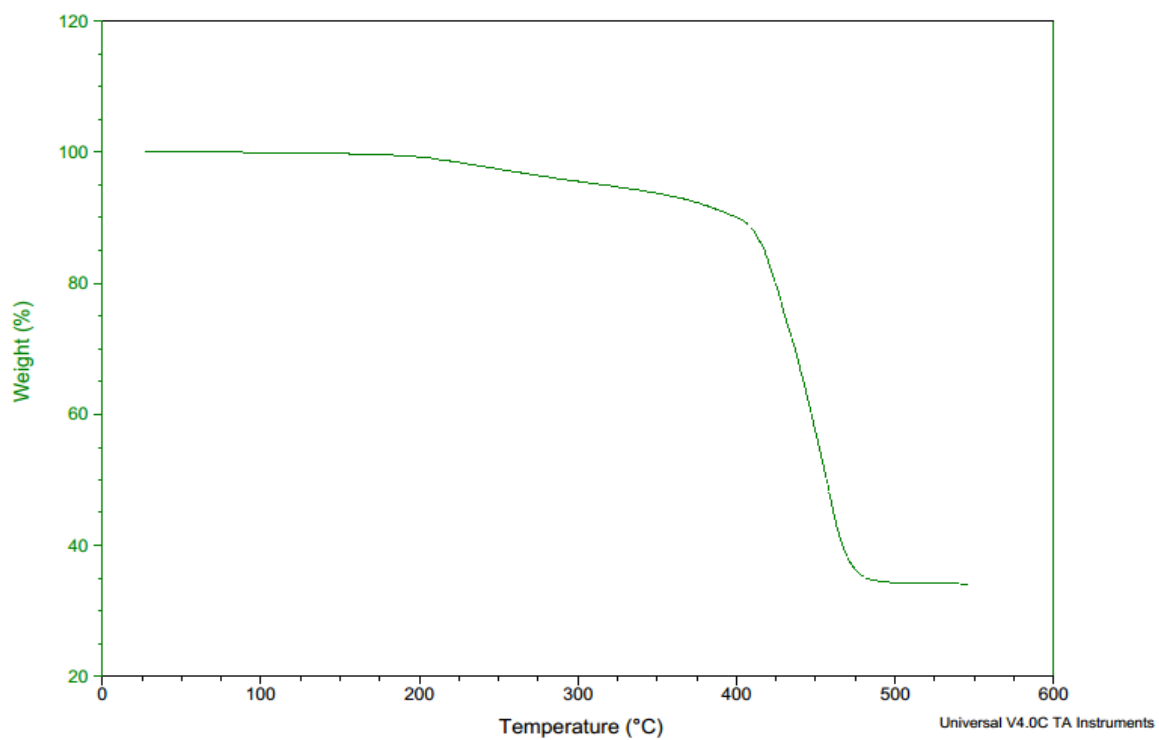Run Date: 2013-08-19 09:39
Instrument: TGA Q50 V6.2 Build 187

Universal V4.0C TA Instruments

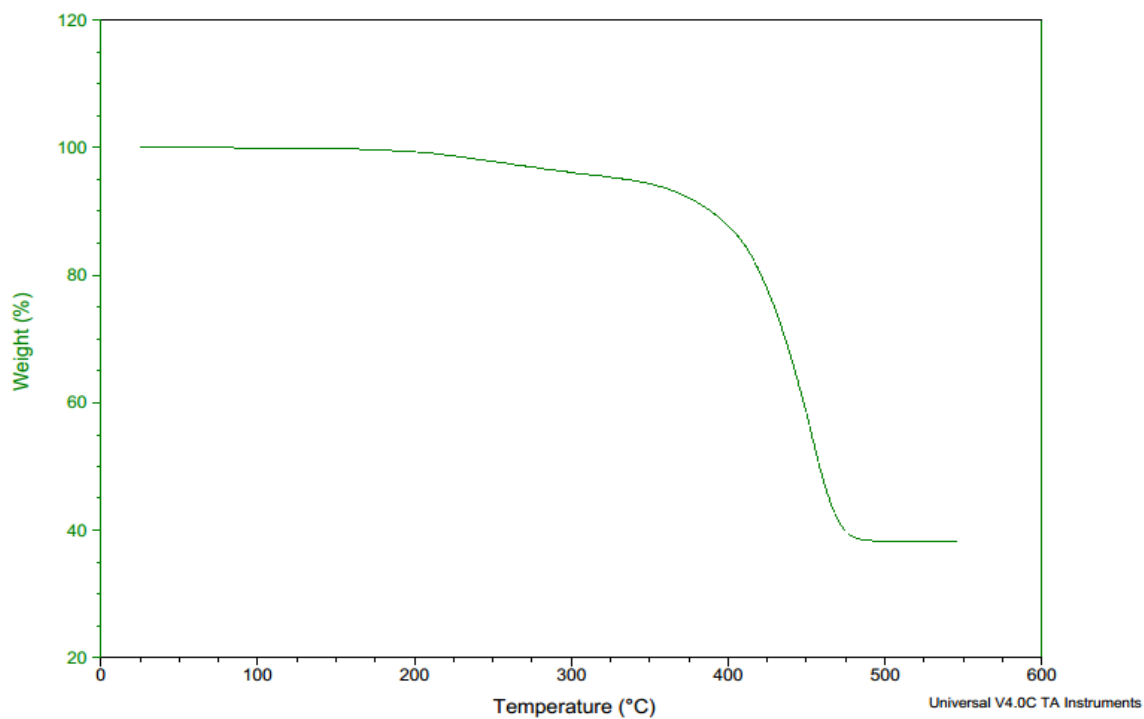Fig 4.19 Wt. loss versus temperature for C-3.

Universal V4.0C TA Instruments

Fig 4.20 Wt. loss versus temperature for C-4.

Sample: C-200
Size: 4.8130 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\C-200.001
Operator: Imran Ameen
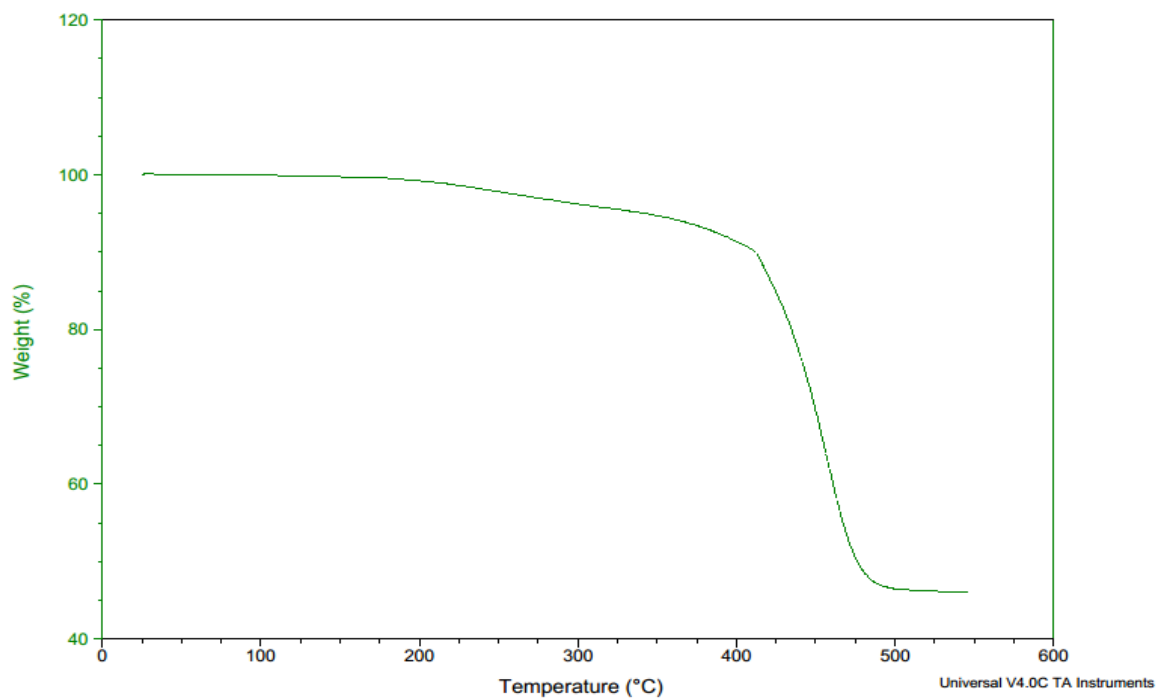Run Date: 2013-08-16 10:08
Instrument: TGA Q50 V6.2 Build 187

Fig 4.21 Wt. loss versus temperature for C-5.

Sample: Si-25
Size: 4.0270 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\Si-25.001
Operator: Imran Ameen
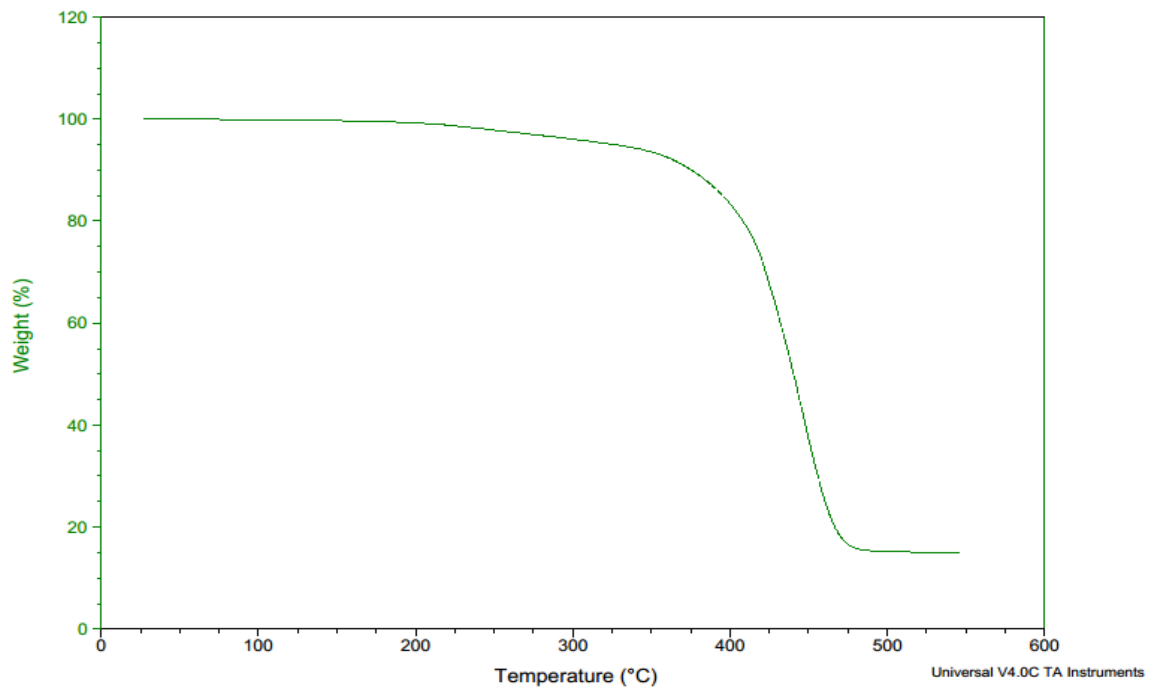Run Date: 2013-08-20 13:10
Instrument: TGA Q50 V6.2 Build 187

Fig 4.22 Wt. loss versus temperature for Si-1.

Sample: Si-50
Size: 4.4910 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\Si-50.001
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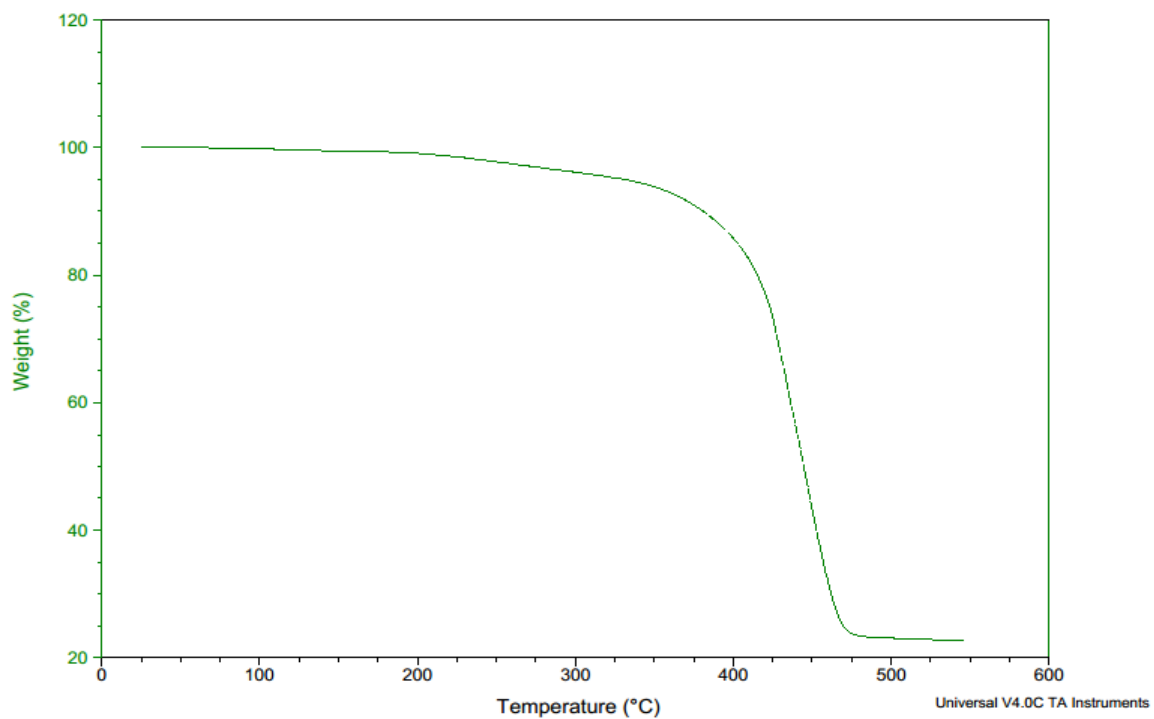Run Date: 2013-08-21 09:37
Instrument: TGA Q50 V6.2 Build 187

Fig 4.23 Wt. loss versus temperature for Si-2.

Fig 4.24 Wt. loss versus temperature for Si-3.

Sample: Si-150
Size: 5.1350 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\Si-150.001
Operator: Imran Ameen
Run Date: 2013-08-22 13:05
Instrument: TGA Q50 V6.2 Build 187

Fig 4.25 Wt. loss versus temperature for Si-4.

Sample: Si-200
Size: 3.9360 mg
Method: Ramp
Comment: Thermal properties

TGA

File: E:\TGA_DSC_2013\TGA\Manzoor\Si-200.001
Operator: Imran Ameen
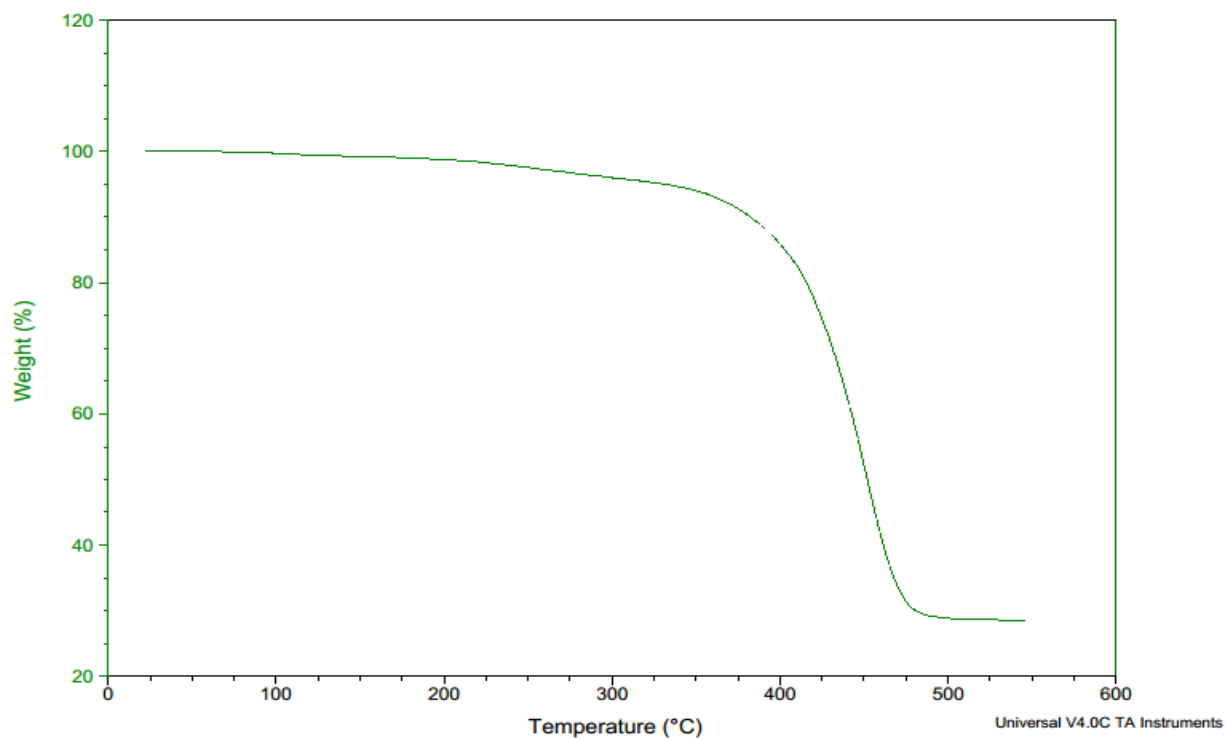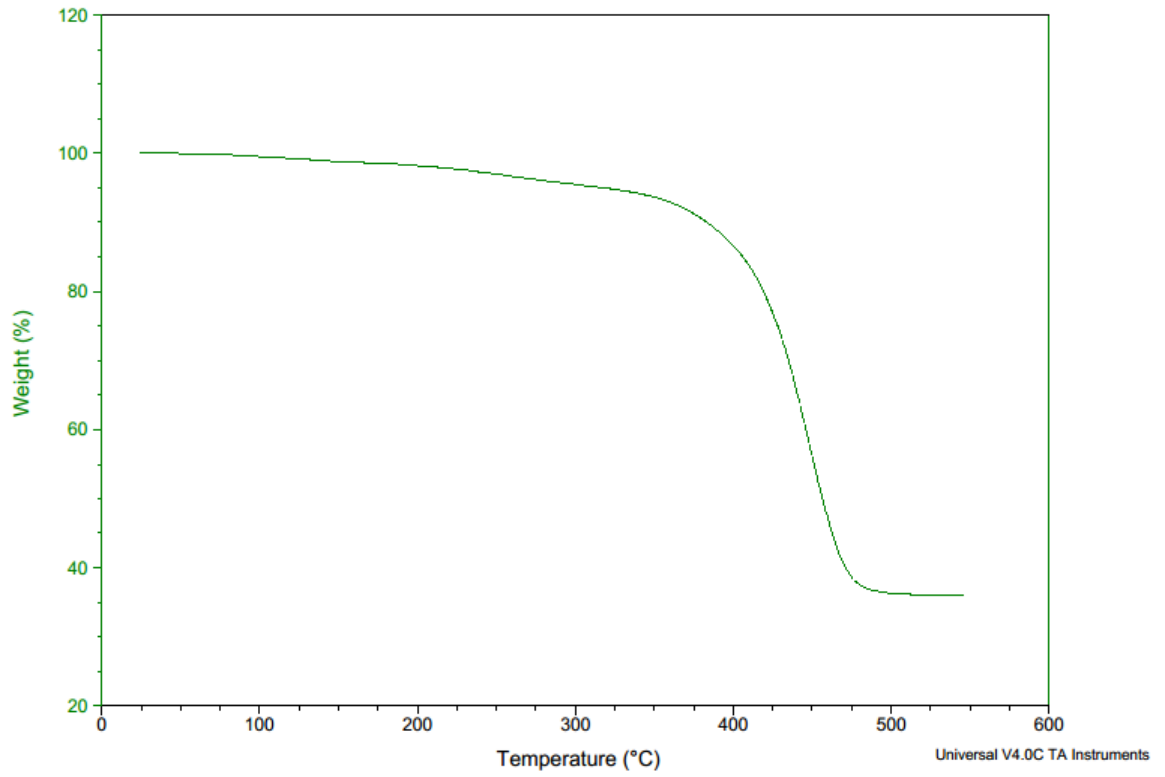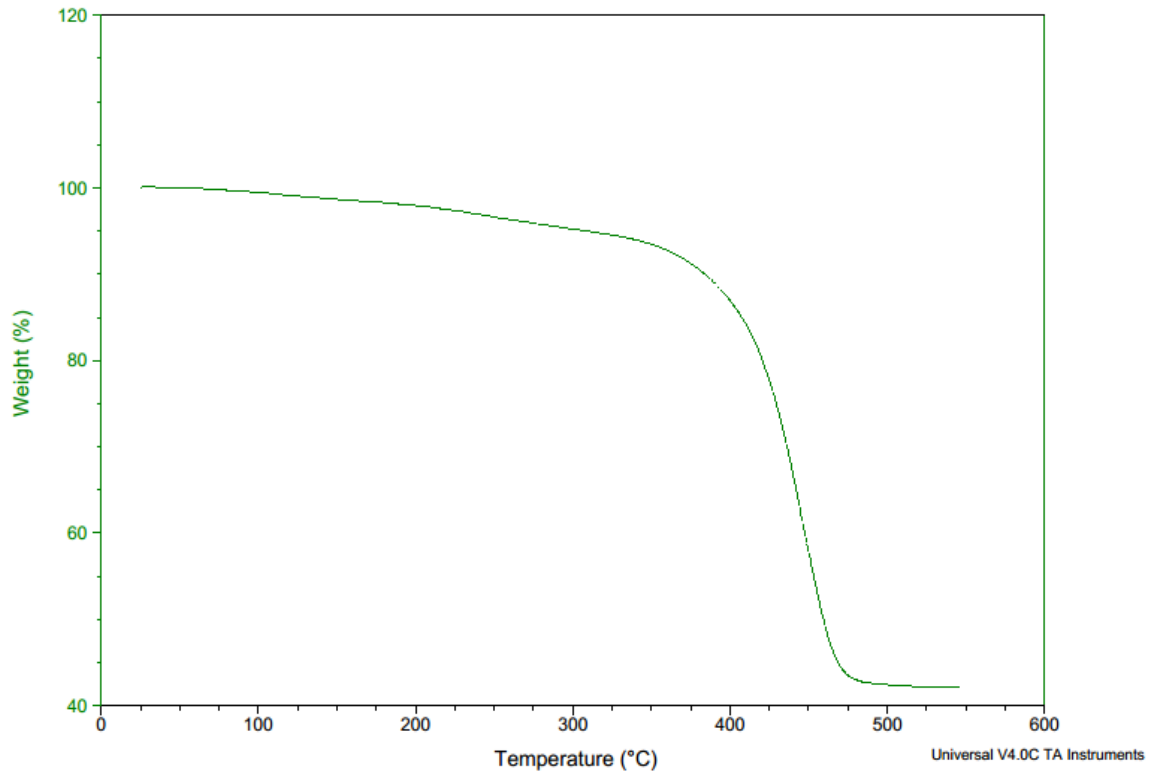Run Date: 2013-08-23 08:53
Instrument: TGA Q50 V6.2 Build 187

Fig 4.26 Wt. loss versus temperature for Si-5.

CHAPTER 5

Conclusions

5.1   Conclusions of results

From this experimental work following conclusions can be drawn:

1.   It is clear that tensile strength increases with the increase of both fillers loading until it reaches some maximum/optimal value and then decreases. This decrease in value is due to the brittleness of the rubber compound with further loading.

2.   It is clear that elongation at break increases with the increase of both fillers loading until it reaches some maximum/optimal value and then decreases. This decrease in value is due to the brittleness of the rubber compound.

3.   Modulus, hardness and density increases with the increase of both type fillers.

4.   It is concluded that the compression set increases with the increase in the silica loading, whereas in carbon black loading there is no significant change in the compression set.

5.   The swelling ratios in the solvents (toluene , ethanol and water) increases with the increase of swelling time until it reaches some optimal values and then fluctuate around the constant value and sometimes decreases very slowly. This decrease in mass with long-term exposure is likely due to extraction of some part of the fillers by the solvents as indicated by Graham.

6.   Normally the swelling ratio decreases with the increase of loading quantities of fillers, it is due to the decreasing of free volume in rubber matrix and as a consequence of the existing pressure involved between the solvent and rubber network that act to expand the rubber network. However it is not always true, but it depends upon the type of filler and solvent used. Thus in true sense it is more suitable to say that swelling ratio is affected by increasing the loading quantity of different fillers.

7.   In toluene the swelling ratio of HNBR composite is greater than ethanol and water; it is due to the closeness of HSPs value of toluene and HNBR as compared to ethanol and water. Thus closer the HSPs value of elastomer and solvent, higher will be the swelling.

8.   Char yield at 550 ^{0}C increases with the increase of fillers loading. It is due to the ash content which increases with the increase of filler quantity. It is also clear that carbon black and silica are stable at this temperature.

5.2 References

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