Fabrication and Characterization of HNBR-Silica/Carbon Phenolic Ablative Composites as an Effective Thermal Protection System (TPS)

By

Naveed Ahmad Tahir

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

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Naveed Ahmad Tahir

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Supervisor Name: Dr. Sarah Farrukh

School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)

H-12 Islamabad, Pakistan

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Dedication

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 anything by myself, in the childhood.

At the last I would like to dedicate this thesis to my wife and my daughters Manha and Faria, because without their support, love and care it might be difficult for me to accomplish this task with convenience.

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ABSTRACT

The increasing demands of thermal protection system (TPS) in aerospace and defense industry focused the scientists and engineers to develop thermal protection/insulation that can with stand at high temperature and pressure environment. These thermal protections are composed of special materials having ablative properties, shielding the space vehicles and defense ammunition from thermal destruction during exposure at high temperatures and flow of flame.

In the present research work the effort has been accentuated to develop a thermal protection/insulation that can meet the requirement of aerospace applications. During the course of research, Two HNBR based thermal protection systems (TPS) were successfully developed using silica phenolic and carbon phenolic as fillers by filler particle size variation and fixing filler amount of filler in different formulations. Both the composite thermal protection systems were characterized for their effectiveness and functional properties by using various analytical techniques.

The fabricated rubber composites demonstrated good mechanical, thermal and ablative properties that can meet requirements of aerospace industry for specific applications. Furthermore; a comparative study was also carried out to perceive the effects of particle size of the filler on thermo-mechanical and ablative properties of both fabricated composites. The results showed that with the decrease of the particle size of the filler. Mechanical properties and thermal stability increase, while ablation rate decreases. The experimental data indicated that the silica Phenolic based composites have better mechanical, thermal and ablative properties as compared to its counterpart carbon Phenolic.

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Lay Out

Recent study has been organized into six chapters,

In Chapter No 1, Introduction will provide general aspects of composites and background of rubber, ablation mechanism, pre requisites of ideal ablators, and statement of problem, need of this research and its contribution

In Chapter No 2, Literature Review will provide an insight about the already performed research work in the same field.

In Chapter No 3, Experimental work is based on the methodology of the research and characterization techniques.

In Chapter No.4, Result and discussion, contains analysis of the results and discussion on the obtained results during the characterization.

In Chapter No 5, Conclusions will highlight the conclusions that are extracted from the current research work.

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LIST of ABBREVATION

TPS	Thermal Protection System
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
TGA	Thermo gravimetric Analyzer
Si-Ph 00	Blank Sample of HNBR without filler
Si-Ph 30~70	Silica Phenolic having particle size retained on 30~70 mesh screen
C-Ph-30~70	Carbon Phenolic having particle size retained on 30~70 mesh screen

Chapter 1: Introduction

1.1 What are composites?

A composite is a special class of materials that are formed by the combination of two or more materials having different nature to create a new material with desirable properties which are not possible to achieve by any the components acting alone. In modern era, composite materials have found numerous applications in every sphere of life. Properties of the composites are optimized to accomplish specific balanced properties for different sort of applications.

1.1.1 Classification of Composites.

Composite materials can be classified in numerous ways. In general, there are two levels of classification of composites i.e. 1st on the basis of matrix material and 2nd is based on reinforcement form.

According to 1st level of classification, on the basis of matrices material is given in fig

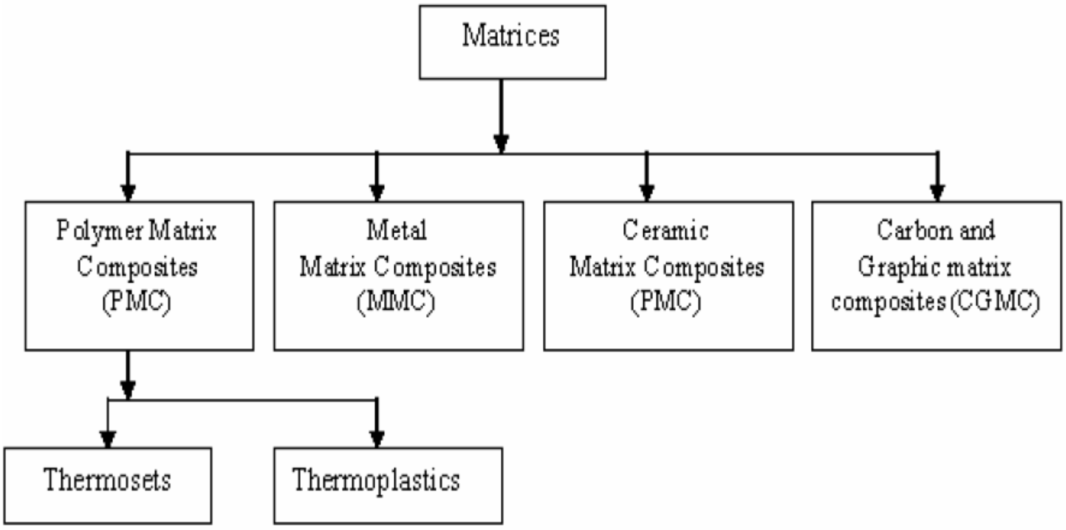


Fig. 1.1 Classification of composites according to matrices materials

Polymers matrix composites can further sub divided into major groups.

- **Thermoplastics**
- **Thermoset**

In case of Thermoplastics, Heating and cooling cycle can be repeated infinitely without any major chemical change to the polymeric chains where as Thermoset polymers undergo chemical reaction known as cross linking, initiated by a chemically reactive substance called initiator to form covalent bonds between molecules and hence heating and cooling cycle are not reversible.

Stiffness and strength of thermoset is greater than thermoplastics by virtue of covalent bonds between molecular chains due to the molecular structure bound together by covalent bonds.

Thermoset heavily dominated in composite applications because of following reasons:

- Easy processing because of low viscosity than melted thermoplastics.
- Good mechanical properties
- Temperature tolerance
- Cost Effective

According to 2nd level of classification, on the basis of reinforcement form is given as

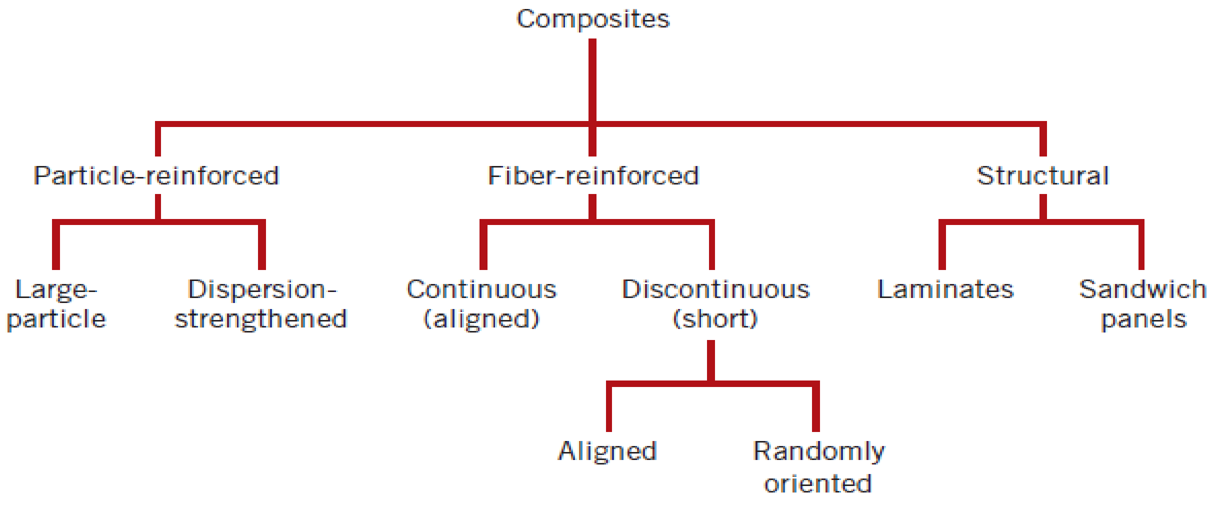


Fig. 1.2 Classification of composites according to reinforcement

1.1.2 Advantages of Composites

- Higher performance as compared to other materials.
- Higher strength as compared to other classes of materials.
- Offers excellent resistance against chemical attack, corrosion and environment**.**
- Reduced production cost
- Good resilience
- Excellent adhesive and coating compatibility
- Outstanding thermal insulation properties
- Present higher safety aspects against fire and high temperature applications.

1.1.3 Disadvantages of Composites

- Brittleness
- Difficult repairing processes
- Difficult transportation
- Requirement of special tooling and equipments

1.2 Ablative composites

Ablative composites are meant to protect certain structural parts or equipment that are exposed to very harsh environmental conditions. Major application area of ablative composites is aerospace industry where ablative composites serves as thermal protection system (TPS) to protect space vehicles and long range ballistic missiles from hypothermal/hypersonic environment during their missions. More over Thermal Protection System (TPS) are composed of ablative materials , which are highly endothermic sacrificial materials.

1.2.1 Pre requisites of Ideal ablative composites

Following are basic requisites to enhance the performance of the ablative composites during practical applications.

- Low linear ablation Rate
- Good insulation properties
- Low thermal conductivity
- Low density
- Less Expensive
- Availability of materials
- Flexible at low temperature

1.2.2 Ablation Mechanism

It is deemed necessary that materials being used in engineering applications must be physically and chemically stable. Since ablative materials are required to be operated at relatively high temperature so thermal stability of the material is also remain in focus while selecting a martial for high temperature applications but in a ultra high temperature environment that is being faced by space vehicles and rockets during their journey from earth to space, ablative materials are designed in such a way to undergo degradation process by physical and chemical means to protect structural parts of space vehicles.

It was explained by Susumu Yamada that thermal protection mechanism by ablators in high temperature environment is completed in three phases.

In 1st phase, ablator undergoes thermal decomposition by the heat generated by highly exothermic reaction and formation of char layer takes place at ablator surface.

In 2nd phase, large amount of energy in the form of heat is being absorbed by endothermic ablative reaction.

In 3rd phase, oxidation of char takes place and it forms an insulation layer that does not allow the further conduction of heat energy to virgin material because of its low thermal conductivity. Detail of ablation mechanism is shown in fig 1.3

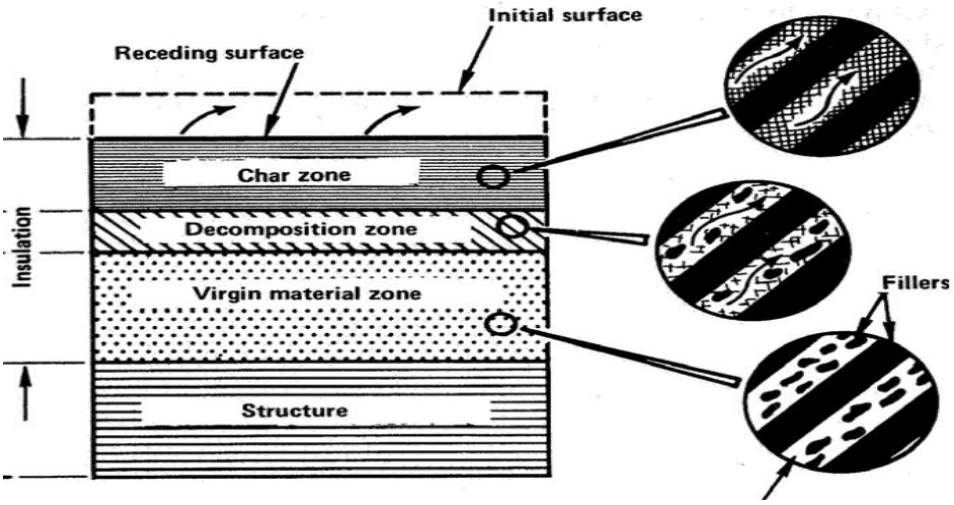


Fig 1.3 Ablation Mechanism

1.3 Elastomers:

Elastomers are the polymeric materials either thermoset or thermoplastic having elastic properties.

Elastomers are often termed as rubber which can be categorized in two major groups:

- Natural Rubber
- Synthetic Rubber

1.3.1 Natural Rubber

Rubber that exists naturally and is not synthesized is known as natural rubber e.g wood, cotton, skin, leather etc. There are a number of countries like Thailand, Indonesia and Malaysia where rubber trees are cultivated, Latex from these trees are poured into containers and processed to form coagulation with the help of acetic acid. About 80% worldwide need is being fulfilled by these countries.

1.3.2 Synthetic Rubber

All kind of rubber which do not occur naturally and hence manufactured by manmade processes e.g Nylon , Polyethylene ,Polyester ,Synthetic rubber etc. In order to achieve optimal properties, additives are also added during rubber compounding.

HNBR as Matrix material for ablative composites

HNBR is also a synthetic rubber that will be utilized as a backbone matrix material during this research.

HNBR itself have good ablative properties along with low physical and mechanical properties. However, these are the major draw backs that prevent its usage as ablative materials to form an effective Thermal Protection system (TPS).

Reinforcement of HNBR by using different fillers is the basic need to overcome its major disadvantages to make it a good ablative choice with better physical and mechanical properties.

1.4 Statement of the Problem

In pure form, HNBR cannot be used as an effective thermal protection system (TPS) because of its low physical and mechanical properties. Reinforcement of HNBR by using different fillers such as carbon Phenolic and Silica Phenolic , is the basic need to overcome its major disadvantages to make it a good ablative choice with better physical and mechanical properties.

1.5 Purpose of the Research:

Major purpose of the current research is focused on the elimination of the limitations of HNBR to an acceptable level and to make it to be used as good ablation material with better physical and mechanical properties by reinforcement of HNBR bt using different particle size of the fillers like carbon phenolic and silica phenolic

1.6 Contributions of the study:

Major contributions after the completion of the study is meant to provide general and broad ideas, highlighting how the properties of HNBR can be optimized by reinforcement by filler particle size variation to make it a popular and accepted choice, being used as an ablative material with good physical and mechanical properties to meet the increasing needs of the aerospace industry.

Chapter 2 Literature Review

2.1 History of ablative materials

In late 1950, which is also known as start up era of space age, the research on thermally stable materials for aerospace industry has been started in top gear. Due to continual advancement in aerospace industry, the hunt for specialized materials based on polymers for thermal protection system (TPS) having good ablation and mechanical properties have increased to an incredible rate.[1, 2]

Requirement of more thermally stable polymer rose significantly when utilization of space vehicles of small size but greater speed for exploration purpose increased. Before 1957, such materials were utilized only for astormy applications only and these polymeric materials retained their desired properties between 100 °C to 150°C for a period of one to five years.[3-5]

In 1960, with further development in aerospace industry, demands for polymeric materials with more thermal and radiation stability became many folds. Major requirement from these Polymers was to function properly in air over range of temperature from 150 °C to 200°C for about one to three years and it will function well at about 500°C over shorter time periods.[4]

Manufacturing of the hardware for large space stations and under water exploration from the material with good physical, mechanical and stable thermal properties rose the demands of new material to serve the purpose.[2, 6-8].

Development of more thermally stable and durable polymers has shown a remarkable progress, supported by defense , aerospace and commercial industry to serve as insulation materials, structural foams and adhesives etc etc. Actually, in early 1960 commercial development of the aromatic polyimide stated new phase of polymer chemistry.[9-11]

For the insulation purpose of intercontinental ballistic missiles and Solid Rocket Motors , that are supposed to be operated at a relatively very high temperature, nano sized fillers such as silica, glass, ceramics and clay were incorporated in NBR, Silicon rubber and EPDM so that an effective and efficient TPS can be formulated.[12-15]

In 2007, VINETA SREBRENKOSKA and GORDANA BOGOEVA-GACEVA characterized the ablative composites based on phenolic resin and different carbon fiber content and length. Optimal were obtained with carbon fiber content up to 60 wt% and mechanical properties were optimized with 25 mm carbon fiber length.[16]

In May 2010, G. Pulci, etc developed a carbon phenolic based TPS and tested it to investigate whether the mechanical and thermal requirement for space vehicles are achievable or not. It was reported that newly manufactured TPS had shown encouraging results with highest mechanical properties with outstanding thermal stability over 1000C for about 20 minutes.[17]

Maurizio [18] Natali, Marco MontiIn, through their experimental work had shown the possibility of producing glass phenolic composites with nanosized silica as an alternative to micron-scaled silicon dioxide. The ablative properties of the produced materials were studied and it was confirmed that nanosized silica particles had improved the ablative significantly.[18, 19]

Vojislav Jovanovic et through their study, investigated the effect of filler (CB) loading on NBR/EPDM blends based composites on mechanical properties and thermal stability .It was concluded that Tensile strength increase while elongation at break decrease while filler loading is increased for all blends of NBR/EPDM and these blends had shown low thermal stability as compared to individual NBR and EPDM based composites.[7, 20]

Srikanth et fabricated carbon/Phenolic ablative composites that were modified by using Zirconia and carbon nano tubes to find out their impact on Physico-mechanical and thermal properties of these composites and it was observed that thermal conductivity had been decreased,moreover presence of Zr also increased the ablation rate due to enhanced solid char conversion to ZrC and CO.CNTs enhance thermal conductivity and ablation rate of carbon phenolic composites.[8]

Yue Guan et studied the ablation properties and mechanism of HNBR composite containing different fillers such as Fused Silica, Organically Modified Micro Tubes, and Expanded Graphite and reported that type of filler has greatly influenced the ablation mechanism and hence shown different ablation performance. It was concluded that HNBR/OMMT had shown lowest linear ablation rate with no char formation, HNBR/FS has highest linear ablation with char formation while HNBR/EG had shown intermediate linear ablation rate.[21, 22]

Zuo-Jia Wang et through the research by thermal analysis on carbon nano tubes and phenolic based ablative composite, concluded that mechanical properties and ablation resistance increased considerably by adding only 0.1and 0.3 wt% of finely dispersed CNTs.[5]

Zahra Eslami et prepared carbon fibers/Phenolic/MWCNT nano composites. Thermal degradation was investigated and it was concluded that thermal stability of these composites improved considerably and it was also reported that linear ablation rate decrease by about 80% with 1% MWCNT loading and by 52% with 2% MWCNT loading.[2]

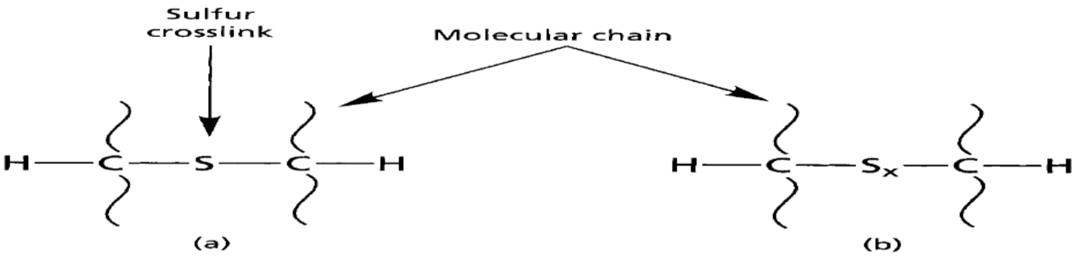
2.2 Rubber Compounding:

Term compounding is generally used to refer a mixing process where intense mixing and a high shearing are used for dispersion of additives in elastomers. Elastomers possess high viscosity, so high shear mixing technique is required.
The most common machine that can perform such high shear mixing is a two roll rubber compounding machine.

2.3 Vulcanization / Cross linking:

HNBR in un vulcanized form possesses long polymeric chains that are entangled throughout the polymeric structure. As a result of stretching these chains may cause slippage which is undesirable for most of the practical applications.[23, 24]

Vulcanization is a special process that is used to lock the movement of these chains which in turn decreases slippage and hence increases the elasticity of the polymers. This process of locking the chain movement to avoid slippage is known as cross linking.
Cross linking of polymeric chains can be obtained by sulphur and Peroxides. However, most of the cross linking is carried out by sulphur in rubber industry known as sulphur vulcanization.[7, 23, 25, 26]



a. S atom linking two polymer chains b. Multiple cross links

2.4 Processing Aids:

In general, elastomeric materials have draw backs of low viscosity as well as low strength along with higher molecular weight, so on application of stress these materials can flow easily when subjected to little stress. Processing aids are the materials that are used to fine tune the cross linking, curing of rubber and other characteristics of fabricated composites known as additives.

2.4.1 Fillers

After the vulcanization most of the elastomers, remain weak so there is a need to reinforce the vulcanized rubber. During compounding of HNBR, fillers are added for reinforcement of polymeric chains that is used to modify and improve the physical and mechanical properties. Since all fillers are not equally created, so a range of reinforcement from very high to very low, corresponding to particle size of filler can be achieved.

Reinforcement mainly depends upon the shape and surface chemistry of the filler particles. Some popular filler are silica, clays, carbon black and chalk. Normally carbon black has highest reinforcement action.[21, 27-30]

2.4.2 Primary Accelerators

These are the chemical substances that are added to accelerate and to complete the cross linking of rubber with sulphur.cross linking process of HNBR with Sulphur is accelerated by 2, 2 Mercaptobenzthiazole Disulfide (MBTS).[1, 31]

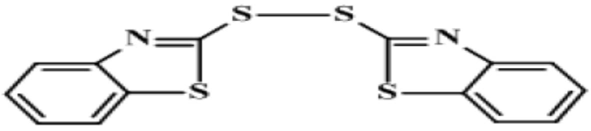


Fig 2.2 Chemical Structure of MBTS

2.4.3 Secondary Accelerator

During the fabrication of ablative composite based on HNBR, secondary accelerator Tetramethylthiuram Disulfide (TMTD) is utilized.[23]

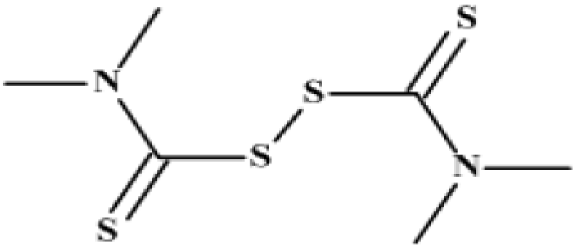


Fig 2.3 Chemical Structure of TMTD

2.4.4 Activators

These are the materials which serve the activation of sulphur cross linking process during process of vulcanization in rubber compounding. Cure system for the rubbers mainly consists of Zinc oxide, Stearic acid, accelerators and suphur. There is a chemical reaction between Zinc Oxide and Stearic acid that results in the formation of Zinc stearate.

Zinc state and accelerators helps to accelerate the reaction to completion in minutes that will take hours to completion with Sulphur alone.

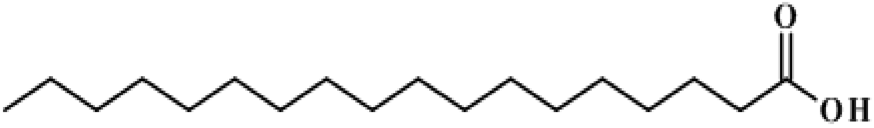


Fig 2.4 Chemical structure of Stearic acid

2.4.5 Plasticizer

Plasticizers are those processing aids during rubber compounding that help to deform the polymeric chains. During rubber compounding of HNBR, oily plasticizer such as dioctyl phathalate (DOP) is also incorporated during the processing to enhance ease of flow by decreasing viscosity and friction of mix for better filler dispersion.

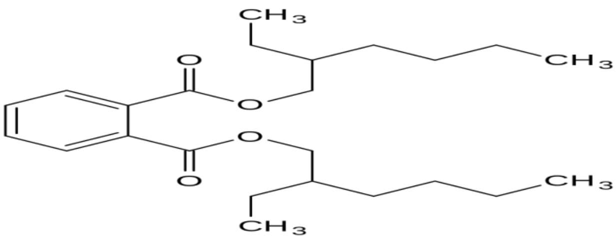


Fig 2.5 Chemical Structure of DOP

2.4.6 Antioxidant

Antioxidants are those chemical substances that are used during rubber compounding to protect organic elastomers by depressing the aging phenomena caused by the presence of free radicals.. Brittleness is observed with aging that is caused by destructive effect of the oxygen, accelerated by heat. Antioxidants are added during rubber compounding to slow down the aging process by removing free radicals.

Phenyl Naphtylamine (PBN) is used as antioxidant. [23]

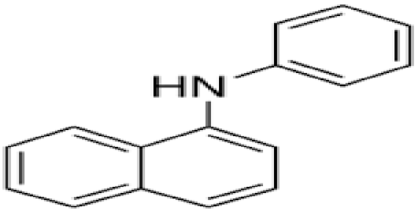


Fig 2.6 Chemical Structure of PBN

Chapter 3 Experimental work

3.1 Introduction

This chapter comprises details of the experimental study that has been carried out during the research phase. Experimental work has been initiated after the arrangement and provisioning of all the materials, in first phase of experimentation, compounding of HNBR with different additives including fillers was carried out followed by curing of the samples. Specimens of different thickness i.e. 2 mm and 6 mm, according to test requirement were prepared and finally testing has been performed.

3.2 Process Flow Chart for Rubber compounding:-

Process Flow chart that has been followed during the research is shown in Fig 3.1

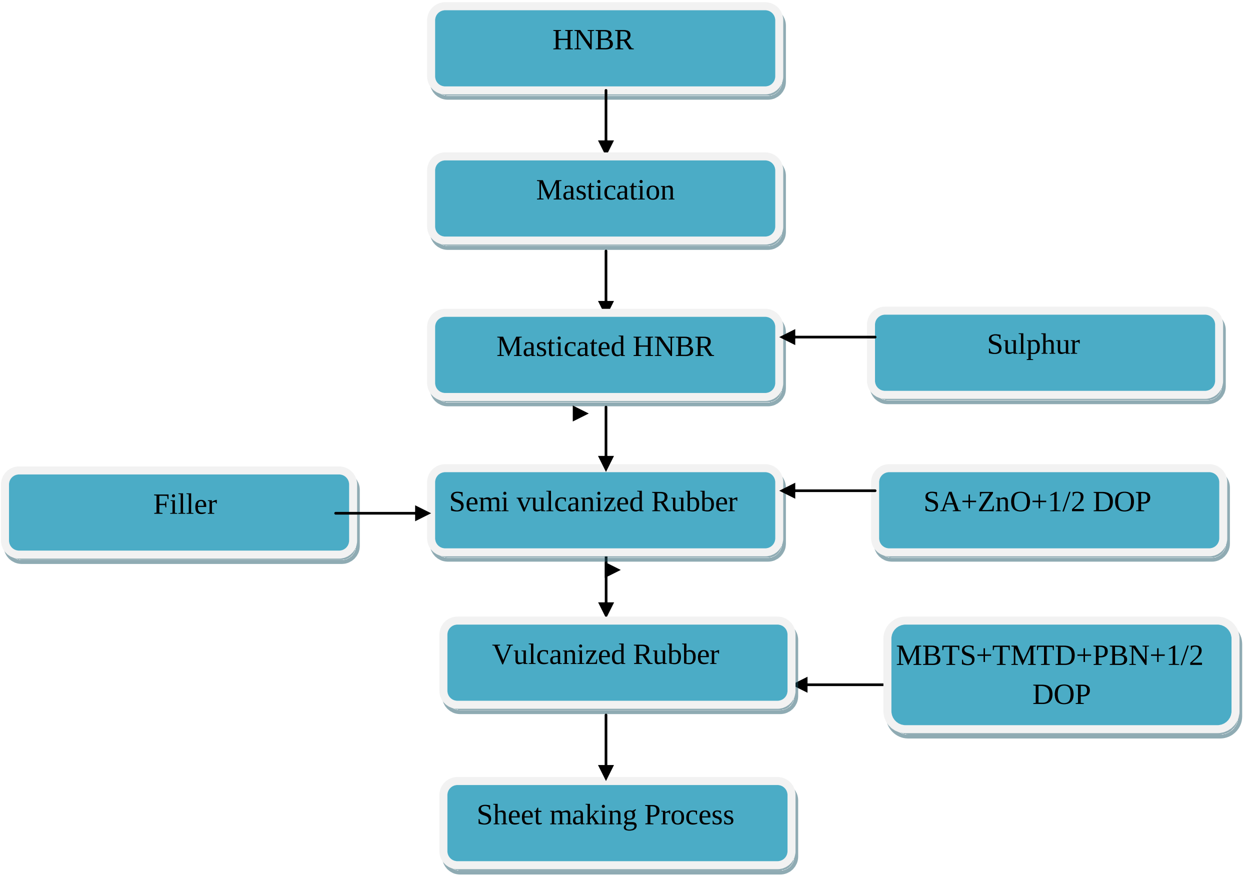


Fig 3.1 Process Flow Chart for Rubber compounding

3.2 Process Flow Chart for Curing

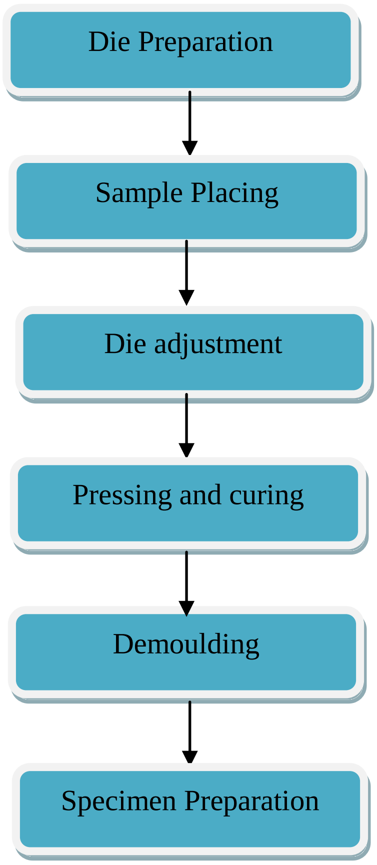


Fig 3.2 Process Flow Chart for curing

3.3 Materials/Ingredients

The different recipes of ablative composites based on HNBR containing different particle sizes of Silica phenolic resin and carbon phenolic resin were prepared. Different processing aids known as additives were also incorporated during mixing/compounding process with basic raw materials. HNBR valculization was activated by using catalyst known as activators e.g. ZnO and Stearic acid. Process is normally accelerated by two types of accelerators, MBTS as Primary accelerator and TMTD as secondary accelerator. Sulphur served the role as cross linker/vulcanizing agent. Phenyl Naphtylamine (PBN) was also mixed during processing which acts as antioxidizing agent. Processing was facilitated by using plasticizer like Dioctyl Phthalate (DOP) to reduce viscosity.

3.4 Sieving Of Fillers

All the materials including natural or synthetic had always found in the disperse form. They possess different shapes and sizes which is known as particle size distribution, which has significant impact on physical and chemical properties.

During this experimental study, effect of particle size variation on ablative composites based on HNBR is the primary objective so after collection of Silica phenolic and carbon phenolic in powder form, vibration sieving was performed to separate fillers according to their particle size, which were saved for further processing.

On the basis of two different fillers, two different formulation were prepared .Amount of the basic ingredients in each formulation was kept fixed and by the variation of particle size for each filler silica phenolic and carbon Phenolic. Detail of each formulation is given in table #. 3.1 and 3.2 respectively.

3.5 Formulation with Silica Phenolic

Material	**A/U**	**Si-Ph 00**	**Si-Ph 40**	**Si-Ph 50**	**Si-Ph 60**	**Si-Ph 70**
HNBR	Phr	100	100	100	100	100
S		3	3	3	3	3
ZnO		10	10	10	10	10
Stearic Acid		2	2	2	2	2
Si-Ph		00	20	20	20	20
MBT		2	2	2	2	2
DOP		5	5	5	5	5
TMTD		1	1	1	1	1
PBN		2	2	2	2	2

Table 3.1 (Formulation with Silica Phenolic Filler)

3.6 Formulation with Carbon Phenolic

Material	A/U	C-Ph 00	C-Ph 40	C-Ph 50	C-Ph 60	C-Ph 70
HNBR	Phr	100	100	100	100	100
S		3	3	3	3	3
ZnO		10	10	10	10	10
Stearic Acid		2	2	2	2	2
Carbon-Ph		00	20	20	20	20
MBT		2	2	2	2	2
DOP		5	5	5	5	5
TMTD		1	1	1	1	1
PBN		2	2	2	2	2

Table 3.2 (Formulation with Carbon Phenolic Filler)

3.7 Mixing/Compounding

Mixing of raw materials as per recipes listed in table 1 was processed by using two roll rubber mixing mill Model XK-160.

Roll Dia: 160 mm

Roll working length: 320 mm

Max working roll nip: 4.5 mm

Total Mixing Time: 35 Min

HNBR was masticated initially and temperature was kept at 40 ^{0}C, water was used as cooling agent. [1, 3, 4, 14]

3.8 Curing

After mixing of all ingredients, curing of the vulcanized HNBR was carried out by using 45 Ton Hydro Press keeping curing at temperature at 165 ^{0}C and pressure 10 MPa for 45 minutes.

3.9 Sampling and Testing

After the completion of curing process, Samples of thickness 2 mm and 6 mm were prepared as per test requirement. Following tests has been carried out.

3.9.1 Mechanical Properties

Mechanical properties provide an insight to the behavior of a material when materials are subjected to an applied load. Mechanical properties provide the following information about the materials.

i. Range of usefulness
ii. Service life
iii. Classification and Identification of materials

3.9.1.1 Tensile Strength

Tensile strength of a material that indicates its ability to withstand applied external forces without breaking.

For the measurement of tensile strength, INSTRON-5966 UTM machine was used. A die was used to form dumbbell shaped specimens from the sheet of 2mm thickness as shown in the fig. The specimen was gripped into the machine and stretching speed was fixed to 100 mm/min. Allied computer with electronic programme was utilized to find out tensile strength, elongation at break and Modulus.

$$\sigma_m = F_{max}/b*d$$

F_{max}=Maximum load

b = Sample width of working area before test

d = Thickness of the sheet before test

3.9.1.2 Elongation at break

It is defined as the ratio of change of length to the original length after the breakage occurrence of the test specimen. It indicates the capability of any material to resist the change in the shape without crack formation.

$$\epsilon_b = (L-L_0/L_0)*100$$

L_0 = Length of sample before test

L= Length of the sample when it breaks

3.9.1.3 Modulus

Ratio of stress to strain in the elastic region is known as Modulus. It is also measured automatically. The modulus is expressed in MPa and provides how stiff a material is.

$$E_0 = P_N * L_0 / A_0 * \Delta L$$

P_N =Load value within elastic region

L_0 = Original guage length of sample before test.

A_0 = Average cross section area

ΔL = Change in length

Sr. #.	Sample	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)
1	**Neat**	**2.32**	**495**	**105**
2	**Si-Ph 30**	**3.98**	**442**	**112**
3	**Si-Ph 40**	**4.18**	**428**	**119**
4	**Si-Ph 50**	**4.52**	**410**	**122**
5	**Si-Ph 60**	**5.02**	**385**	**136**
6	**Si-Ph 70**	**5.25**	**360**	**141**
7	**C-Ph 30**	**3.69**	**398**	**109**
8	**C-Ph 40**	**3.85**	**374**	**114**
9	**C-Ph 50**	**4.05**	**357**	**120**
10	**C-Ph 60**	**4.30**	**334**	**126**
11	**C-Ph 70**	**4.88**	**3.15**	**132**

Table 3.3 Mechanical Properties of fabricated composites

3.9.2 Physical Properties

3.9.2.1 Hardness

Most common instrument that is used to measure hardness of elastomers and rubber is known as Durometer which contains a calibrated spring to apply a specific pressure to conical or spherical shaped indenter foot. An attached scale is used to measure the depth of indentation. A variety of models are available, the Model A is used for soft materials while Model D is used for harder materials.[31]

Sr.#.	Sample I.D.	Hardness (Shore A)
1	Neat	70
2	Si-Ph 30	82
3	Si-Ph 40	88
4	Si-Ph 50	98
5	Si-Ph 60	109
6	Si-Ph 70	115
7	C-Ph 30	78
8	C-Ph 40	85
9	C-Ph 50	93
10	C-Ph 60	100
11	C-Ph 70	108

Table 3.4 Hardness of fabricated composites

3.9.2.2 Density

Mass per unit volume of a substance is known as density having units of kg/m^3 or g/cm^3. Sample sheets of 2mm thickness were used to measure density according to ASTM D-4018.[35].

Sample sheets were conditioned at 20±2 ċ for one hour before the start of the test.

Density was calculated by using the formula:

$$\rho = m_1 * \rho_1 / m_1 - (m_2 - m_3)$$

m_1= Mass of sample in air (gm)

m_2= Mass of sample + metal wire immersed in paraffin oil (gm)

m_3 = Mass of metal wire immersed in paraffin oil (gm)

ρ_1 = Density of paraffin oil (gm/cm^3)

Sr.#.	**Sample I.D.**	**Density (g/cm^3)**
1	Neat	1.035
2	Si-Ph 30	1.046
3	Si-Ph 40	1.05
4	Si-Ph 50	1.055
5	Si-Ph 60	1.061
6	Si-Ph 70	1.067
7	C-Ph 30	1.042
8	C-Ph 40	1.047
9	C-Ph 50	1.052
10	C-Ph 60	1.056
11	C-Ph 70	1.061

Table 3.5 Density of fabricated composites

3.10 Measurement of Thermal Properties

3.10.1Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis is tool based on thermal analysis that measures the physical or chemical changes that occurred as a function of increasing temperature by employing constant rate of heating.

Thermal stability of newly fabricated ablative composites based on HNBR was characterized by using thermo gravimetric analysis (TGA).Fixed mass of the sample was subjected to thermal analysis.TGA instrument continually weigh the sample as temperature in increased to 550 c^0 at a constant rate.

With the increase in the temperature, volatile components decomposed and there is a constant decrease in the mass is observed till a point is reached where there is no weight loss of the sample occurred. This residue is known as char yield.

Instrument: TGA Q50 V6.2 Build 187

Heating Rate: 10 C^o/min

Sample Size: 6±0.5 mg

Results of Thermal Stability by TGA

Sample Code	Initial Weight (mg)	T_{10} (^oC)	T_{50} (^oC)	% Char Yield
Si-Ph 30	5.987	347	430	14.6
Si-Ph 40	6.004	355	437	25.4
Si-Ph 50	6.010	362	448	27.5
Si-Ph 60	5.989	366.7	454.15	29.9
Si-Ph 70	6.019	375	469	31.5

Table 3.6 Thermal stability by TGA (Silica Phenolic)

Sample Code	Initial Weight (mg)	T_{10} (^oC)	T_{50} (^oC)	% Char Yield
C-Ph 30	5.997	354	433	11.7
C-Ph 40	6.014	375	440	15.1
C-Ph 50	6.018	360	450	17.3
C-Ph 60	5.998	378	448	19.4
C-Ph 70	6.013	379	452	21.6

Table 3.7 Thermal stability by TGA (Carbon Phenolic)

3.10.2 Thermal Conductivity

Thermal conductivity of known thickness and area of both samples of silica phenolic and Carbon Phenolic was measured by using Guarded Hot Plate apparatus according to ASTM C177-97. Results are tabulated below

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Sr. #.	Sample I.D.	Thermal conductivity(W/m.K)
1	Neat	1.043
2	Si-Ph 30	1.039
3	Si-Ph 40	1.0387
4	Si-Ph 50	1.037
5	Si-Ph 60	1.037
6	Si-Ph 70	1.037
7	C-Ph 30	1.038
8	C-Ph 40	1.038
9	C-Ph 50	1.036
10	C-Ph 60	1.036
11	C-Ph 70	1.036

Table 3.8 Thermal conductivity

3.11 Ablation Properties:

3.11.1 Linear Ablation Rate

Thermal ablation characterization of samples was carried out by using Oxy-acetylene torch method according to ASTM E-285-80 standard. Samples are formed in the shape of circular disc and were exposed to high temperature environment by providing stable oxy-acetylene flame as a heat source to burn the circular disc samples at an angle of 90^0 at about 3000 ± 100 C^0 temperature. The distance between the samples and nozzle was kept at 10 ± 0.2 mm and the exposure time was 20 sec. linear ablation rate was calculated by the formula.

$$\mathbf{R = L_1 - L_2 / t}$$

Where L_1 is the initial thickness and L_2 is the final thickness of the samples after exposure of the sample piece to ablation time t.[1,3-4, 6,]

Sr. #.	**Sample I.D.**	**Linear Ablation Rate (mm/Sec)**
1	**Neat**	**0.852**
2	**Si-Ph 30**	**0.398**
3	**Si-Ph 40**	**0.351**
4	**Si-Ph 50**	**0.341**
5	**Si-Ph 60**	**0.302**
6	**Si-Ph 70**	**0.292**
7	**C-Ph 30**	**0.712**
8	**C-Ph 40**	**0.653**
9	**C-Ph 50**	**0.608**
10	**C-Ph 60**	**0.597**
11	**C-Ph 70**	**0.595**

Table 3.9 Linear ablation Rate

Chapter 4 Results and Discussion

4.1 Introduction

This chapter depicts the results in graphical form after the completeness of tests results that are already reported in the previous chapter in tabulated form. For the purpose of comparison and discussion, results for both fillers silica aphenolic and carbon phenolic are presented on same axes.

4.2 Physico-Mechanical Properties

4.2.1 Density

It is clear from the fig 4.1 that density of ablative composites based on HNBR increases for the both types of the fillers with decrease in particle size. This increase in density is due to increase in surface area and good compaction of filler with matrix material as the particle size decreases. Moreover, density of the fabricated composite is also dependent on the specific gravity of additives and since specific gravity of silica Phenolic (1.23) is higher that neat sample of HNBR having specific gravity (1.035).It can also be concluded that silica phenolic gives slightly higher values of the density as compared to its counterpart.

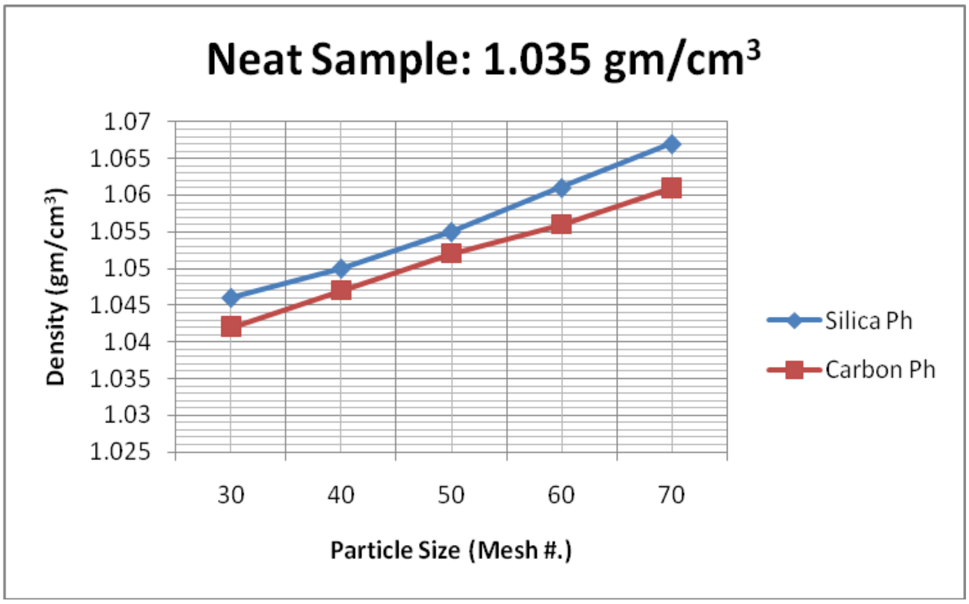


Fig 4.1 Comparison of Density

4.2.2 Hardness

The effect of particle size variation on the hardness of the composite is shown in the fig 4.2. It is quite evident that hardness of Ablative composites based on HNBR increases as the particle size of the filler decrease for the both types of the fillers. This increase in hardness is because more rigid filler particles replace the relative softer part of the rubber which also lowers the elasticity of the polymeric chains of the rubber. It can also be concluded that silica Phenolic gives slightly higher values of the hardness.

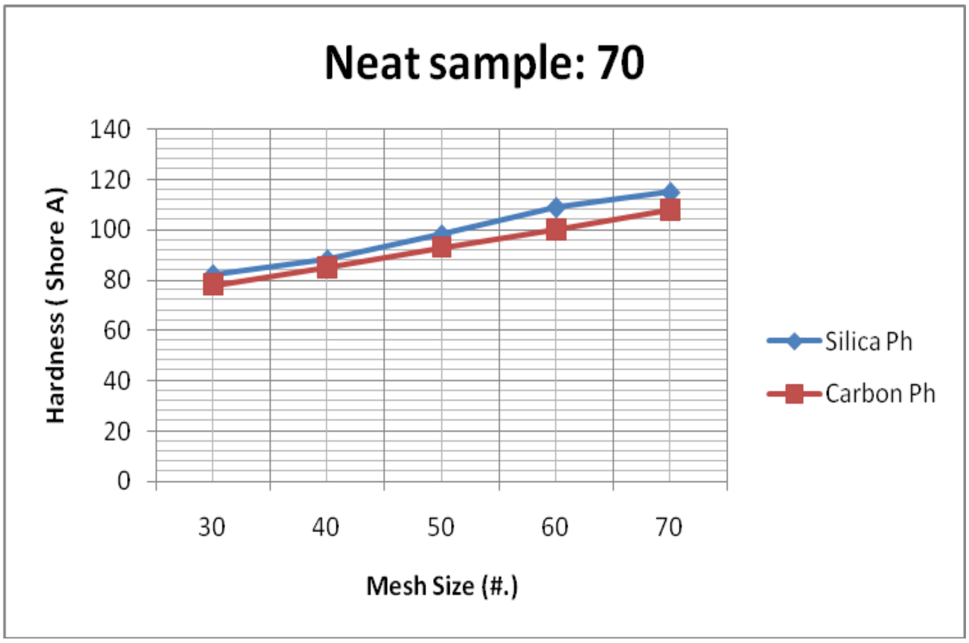


Fig 4.2 Comparison of Hardness

4.2.3 Tensile Strength

The effect of particle size variation on the tensile strength of the fabricated ablative composite is shown in the fig 4.3. It is evident that tensile strength of composites increases as the particle size of the filler decrease for the both types of the fillers. This increase in tensile strength can be explained by the fact that rubber filler interaction improves as the particle size of the filler decreases i.e. smaller the particle size higher will be interaction. It can also be concluded that silica Phenolic gives slightly higher values of the hardness.

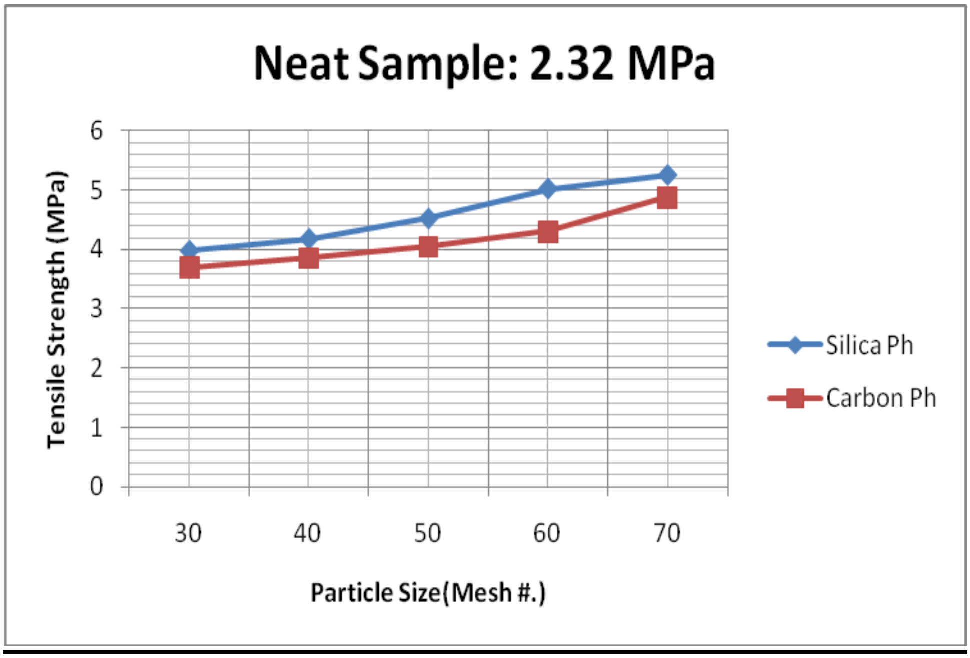


Fig 4.3 Comparison of Tensile Strength

4.2.4 Elongation at Break

The effect of particle size variation on the elongation at break of the composite is shown in the fig 4.4. It is clear that elongation at break of fabricated ablative composites decreases as the particle size of the filler decreases for the both types of the fillers. Since elongation at break measures the elastic behavior of the material ,this decrease in elongation at break is because more rigid filler particles replace the relative softer part of the rubber which also lowers the elasticity of the polymeric chains of the rubber. Moreover, Silica phenolic filler gives lower values of the elongation at break in comparison to its counterpart Carbon Phenolic.

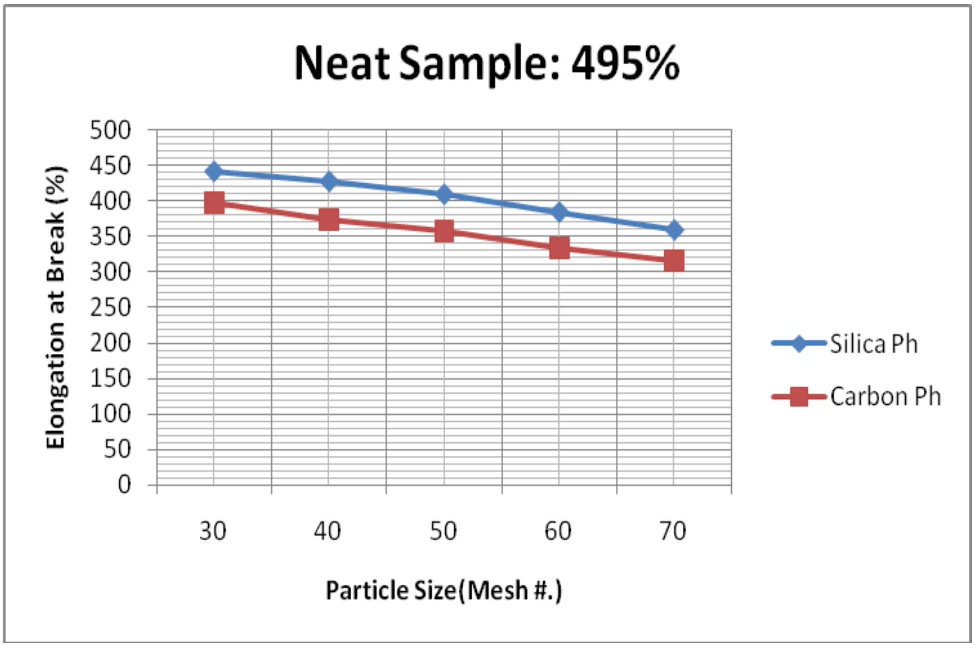


Fig 4.4 Comparison of Elongation at break

4.2.5 Initial Modulus

The effect of particle size variation on the initial modulus of the composite is shown in the fig 4.5. It is clear that the value of initial modulus of fabricated ablative composites increases as the particle size of the filler decreases for the both types of the fillers. Since initial modulus is the ratio of tensile strength and elongation at break, as tensile strength increases and elongation at break decrease as filler particle size decrease, so value of initial modulus increases. It can also be seen here also that Silica phenolic filler gives higher values as compared to its counterpart carbon phenolic.

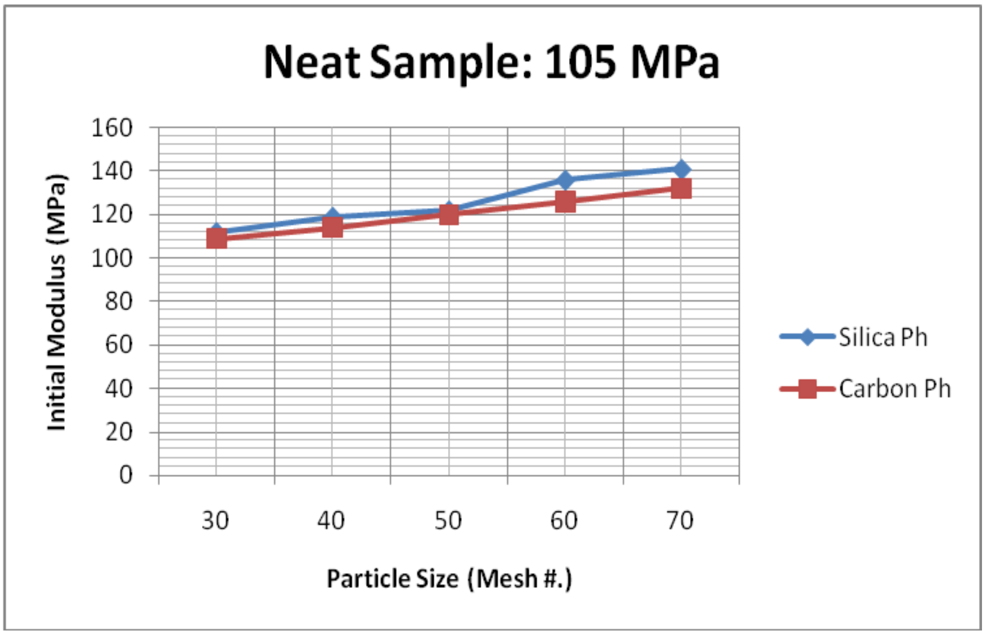


Fig 4.5 Comparison of Initial Modulus

4.3 Thermal Properties

4.3.1 Thermal stability Comparison

4.3.1.1 Silica Phenolic Filler

Thermal stability comparison of fabricated ablative composite using silica phenolic as filler is shown in fig 4.6 .Results obtained by TGA suggests that composites had superior thermal stability than the neat matrix of HNBR. It is also clear from The TGA patterns that thermal stability improves as particle size is reduced by considerable improvement in resistance to oxidation.

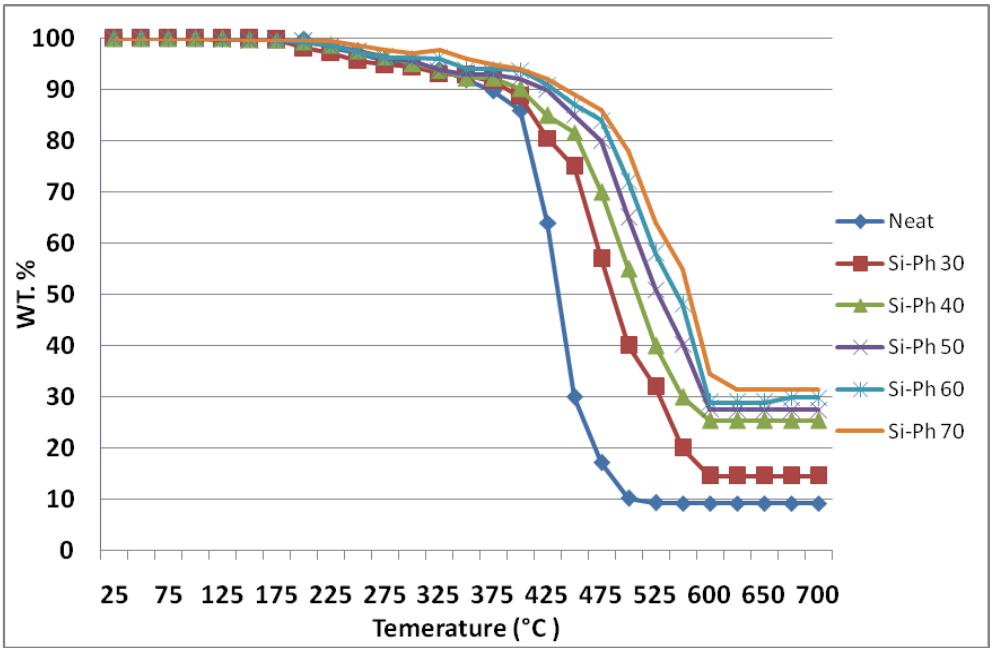
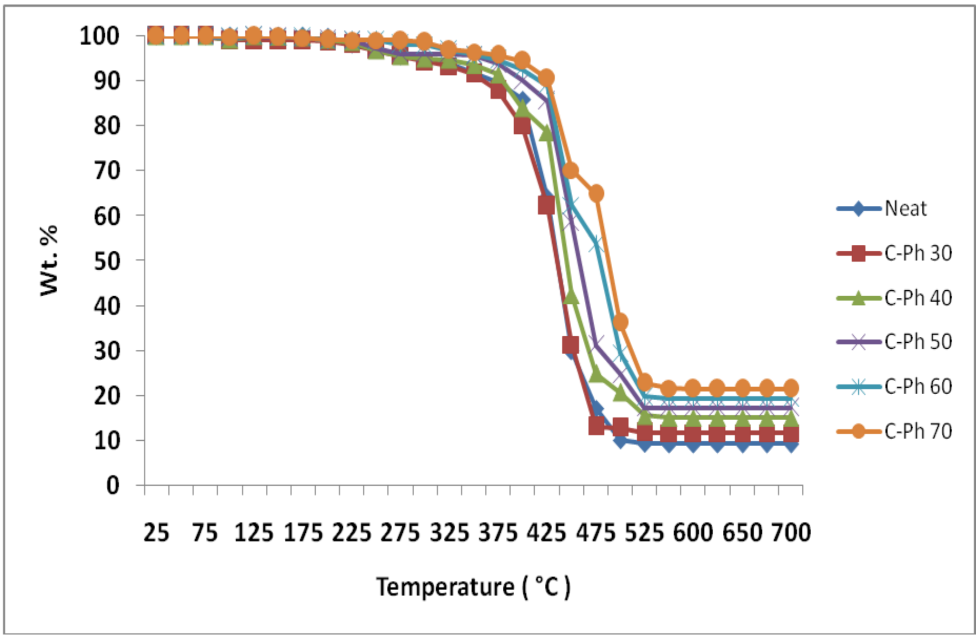


Fig 4.6 Comparison of Thermal stability (Silica Phenolic)

4.3.1.2 Carbon Phenolic Filler

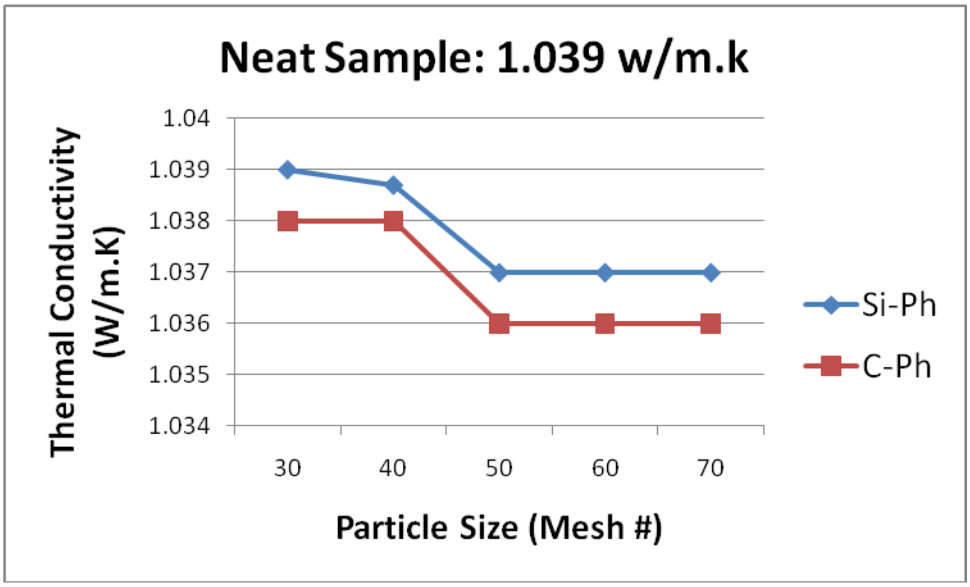
Thermal stability comparison of fabricated ablative composite using silica phenolic as filler is shown in fig 4.7 .Results obtained by TGA suggests that composites had superior thermal stability than the neat matrix of HNBR. It is also clear from The TGA patterns that thermal stability improves as particle size is reduced by considerable improvement in resistance to oxidation.



4.7 Comparison of Thermal stability (Carbon Phenolic)

4.3.2 Thermal conductivity

The effect of particle size variation on the thermal conductivity of the composite is shown in the fig 4.8. It is clear that thermal conductivity of fabricated ablative composites decreases as the particle size of the filler decreases for the both types of the fillers.. Moreover, Silica phenolic filler gives lower values of the elongation at break in comparison to its counterpart Carbon Phenolic.



4.8 Comparison of Thermal conductivity

4.4 Ablation Properties

Figure 4.9 shows the effect of filler particle size variation on the linear ablation rate on HNBR based ablative composites. It gives clear picture that as the particle size of the filler decreases, linear ablation rate also decreases .As the neat matrix is exposed to high temperature, matrix became charred and becomes unable to hold the burnt substrate and thus causes to increase the erosion rate. Results also indicates that incorporation of silica/carbon phenolic fillers into neat samples of HNBR helps to considerably reduce erosion rate because as the fabricated composites melt, they tend to produce a more viscous layer of residue that binds to substrate It can also be concluded that Silica phenolic filler gives good ablation results as compared to its counterpart carbon phenolic.

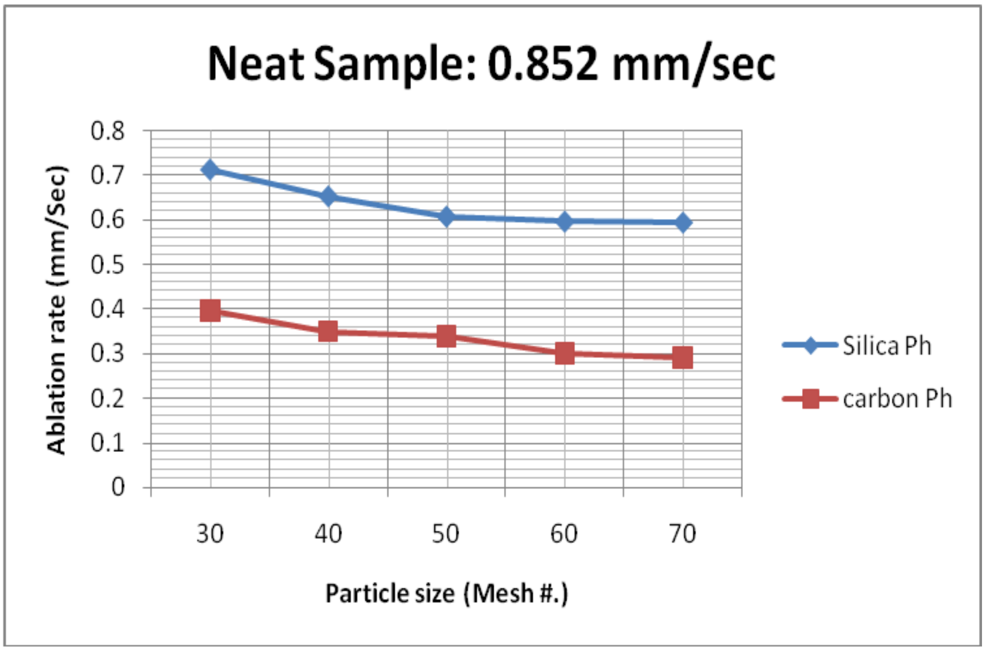


Fig 4.9 Comparison of Ablation rate

Chapter 5 Conclusions

During this experimental study, Ablative, Thermo mechanical and Physical properties of fabricated ablative composites based on HNBR by using Silica/carbon phenolic fillers of different particle size keeping amount of filler in each formulation fixed to 20 Phr (Parts per hundred rubber) were studied.

Following conclusions can be drawn from the study.

1. It can be depicted from experimental study that tensile strength increases with the decrease of filler particle size for both fillers, this increase is 126% for silica phenolic fillers and 100% for carbon Phenolic fillers as compared to neat HNBR without fillers. Silica phenolic fillers give better results of tensile strength as compared to its counterpart carbon phenolic.
2. It can be concluded that elongation at break decreases with the decreases of filler particle size for both of the fillers, this decrease is 27% and 36% for silica phenolic and carbon phenolic fillers respectively as compared to neat HNBR.
3. An increase in the values of initial Modulus of the composite was also found as filler particles became coarse to fine , this increase is 34 % for silica phenolic fillers and 26 % for carbon phenolic fillers. Silica Phenolic fillers give better results of tensile strength as compared to its counterpart carbon Phenolic.
4. There was also increasing trend among density and hardness results of newly fabricated ablative composites as filler particle size was decreased for both fillers. This increase in density was 3 % and 2.5 % for silica phenolic and carbon phenolic respectively and increase was 64 % and 55 % for silica phenolic and carbon phenolic fillers respectively.
5. There is a slight decrease in the thermal conductivity of composites when size of filler particles is decreased and no change in results were found after 50 mesh size of both fillers. The decrease is 0.2 % and 0.3 % for silica and carbon phenolic fillers respectively.
6. TGA results also indicated that thermal stability of newly fabricated ablative composites improved as compared to original neat sample of HNBR without fillers incorporation. Thermal stability was improved to 32 % and 19 % by filler particle size variation for silica phenolic and carbon phenolic fillers respectively.

7. Results of linear ablation rate also showed the ablation effectiveness of newly fabricated HNBR based ablative composites as compared to neat sample of HNBR without filler incorporation. It can be depicted from experimental study that linear ablation rate decreases with the decrease of filler particle size of both fillers, this decrease was 66 % for silica phenolic fillers and 33 % for carbon Phenolic fillers. Silica Phenolic fillers give better results of tensile strength as compared to its counterpart carbon Phenolic.

8. In general, Physico-mechanical, Thermal properties and Ablative properties of HNBR based composites can be improved effectively for optimal and desired results by decreasing particle size of the filler. Silica Phenolic with decrease in particle size has presented better results in terms of decrease in linear ablation rate, improved thermal stability, better mechanical and physical properties as compared to its counterpart carbon Phenolic filler.

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