STUDY ON SULPHUR CURED ETHYLENE PROPYLENE DIENE TERPOLYMER BASED INSULATION FOR LARGE COMPOSITE ROCKET MOTOR CASING

Submitted in partial fulfilment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

IN

CHEMICAL ENGINEERING

By

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CERTIFICATE

This is to certify that the thesis entitled "**Study on Sulphur Cured Ethylene Propylene Diene Terpolymer based insulation for large Composite Rocket Motor Casing"** being submitted by **Mr. I. KINGSTONE LESLEY JABEZ (Roll No: 718056)** for the award of the degree of Doctor of Philosophy (Ph.D) in Chemical Engineering to the National Institute of Technology, Warangal, India is a record of the bonafide research work carried out by him under our supervision. The thesis has fulfilled the requirements according to the regulations of this Institute and in our opinion has reached the standards for submission. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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<u>DECLARATION</u>

This is to certify that the work presented in the thesis entitled "**Study on Sulphur Cured Ethylene Propylene Diene Terpolymer based insulation for large Composite Rocket Motor Casing "** is a bonafide work done by me under the supervision of **Dr. Sarath Babu Anne and Dr. R. Manivannan** and was not submitted elsewhere for award of any degree.

I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included, I have adequately cited and referenced the original source. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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I.KINGSTONE LESLEY JABEZ

ABSTRACT

Internal insulation for large Composite Rocket Motor Casing (CRMC) is primarily intended as heat barrier material between the inner surface of the CRMC and the propellant in order to prevent the casing from reaching temperature which will endanger its structural integrity. Nitrile Rubber (Copolymer of acrylonitrile and butadiene) based insulation is popular for large CRMC and its performance as rocket motor insulation has been proven in several static tests and flight tests. Nitrile rubber based insulation, however, has certain disadvantages viz. higher specific gravity, lower ageing resistance (and hence limited life) and poor low temperature flexibility. These limitations made the propulsion experts think of alternative insulation having lower specific gravity, improved ageing resistance and better low temperature flexibility. Ethylene Propylene Diene Terpolymer (EPDM) Elastomer based insulation was identified to be a better alternative for Nitrile Rubber based insulation because of its lower specific gravity (EPDM rubber has the least specific gravity among the available elastomers), better ageing resistance and hence longer life and improved low temperature flexibility. This is because, EPDM Elastomer has unsaturation in the side chain (unlike Nitrile Rubber which has unsaturation in the backbone) and EPDM Elastomer based insulation has lower glass transition temperature than Nitrile Rubber based insulation. Despite, the abundant literature on EPDM Elastomer based insulation, its adoptability to large CRMC was remaining a distant dream due to non-availability of data on achieved physical, mechanical, thermal properties, erosion rate, heat of ablation and interface properties as required by insulation designer. This gave impetus to take up the research entitled "Study on sulphur cured Ethylene Propylene Diene Terpolymer based insulation (EPDM-S) for large Composite Rocket Motor Casing". In the research work, two potential formulations viz. EPDM with Kevlar and Silica as reinforcing fillers (herein after called EPDM with Kevlar) and EPDM with only silica as reinforcing filler (herein after called EPDM without Kevlar), meeting the insulation requirements were considered for the study. Cure behaviour of EPDM with Kevlar based insulation was studied in detail through novel approach with the help of instrumental techniques viz. DSC, TGA and FTIR leading to evolution of optimum cure cycle/cure condition. Process for production batch of size 10 kg was established for EPDM with Kevlar and EPDM without Kevlar. Insulations based on EPDM with Kevlar and EPDM without Kevlar were characterized for physical, mechanical, thermal properties, erosion rate, heat of ablation, thermal degradation behaviour through DSC and TGA, water absorption and drying behaviour, FTIR Spectroscopy and morphological study through Scanning Electron Microscope (SEM) and compared with proven Nitrile Rubber based insulation. Further, limited accelerated ageing study was carried out for insulation based on EPDM with Kevlar. Research brought out clearly the relative advantages and disadvantages of EPDM with Kevlar and EPDM without Kevlar and advantages and disadvantages of EPDM with Kevlar and EPDM without Kevlar over proven Nitrile Rubber based insulation against the requirements of insulation for large CRMC. The research paved way for the adoption of sulphur cured EPDM (EPDM-S) with Kevlar based insulation for large CRMC.

Key Words: EPDM; Kevlar; Large Composite Rocket Motor Casing; Insulation; ***Cure behavior;*** Cure ***Condition; Rheometer; Degree of Cure; Accelerated ageing;***

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LIST OF ABRREVIATIONS USED IN THE THESIS

Abbreviation	Expansion
EPDM	Ethylene Propylene Diene Terpolymer
EPDM-S	Sulphur cured Ethylene Propylene Diene Terpolymer based insulation
ENB	Ethylidene nor-bornene
DSC	Differential Scanning Calorimetry
TGA	Thermo Gravimetric Analysis
TMA	Thermo Mechanical Analysis
FTIR	Fourier Transformed Infrared spectroscopy
SEM	Scanning Electron Microscopy
MDR	Moving Die Rheometer
UTM	Universal Testing Machine
TDQ	2,2,4-trimethyl-1,2-dihydroquinone
TMTD	Tetramethyl thiuram disulphide
MBTS	Mercapto benzothiazyl disulphide
KP	Kevlar Pulp
CCF	Chopped Carbon Fiber
AP	Ammonium Polyphosphate
CB	Carbon black filler
CF/EP	Carbon Fiber/Epoxy Composite
PEG	Polyethylene glycol
CRMC	Composite Rocket Motor Casing
Rocasin	Nitrile Rubber based insulation (most commonly used for CRMC)
NBR	Nitrile Rubber (Acrylonitrile butadiene copolymer)
Perbunan 3445	A standard grade of Nitrile Rubber with medium acrylonitrile content
CSE	Chlorosulphonated polyethylene
EHSM	Elastomeric Heat Shielding Materials
MAH	Maleic anhydride
HTPB	Hydroxyl terminated polybutadiene (commonly used binder for solid propellant)
BEM	Ballistic Evaluation Motor
PAN	Polyacrylonitrile

Abbreviation	**Expansion**
TC90	Optimum cure time
TS2	Scorch time
ΔH	Heat of Exotherm
Q	Heat flux
A	Cross section area of specimens
t	Time of exposure
m_1	Initial mass of specimen before erosion testing
m_2	Final mass of specimen after erosion testing
T_g	Glass transition temperature

CHAPTER 1

INTRODUCTION

STUDY ON SULPHUR CURED ETHYLENE PROPYLENE DIENE TERPOLYMER BASED INSULATION FOR LARGE COMPOSITE ROCKET MOTOR CASING

Introduction:

Composite Rocket Motor Casing (CRMC) is realized by filament winding technique using PAN based carbon fibre (T-700, 12 K) and Epoxy resin (Epofine 1555 resin system and FH5200 hardener mixed in the ratio 100:27 by weight). Figure-1 represents the sectional view of CRMC with propellant, assembled with Nozzle and Igniter. Typical size of the CRMC for strategic system is as small as 1 metre diameter x 3.5 metre length (boss to boss) and as big as 2.2 metre diameter x 10 metre length (boss to boss). CRMC offers a weight saving of 30-40% as compared to metallic rocket motor casing made of maraging steel (MDN250). Besides that, the lead time of realization is also less for CRMC. Thus, CRMC is preferred over metallic rocket motor casing.

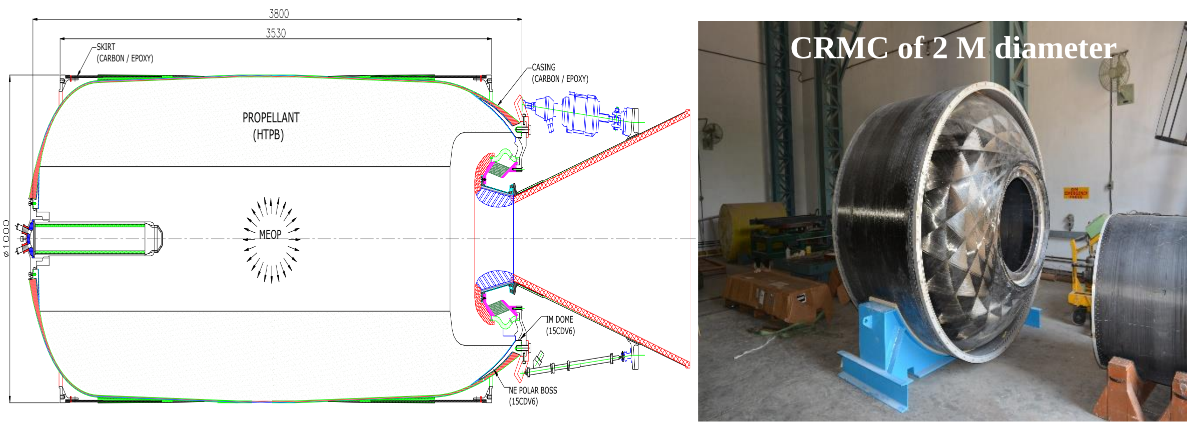


Figure-1 CRMC with Propellant after being assembled to Nozzle

Internal insulation of a rocket motor is a layer of low conducting material (preferably an elastomer) between the inner surface of the casing and the composite solid propellant. Internal insulation has to primarily protect the casing from hot combustion gases by preventing it from reaching temperature at which the composite material will lose its strength appreciably, thereby its structural integrity will be endangered. The secondary functions of insulation are as follows:

- Shields the propellant from casing strain.
- Ensures that the products of combustion do not impinge on the casing.

- Prevents the loss of pressure and damage from hot combustion products by sealing the casing joints.
- Guides combustion products into the nozzle in laminar flow to the greatest extent possible.

Insulation material is expected to have low specific gravity, high specific heat capacity, low thermal conductivity, high elongation and low erosion rate. For large Rocket Motors, Nitrile Rubber based insulation has been well established and proven in Static and Flight Tests. However, it has low shelf life thereby limits the useful life of Rocket Motor. This, in turn, reduces the overall life of Strategic Missiles delivered to the armed forces. Further, Nitrile Rubber based insulation has higher specific gravity (adding up inert mass). This is the background which gave impetus to take up the research work as EPDM Elastomer has the lowest specific gravity among the elastomers and long shelf life as compared to existing Nitrile Rubber based insulation. Besides the above, EPDM Elastomer based insulation is reported to have improved low temperature properties. Therefore, the research work entitled "**Study on Sulphur Cured Ethylene Propylene Diene Terpolymer (EPDM) based insulation for large Composite Rocket Motor Casing"**, was undertaken, wherein, two potential formulations of sulphur cured EPDM (EPDM-S) insulation viz. EPDM with Kevlar and EPDM without Kevlar were extensively studied and evaluated against the proven Nitrile Rubber based insulation for the requirements of insulation.

Requirements of insulation, originally considered to evaluate/qualify the Nitrile Rubber based insulation were taken as the basis for the evaluation of EPDM Elastomer based insulation too. The same are given in Table-1.

Table-1: Requirements of insulation for large CRMC

Sl. No.	Properties	Specification
1.	**Physical Properties**	
1.1	Shore- A Hardness	60 min
1.2	Density, g/ cm^3	As low as possible
1.3	Tensile Strength, kg/cm^2	100 min
1.4	% Elongation	600 min
2.	**Thermal Properties**	
2.1	Thermal conductivity, at 80°C cal/cm/sec/° C	$6.5x10^{-4}$ max

2.2	Specific heat at 80°C, cal/g/ ˚C	0.35 min
2.3	Coefficient of linear thermal expansion, $°C^{-1}$	$3X10^{-4}$ max
2.4	Erosion rate (@300 W/cm^2), mm/sec	0.20 max
3.	**Interface Properties**	
3.1	Rubber to Composite Peel Strength kgf/cm	5.0 min
3.2	Rubber to Propellant Peel Strength kgf/cm	0.6 min

CHAPTER 2

LITERATURE SURVEY

LITERATURE SURVEY

2.1 Literature Survey:

Extensive literature survey was carried out. 33 papers were identified in the field of EPDM as insulator and few others in the relevant areas. Literature garnered was up to date. Papers published in the year 2020 were also part of the collected literature. Literature was scrutinized and papers relevant to the topic of Research were segregated. Work already carried out in the relevant area, as evident from these papers, are summarized in Table-2.

Table-2: Summary of work already carried out as evident from Literature

Paper Details	Summary of work carried out/Findings
Jiang Li et al., (2018)	Ablation and erosion characteristics of EPDM composites under realistic solid motor conditions were studied using an ablation motor and an overload simulation erosion motor. Combined use of silica and aramid fibres can make the char layer form a uniform network like structure with a compact surface and a loose interior, improving both the heat shielding and erosion resistance performances of char layer. By increasing the silica and aramid fibre contents, the erosion resistance of EPDM composite was improved.
El-Dakhakhny et al., (2015)	Using hybrid reinforcement content Kevlar Pulp+ Alumina+Silica (KP + Al + Si) inside EPDM improves the performance of EPDM w.r.t. mechanical, thermal properties, ablation resistance and decomposition resistance. The best volume fraction which gives the best performance of the insulation material is 10phr KP+ 5 phr Al+5 phr Si.
El-Dakhakhny et al., (1989-1995)	Reinforcement of ethylene propylene diene monomer with Kevlar improves the performance of the material with respect to mechanical and thermal properties, while not improving well the performance with respect to ablation resistance. Using hybrid reinforcement (KP

	+ alumina + silica) within ethylene propylene diene monomer improves the performance of ethylene propylene diene monomer with respect to mechanical properties, thermal properties, ablation resistance and thermal decomposition resistance.
Jamal Gul et al., (2012)	Ballistic evaluation motor (BEM) results showed that Kevlar significantly enhanced ablative properties of EPDM by forming a tough uniform char layer on the surface. Experimental results revealed that mechanical properties such as tensile strength and hardness also increased with addition of Kevlar to EPDM. However, elongation at break of the EPDM drastically decreased with the addition of Kevlar loading. Thermal gravimetric analysis showed that Kevlar also enhanced thermal properties of EPDM.
Kesiya George et al., (2020)	The results demonstrated that nanosilica reinforced EPDM has shown significant enhancement for the tensile strength (up to 109%) and modulus. And the thermal conductivity of EPDM has been further lowered with the silica nanoparticles in addition to maintaining a lower density.
Sangita Singh et al., (2013)	EPDM when grafted with maleic anhydride (MAH) imparted polarity in the nonpolar EPDM matrix. Nanosilica imparts specifically better erosion resistance. Polyimide, nanosilica filled MAH-g-EPDM elastomer nanocomposites have been successfully prepared. Low density ($<1 g/cm^3$) and enhancement of desirable mechanical properties for the chemically grafted EPDM elastomer nanocomposites were achieved.
Santanu Datta et al., (1996)	Incorporation of up to 20phr of precipitated silica filler into a thermoplastic elastomer of composition 100 phr maleated EPDM rubber, 10phr zinc oxide, 1 phr stearic

	acid, 30 phr zinc stearate, results in an improvement of physical properties such as modulus, tensile strength and tear resistance. While the glass transition temperature (T_g) of the thermoplastic elastomer occurring around -37°C remains unaltered in the presence of the filler, the ionic transition (Ti) occurring around +50°C is shifted to higher temperature on filler incorporation. It is believed that, the ionic domains in the thermoplastic elastomer interact strongly with the polar sites on the filler surface.
Ashraf Fathy Ahmed et al., (2011)	A new method for the development (design, fabrication and characterization) of asbestos-free rubbers for use as rocket motor insulators is presented. Such insulation is based on chopped carbon fibre (CCF) and aramid fibre in pulp form as reinforcement for ethylene propylene diene monomer (EPDM) along with ammonium polyphosphate (AP) flame retardant agent. Six mm long CCFs and/or Kevlar pulp (KP) are dispersed in the EPDM polymeric matrix to obtain a homogeneous master batch for curing. Laminates composed of six alternative layers of these prepregs have been shown to exhibit better thermal, mechanical, physical, and ablative properties than their non-laminated counterparts.
Macro Rallini et al., (2018)	EPDM based Elastomeric Heat shielding materials (EHSMs) combined with glass microspheres at different percentages are evaluated. Material containing 20 phr micro balloons evidenced the best trade-off among all properties.
Macro Rallini et al., (2018)	In order to increase the thermo-oxidation resistance and char retention of EPDM/aramid fibre ablatives, boron based fillers can be considered in the material formulation of the SRM insulation liner. According to

	experimental results, all boron containing fillers allowed to increase the char yield. Boric Acid outperformed all the other boron containing fillers in all the metrics promoting an increased young modulus and deformability, combined with an improved thermal and ablation resistance. Boric Acid based formulation exhibited a good workability and the lowest density among all formulations (~0.97 ± 0.02 g/cm³).
Vojislav Jovanovic et al., (2013)	The paper investigated the effect of carbon black filler (CB) (loading 60-100 phr) in the cure kinetics, mechanical properties, morphology and thermal stability of NBR/EPDM rubber blends. Hardness and tensile strength increased but elongation at the break decreased with the increase in CB content for all NBR/EPDM rubber blend composites. NBR/EPDM/CB rubber blend composite is a less stable system according to lower temperatures of degradation compared to NBR and EPDM individually.
Çavdar S et al., (2010)	Thermal gravimetric analysis with in situ Fourier transform infrared (FTIR) spectra was taken, and the thermal degradation of the EPDM rubber was observed for varying amounts of vulcanising agent and filler content. Although the vulcanising agent improved the mechanical properties of the EPDM initially, a further increase in the vulcanising agents deteriorated the mechanical properties. Attenuated total reflectance FTIR spectrum confirmed the decrease in the relative degree of cross-linking with the increase in the vulcanising agent content.
Maurizio Natali et al., (2013)	In this study, Kynol fibre, a phenolic based reinforcement with high mechanical and thermal properties, was evaluated on this class of ablatives: It was found that EPDM/Kynol composition produced the

	char with the smaller dimensional change and the higher adhesion on the virgin material.
Tohid Farajpour et al., (2015)	The effect of Borax on the mechanical and ablation properties of three different ethylene propylene-diene terpolymer (EPDM) compounds containing 20 phr carbon fibre, 20 phr Kevlar or 10 phr/ 10 phr carbon fibre/ Kevlar was investigated. All formulations contained 30 phr fumed silica powder and 10 phr paraffinic oil. It was found that adding Borax to the composite samples containing carbon fibre or Kevlar fibre or their mixture with an equal ratio can increase the tensile strength, elastic modulus and hardness with a slightly decrease in the elongation at break of the rubber samples. The results of thermo-gravimetric analysis (TGA) on the various samples showed significant increase in the char yield at 670°C by adding Borax to the rubber compounds. Moreover, ablation resistance of samples was also improved by increasing Borax content. Meanwhile, density and thermal conductivity of the insulator were also reduced up to about 10% when the carbon fibre was replaced with the Borax.
Xialong Jia et al., (2013)	Effect of epoxy phenolic resin (EPR) on ablative and interfacial bonding properties of EPDM composites were evaluated. Ablative properties of EPDM composites were enhanced by two folds by incorporating 10 phr EPR. Interfacial shear strength of EPDM composites with carbon fibre/ epoxy (CF/EP) composites was increased by 55.6% by incorporating 10 phr EPR due to interfacial chemical reaction of epoxide group of EPR molecule from EPDM

	composites with amine group of hardener from CF/EP composites.
Suresh Kumar M S et al., (2008)	Bonding properties are found to improve when EPDM is blended with other polar rubbers like polychloroprene, chlorosulphonated polyethylene (CSE), etc. This type of polar polymer when blended with EPDM rubber enhances the insulator-to-propellant interface bonding. An attempt has been made to study the properties of EPDM–CSE based insulator by incorporating HTPB, a polar polymer as well as a polymeric binder, as an additive to the EPDM–CSE blend by varying the HTPB concentration.

2.2 Assessment of Literature and Gaps Identified:

Studies have been carried out to understand the effect of aramid fibre, carbon fibre, hybrid reinforcement (Kevlar pulp + alumina + silica), Nano silica, varying concentration of vulcanizing agent on the achieved properties/performance of EPDM insulator. Literature is available on improving the interface bonding properties of EPDM insulator to propellant by incorporating & varying the concentration of CSE & HTPB based bonding agent. Study on vulcanization kinetics, ageing in water & thermal degradation behaviour of EPDM insulator have also been reported. Extensive studies are reported on characterization/performance of EPDM insulation reinforced with glass micro balloons, Boron, Borax and Kynol fibre. Studies on EPDM/NBR blend, EPDM grafted with maleic anhydride are also reported.

Data (physical, mechanical, thermal, ablative, interface properties, water absorption, thermal degradation & ageing behaviour) required for evaluating the performance of EPDM insulation against the proven Nitrile Rubber based insulation for the insulation requirements of large Composite Rocket Motor Casing (CRMC) are not available in literature. This has made the more advantageous EPDM still a distant dream for large CRMC. In order to bridge the above gap, the research work entitled "Study on sulphur cured EPDM Elastomer based insulation for large composite rocket motor casing" was undertaken with the prime objective of characterizing the most potential formulations of EPDM-S Elastomer based insulation in comparison with the proven Nitrile Rubber based insulation thereby generate the data and instil confidence to the CRMC manufacturer and propulsion designer to accept EPDM-S Elastomer based insulation for large CRMC.

2.3 Schools of thought considered towards finalizing the objectives of Research:

As reported in the literature, nano-silica was thought of as filler in order to have better reinforcement in the EPDM-S insulation. However, keeping in view of the end application of the outcome of research, which is large CRMC internal insulation, which warrants seamless supply and consistent quality of filler for sustained production, it was decided to fulfil the requirements of insulation for large CRMC by reinforcing EPDM elastomer with only proven and indigenously available precipitated silica. As the requirement of insulation warrants thermal conductivity as low as possible, carbon fibre was not chosen as reinforcing filler as it can increase the overall thermal conductivity of the insulation. Further, in order to achieve better homogeneity of rubber compound, using twin screw extruder/kneader was thought of. However, the same was not considered due to the fact that fibrous filler viz. polyamide pulp (Kevlar pulp) used in the formulation may get damaged during the process of extrusion/ kneading thereby affect the end properties. Finally, it was decided to identify potential EPDM insulation formulation based on conventional fillers, carry out the compounding using two roll mill and characterize the same against the proven Nitrile Rubber based insulation for the requirements of insulation for large CRMC. Accordingly, the objectives of the Research were finalized as given in the subsequent section.

CHAPTER 3

OBJECTIVES OF RESEARCH AND RESEARCH METHODOLOGY

3.1 Objectives of the Research:

3.1.1 Assess the suitability of available formulation based on sulphur cured EPDM Rubber (EPDM-S) for the requirements of insulation for large CRMC.

3.1.2. Study on cure behaviour and optimization of cure condition for the sulphur cured EPDM Rubber based insulation (EPDM-S).

3.1.3. Evaluation of EPDM rubber against proven Nitrile rubber for the insulation requirements of large CRMC.

3.1.4. Comparative analysis of results to identify relative advantages and disadvantages w.r.t Nitrile rubber based insulation and improvement methodology to overcome the major disadvantages of EPDM rubber based insulation.

3.1.5. Limited accelerated ageing study to predict the life of EPDM rubber based insulation (EPDM-S).

3.2 Finalized Research Methodology:

The Research Methodology envisaged and followed is detailed below.

- ➢ Conducting trial to assess suitability of the available formulation with Kevlar & Silica as reinforcing fillers for the insulation requirements of large Composite Rocket Motor Casing (CRMC) (Discussed in Chapter 4)
- ➢ Customizing/optimizing cure cycle to suit the requirements of CRMC manufacturer for the finalized formulation based on: (Discussed in Chapter 5)
    - Rheometer characterization
    - Curing of mechanical slabs at the given temperature for varying duration
    - Evaluating mechanical properties, degree of cure by DSC and FTIR Spectroscopic Characterization of cured slabs.
    - Isothermal DSC and TGA run for cured slabs, if required, and finalizing the optimum cure cycle based on analysis of test data.
- ➢ Production of 10 kg batch for each of EPDM with Kevlar and Silica (herein after called EPDM with Kevlar), EPDM with only Silica (herein after called EPDM Without Kevlar) and proven Nitrile rubber based insulation and characterizing them comparatively for the requirements of large CRMC in terms of (Discussed in Chapter-6):

- Rheometer characterization
- Physical & mechanical properties
- Thermal properties viz. Thermal conductivity, Specific heat capacity & Coefficient of thermal expansion
- Ablative performance by Plasma Arc Jet testing for erosion rate and heat of ablation
- Water absorption and drying behaviour.
- Thermal stability by DSC & TGA
- Evaluation of interface properties of various interfaces encountered during insulation lining of CRMC
  - Composite-Rubber
  - Rubber- Rubber
  - Rubber – Propellant

- Analysis of characterization results leading to findings on merits/demerits of EPDM over proven Nitrile rubber based insulation (Discussed in Chapter 6)
- Corroboration of findings by instrumental techniques viz. SEM, FTIR Spectroscopy. (Discussed in Chapter 6)
- Limited accelerated ageing study to predict the life of sulphur cured EPDM insulation (Discussed in Chapter 7)

CHAPTER 4

TRIAL TO ASSESS THE SUITABILITY OF AVAILABLE FORMULATION BASED ON SULPHUR CURED EPDM RUBBER

TRIAL TO ASSESS THE SUITABILITY OF AVAILABLE FORMULATION BASED ON SULPHUR CURED EPDM RUBBER

4.1 Formulation:

Trial batch of size 4 kg was carried out by drawing guidelines from the literature and Formulation originally developed by High Energy Materials Research Laboratory (HEMRL, Pune). Baseline formulation adopted for the trial is given in Table-3. Base EPDM Rubber used in the trial is TER-4038 (Make: Versalis, Italy) as against H412 recommended by HEMRL. EPDM rubber compound with the formulation given in Table-3 is hereinafter called EPDM with Kevlar. Primary objective of the trial is to confirm the suitability of Formulation given in Table-3 for the requirements of insulation for large CRMC.

Table-3: Baseline Formulation used in 4 kg trial

Ingredients	Parts Per Hundred Rubber (PHR)
EPDM (TER 4038) + Liquid EPDM (Trilene 77)	100
Kevlar Pulp (RHENOGRAN P91-40/EPDM)	9
Silica (Ultrasil VN-3)	35
Zinc Oxide + Stearic acid	6
Sulphur + TMTD + MBTS	3.5
Rubber Oil-501 + Tackifier + Polyethylene glycol (PEG-400)	22
Titanium dioxide + Antimony trioxide + TDQ	3
Total	178.5

TMTD: Tetramethyl thiuram disulphide MBTS: Mercapto Benzothiazyl Disulphide

TDQ: Polymerized 2,2,4-Trimethyl 1,2-dihydroquinone

4.2 Specifications for Ingredients used:

Specifications for various ingredients used for the preparation of sulphur cured EPDM Rubber (EPDM-S) based insulation are given in Table-4 to Table-17. Specifications are intended to ensure the quality of ingredients in order to achieve batch to batch consistency in quality of insulation produced and to obtain reproducible results.

Table-4: EPDM-TER-4038 (Source-M/s Lotte Versalis Elastomers Co. LTD)

Mooney Viscosity [ML(1+4) 125^{o}C]	58 ± 5
ENB Content (%)	3.5 – 5.0
Propylene Content (%)	30 ± 5
Specific Gravity	0.85±0.05
% Volatile Content	1.00 (maximum)
% Ash content	0.75 (maximum)

Table-5: Liquid-EPDM- Trilene 77 (Source-M/S Lion Elastomers)

Specific Gravity	0.85±0.05
% Volatile Content at 100^{o}C	1.00 (maximum)
% Ash Content	0.75 (maximum)
% ENB Content	8-12
% Propylene Content	22-29
Melting Transition by DSC (°C)	40-60

Table-6: Kevlar- Rhenogran P91-40/EPDM (Source-M/s Lanxess)

Density at 20^{o}C (Compression) [g/ cm^3]	1.03 -1.09
% Residue of Ignition	1.5 - 4.5
% Kevlar as Fibre	36.5 to 41.5

Table-7: Ultrasil-VN-3 (Source-M/s Evonic Co. LTD)

Physical form	Fine white powder
Specific gravity	1.90 – 2.10
Silica as SiO_2	85% min.
Weight loss at 105^0C	7% max.
Weight loss on ignition	12.5% max.
PH of aqueous slurry	6.0 ± 0.5

Table-8: Diamond Sulphur DS-90

Specific gravity	1.90 – 2.10
Purity	99% (min.)
Insoluble Sulphur	Over 90 %
Acidity	Max. 0.15 %
Ash	Max. 0.15 %

Table-9: Zinc oxide and Stearic acid

Zinc oxide	
Physical form	White powder
Specific gravity	5.4 – 6.0
Particle size	4 μ max.
Purity	95 min.

Stearic acid	
Physical form	White wax like solid
Specific gravity	0.94 – 0.98
Melting point	68 – 70 ^{0}C
Purity	98% (min.)

Table-10: Vulkanol FH (Tackifier)

Appearance	Bright yellow viscous liquid
Viscosity at 50^{o}C	6000-15000 mPa.s
Refractive index at 50^{o}C	1.560-1.5750
Density at 50^{o}C (g/ cm^{3})	1.04-1.08

Table-11: Polymerized 2,2,4-Trimethyl 1,2-dihydroquinone (TDQ)

Appearance	Brown granules, free from agglomerates
Assay	90% (minimum)
Softening Point	87 - 93^{o}C
Specific gravity at 27^{o}C	1 to 3 %
% Volatile content	0.50 (maximum)
% Ash Content	0.25 (maximum)

Table-12: Polyethylene glycol (PEG-400)

Appearance	Clear liquid
Moisture Content	0.20% (maximum)
Residue on Ignition	0.05% (maximum)
Hydroxyl Value (mg KOH/g)	265.0- 295.0

Table-13: Rubber Oil-501 (Naphthenic oil)

Specific Gravity	0.85 to 0.90
Flash point	160^{o}C
Aniline Point	70-85^{o}C

Table-14: Titanium dioxide (TiO_2)

Appearance	White powder
Specific Gravity at 27^{o}C	3.7 to 3.9
Volatile matter at 105^{o}C	0.5% (maximum)

Table-15: Antimony Trioxide (Sb_2O_3)

Appearance	White powder
Purity	98% (minimum)
Volatile matter	0.1% (maximum)

Table-16: Tetramethyl Thiuram Disulphide (TMTD)

Physical form	Yellowish powder
Specific gravity at 30^{0}C	1.4 – 1.5
Total Sulphur content	51-53 %
Melting point	140^{0}C (Min)

Table-17: Mercapto Benzothiazyl Disulphide (MBTS)

Physical form	Yellow white to grey white powder
Specific gravity at 30^{0}C	1.3 – 1.4
Melting point	174 – 180^{0}C
Total Sulphur content	36-39 %

4.3 Mixing/Compounding Process:

Based on systematic lab scale endeavour, sequence of addition of ingredients and Mixing/Compounding Process was finalized. Finalized mixing/compounding process as followed in this trial is described in Table-18 and Table-19. Rubber mixing was carried out in two stages viz. premixing & final mixing, in two roll mill and 2 mm thick sheet was drawn. Table-18 summarizes the mixing activities performed during premixing and Table-19 summarizes the mixing activities performed during final mixing. During premixing, all ingredients other than sulphur and accelerators (TMTD & MBTS) are mixed and sulphur and accelerators are added during final mixing.

Table-18
Compounding: Premixing

Activity	No. of Passes between rolls / time of mixing
Cross mix Liquid EPDM (Trilene) with Rhenogran (Kevlar) on the mixing mill.	10-12 pass
EPDM (TER-4038) is taken on the mixing mill (with a close nip) for mastication.	5-7 pass
Cross mix EPDM and Liquid EPDM with Kevlar. If any trace of ingredients falls out from the rollers on the pan, it should be put back to the mix. The band is frequently parted off from the mill using scraper blades and returned to the nip.	5-7 minutes cross mixing
EPDM - Liquid EPDM-Kevlar blend +TDQ	5-7 pass
Half quantity of Precipitated Silica is incorporated in number of small lots with frequent addition of Stearic Acid, Rubber Oil & Vulkanol FH (tackifier) to reduce the torque load on the mill. Remaining Precipitated Silica is incorporated in number of small lots with the assistance of Rubber Oil, Mono PEG – 400 & tackifier.	Cross mixing 7-10 minutes
Add Zinc Oxide, Titanium Dioxide, Antimony Trioxide and carry out Cross mixing	5-7 minutes
After completing all the above additions, mixing is continued to get a uniform dispersion. The mix is released from the mill as continuous sheeting of about 2 to 3 mm thick. This is rolled up and kept in ambient condition for a minimum of 24 hours for cooling and de-aeration.	5-10 minutes

Table-19
Compounding: Final mixing

Activity	No. of Passes between rolls /time of mixing/Remarks
The Premix is once again taken up on the mill after minimum 24 hours of de-aeration and is warmed up by mastication.	5-7 pass
MBTS, TMTD and Sulphur addition and cross mixing in Mixing mill	5-7 minutes
Mix is drawn in the form of Sheet	Thickness of the sheet is maintained within 2 ± 0.2 mm

During final mixing, internal cold water (at 24-26°C) circulation at required flow rate is maintained within the rolls of the two roll mill so that the surface temperature of the rubber does not exceed 65°C at any point of time. This is due to the reason that any increase in the temperature of the insulation beyond 70°C because of frictional heat build-up could lead to scorching/premature vulcanization, resulting in deterioration of the mechanical properties of the insulation. Figure-2 depicts the Rubber Compounding stage of the 4 kg trial.

Figure-2: Rubber Compounding in progress

4.4 Rheometer Characterization:

Samples were drawn from unvulcanised EPDM Rubber compound in the form of sheet and subjected to Rheometer Characterization using MDR 3000 at frequency of 1.67 Hz and amplitude of 0.50°. Rheometer characterization was carried out at 140° for 4 hours (cure condition in general followed for EPDM Elastomer) and 120° for 6 hours (cure condition preferred for CRMC owing to Glass Transition Temperature (T_g) constraints). Figure-3 represents the Rheometer curve generated at 140°C/4 hours and Figure-4 represents the Rheometer curve generated at 120°C/6 hours.

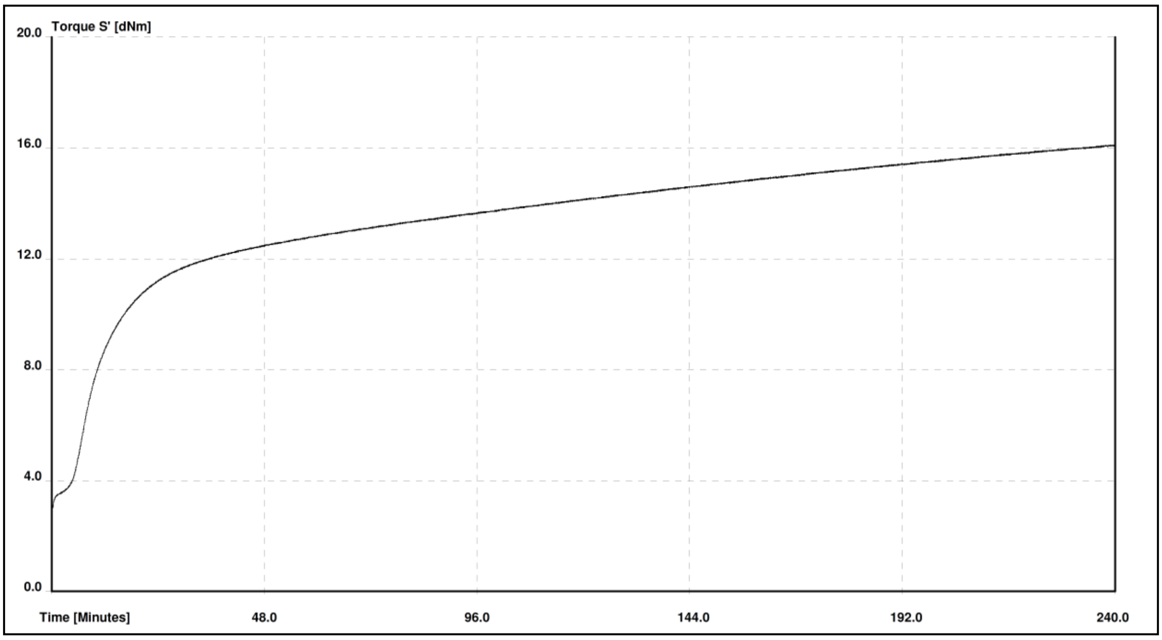


Figure-3: Rheometer curve generated at 140°C/4 hours

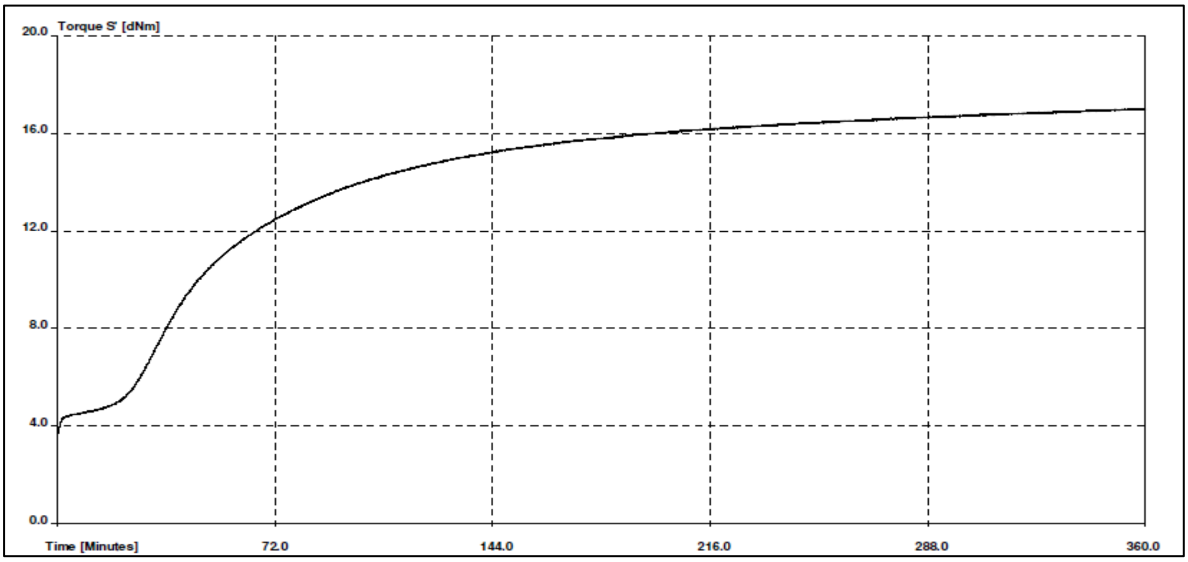


Figure-4: Rheometer curve generated at 120°C/6 hours

Maximum and Minimum Torque, scorch time (TS2) and optimum cure time (TC90) as obtained from the Rheometer data are summarized in Table-20 for both the cure conditions,

Table-20: Rheometer Characteristics

Cure Condition	Maximum Torque (dNm)	Minimum Torque (dNm)	Scorch Time TS-2 (minutes)	TC-90 (minutes)
140°C/4hrs	16.10	3.00	4.76	154.63
120°C/6hrs	17.00	3.67	12.79	170.03

As evident from Figure-3 and 4, curing does not reach completion at 140°C/4 hours and 120°C/6 hours as Rheometer curves are progressive at both these temperatures. However, curing was carried out at these temperatures to check if required mechanical and thermal properties will still be achieved.

4.5 Physical and Mechanical Properties:

From the 2 mm thick sheet drawn (Section 4.3) from the unvulcanised EPDM Rubber compound, four number of 150 mm x150 mm size slabs (thickness of 2 mm) were drawn and assembled inside the sheet mould. Two slabs were cured at 140°C/4 hours and the other two were cured at 120°C/6 hours in calibrated oven. Shore-A hardness of the cured slabs was tested as per ASTM D 2240 and density was tested as per ASTM D 792 by drawing samples from the cured slabs. Dumbbells conforming to ASTM D412 were cut in warp (longitudinal) direction in one slab and weft (transverse) direction in the other slab (out of 2 slabs cured at each cure condition) using standard dumbbell cutter and tested for mechanical properties as per ASTM D412. Test results of Physical and Mechanical properties thus evaluated are given in Table-21. Value in the parenthesis indicates minimum and maximum of test results for the given property.

As evident from Table-21, achieved mechanical properties are better in case of slabs cured at 120°C/6 hours as the average tensile strength and % Elongation achieved at this cure condition are well above the respective minimum required values and the scatter in the test results is also quite less. But, in case of slabs cured at 140°C/4 hours, scatter is quite high in the achieved mechanical properties and % Elongation (560) in the warp direction is lower than the minimum required value of 600.

Table-21

Physical and Mechanical Properties

Property	Requirements	Test Result for slabs cured at 140°C/4 hours	Test Result for slabs cured at 120°C/6 hours	Test Method/ Standard
Physical Properties				
Density g/cm^3	As low as possible	1.04-1.06	1.02-1.06	ASTM D792
Shore-A hardness	60 (min)	62-72	62-70	ASTM D2240
Mechanical Properties				
Tensile Strength kg/cm^2 Warp Weft	100 (min)	126 (110-142) 111 (85-157)	165 (158-175) 105 (90-124)	ASTM D 412
% Elongation Warp Weft	600 (Min)	560 (530-586) 615 (572-650)	656 (638-669) 614 (599-635)	ASTM D 412

4.6 Thermal Properties:

From the 2 mm thick sheet drawn (Section 4.3) from the unvulcanised EPDM Rubber compound, two number of 150 mm x 150 mm size slabs (thickness of 6 mm) were made by placing three numbers of 150 mm x 150 mm size slabs, one over the other inside the appropriate sheet mould. One slab was cured at 140°C/4 hours and the other was cured at 120°C/6 hours in calibrated oven. From each 6 mm thick slab thus made, specimen of diameter 50 mm and thickness of 6 mm was cut and subjected to thermal conductivity determination using Guarded Heat Flow Meter as per ASTM E1530. Further, specimens were drawn from above 6 mm thick slabs and specific heat was measured using DSC (TA Instrument Discovery DAC) as per ASTM E1269 and coefficient of linear thermal expansion was measured using TMA as per ASTM E831. Cylindrical specimens of diameter 10 mm and length 25 mm were moulded at 140°C/4 hours and 120°C/6 hours using specially designed moulds for testing of erosion rate. Erosion test was carried out in the Plasma Arc Jet Facility by simulating a heat flux of 300 W/cm^2. VSSC, ISRO rendered necessary testing support for evaluation of all the above thermal properties and erosion rate. Test results of thermal properties and Erosion Rate, thus evaluated at VSSC, ISRO, are given in Table-22.

Table-22: Thermal Properties and Erosion Rate

Properties	Requirement	Test Result for slab cured at 140°C/4 hours	Test Result for slab cured at 120°C/6 hours	Test Method/Standard
Thermal conductivity, at 80°C, Cal/cm. sec.°C (Max)	6.5×10^{-4}	5.4×10^{-4}	5.4×10^{-4}	ASTM E 1530
Specific heat at 80°C Cal/g.°C (Min)	0.35	0.44	0.45	ASTM E 1269
Coefficient of linear thermal expansion $°C^{-1}$ (Max)	3.0×10^{-4}	3.1×10^{-4}	3.0×10^{-4}	ASTM E 831
Erosion rate at 300 W/cm^2 mm/sec (Max)	0.20	0.12-0.13	0.11	By plasma arc jet

As evident from Table-22, achieved thermal properties and Erosion Rate are well comparable for both the cure conditions. Further, thermal conductivity, specific heat and Erosion Rate meet the respective requirements irrespective of whether cured at 140°C/4 hours or 120°C/6 hours. Coefficient of thermal expansion is slightly on the higher side, however, very marginally. It may be noted that the requirements given above have been evolved for the large CRMC on the basis of proven Nitrile Rubber based insulation.

4.7 Findings:

Available potential formulation, given in Table-3, has been verified for the insulation requirements of large CRMC through 4 kg trial batch. Physical and Mechanical properties of insulation (made in the trial batch of 4 kg), cured at 120°C/6 hours, are found to meet the requirements and the achieved mechanical properties at this cure condition are found to have less scatter. Physical properties of insulation cured at 140°C/4 hours are found to meet the requirements, whereas, their mechanical properties are found to be more scattered and % Elongation in the warp direction is found to be lower than the minimum required value of 600. Thermal properties and Erosion rate are almost meeting the requirements irrespective of the cure condition. Thus, Formulation given in Table-3 (herein after called EPDM with Kevlar) is found to be suitable for the requirements of insulation for large CRMC, if insulation made

of this is cured at appropriate cure condition. As per the data generated in this 4 kg trial batch, 120°C/6 hours seems to be better cure condition than 140°C/4 hours. The above observation, in combination with the fact that Rheometer curves (Figure-3 and Figure-4) at 140°C (run for 4 hours) and 120°C (run for 6 hours) are progressive (torque increases with time), has given the necessary impetus to carry out the detailed study on the cure behaviour of sulphur cured EPDM insulation based on formulation given in Table-3. The prime objective of the study on the cure behaviour is to understand scientifically why the properties achieved at 120°C/6 hours are better and the study was further aimed to find out optimum cure condition/cycle in order to reap the full benefits of sulphur cured EPDM (EPDM-S) insulation. The study on cure behaviour, thus carried out, is discussed in Chapter-5. Further, the scatter in the achieved mechanical properties raised scepticism over the distribution of Kevlar on EPDM matrix. Therefore, in order to understand the influence of Kevlar on the overall achieved properties of insulation, it was decided to evaluate the characteristics of insulation by using only precipitated silica as reinforcing filler. Accordingly, in the formulation given in Table-3, 35 phr of silica and 9 phr of Kevlar Pulp (RHENOGRAN P91-40/EPDM) were replaced by 44 phr of silica alone and 10 kg batch of insulation was made, which is hereinafter called EPDM without Kevlar. 10 kg insulation made using EPDM with Kevlar formulation and 10 kg with insulation made using EPDM without Kevlar were characterized in comparison with proven Nitrile Rubber based insulation. Comparative characterization thus carried out, is discussed in Chapter-6. Thus, Chapter-4 laid foundation for Chapter-5 and Chapter-6.

CHAPTER-5

STUDY ON CURE BEHAVIOUR AND OPTIMIZATION OF CURE CONDITION FOR EPDM-S INSULATION

STUDY ON CURE BEHAVIOUR AND OPTIMIZATION OF CURE CONDITION FOR EPDM-S INSULATION

5.1 Introduction:

As per the findings of Chapter-4, 120°C/6 hours seems to be better cure condition than 140°C/4 hours for insulation based on EPDM with Kevlar. Rheometer curves (Figure-3 and Figure-4 of Chapter-4) at 140°C (run for 4 hours) and 120°C (run for 6 hours) are progressive (torque increases with time). Above findings of Chapter-4, has given the necessary impetus to carry out the detailed study on the cure behaviour of insulation based on EPDM with Kevlar as per formulation given in Table-3 of Chapter-4. The prime objective of this study is to understand scientifically why the properties achieved at 120°C/6 hours are better and to evaluate the most optimum cure condition for EPDM-S insulation as a spin off.

5.2 Recipe/Formulation used for Study:

EPDM elastomer with Kevlar pulp and precipitated Silica as reinforcing filler compounded in accordance with baseline recipe detailed in Table-3 of Chapter-4, was considered for the study. EPDM of grade TER-4038 of 74% Ethylene content and Mooney viscosity 62 (ML 1+4 (125°C)), was the primary polymer. Trilene-77 of 10.5 % Diene content was the secondary polymer in the recipe. EPDM and liquid EPDM were used as the base rubber. 10 kg of EPDM rubber, as per the formulation given in Table-3 of Chapter-4, was produced as per Compounding process detailed in Table-18 and Table-19 and drawn into sheet of length 6 meter, width 660 mm and thickness 2 mm. Test specimens were removed and subjected to Rheometer characterization. Samples were cured for physical and mechanical properties evaluation at different temperatures say 120°C, 140°C, 150°C and 160°C for varying durations.

5.3 Rheometer Characterization:

Rheometer study was carried out using MDR 3000 at frequency of 1.67 Hz and amplitude of 0.50°. Rheometer data was generated at four temperatures. Rheometer curves generated at 120°C, 140°C, 150°C and 160°C are given in Figure- 5, 6, 7 and 8 respectively.

As evident from the Figure-5, 6, 7 and 8, Rheometer curves are progressive up to test duration of 8 hours at 120°C. They are progressive up to 2 hours and 3 hours at 150° and

160°C respectively. Thereafter, the curves seem to be saturated for a short while before becoming progressive once again (secondary rise) even up to 6 hours at 150°C and 7 hours at 160°C. This observation is quite contradictory to that of proven Nitrile Rubber based insulation, whose Rheometer curves at 120°C and 150°C are given in Figure 9 and 10 respectively.

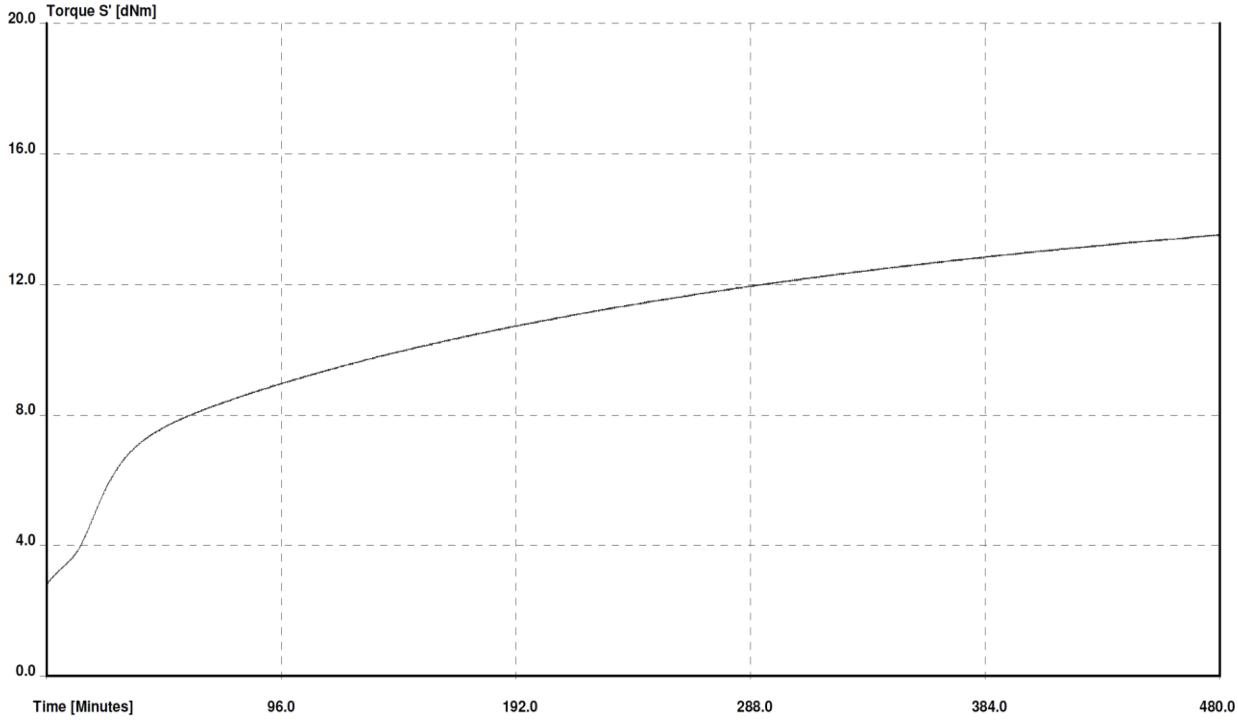


Figure-5: Rheometer Curve generated at 120°C up to 8 hours for EPDM-S

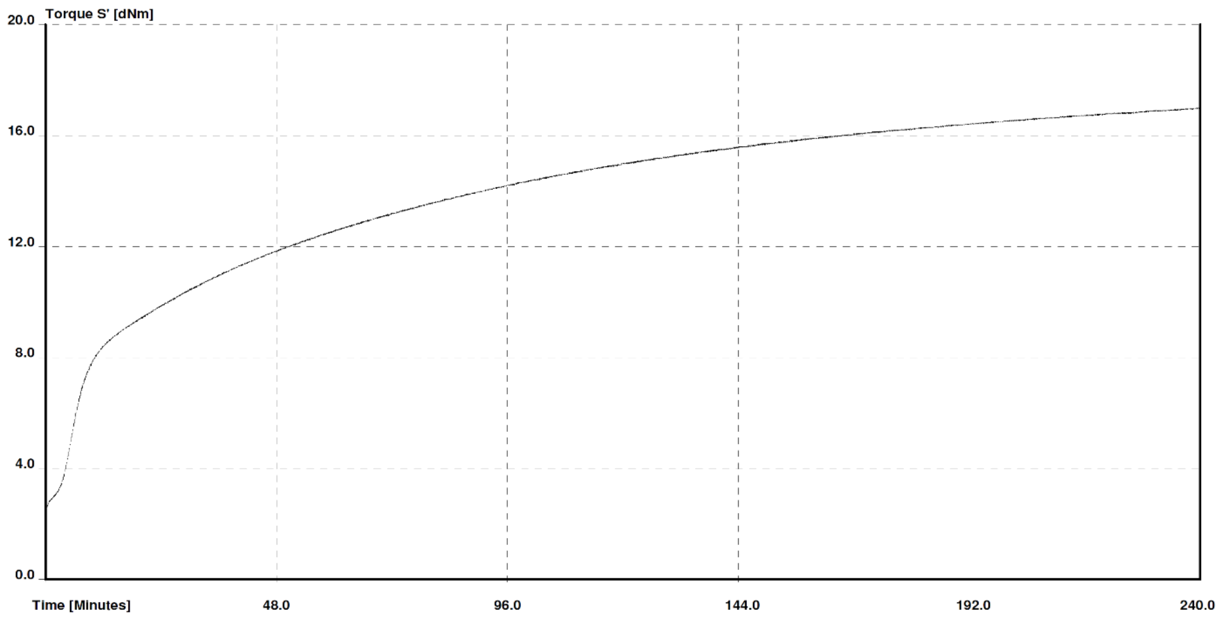


Figure-6: Rheometer Curve generated at 140°C up to 4 hours for EPDM-S

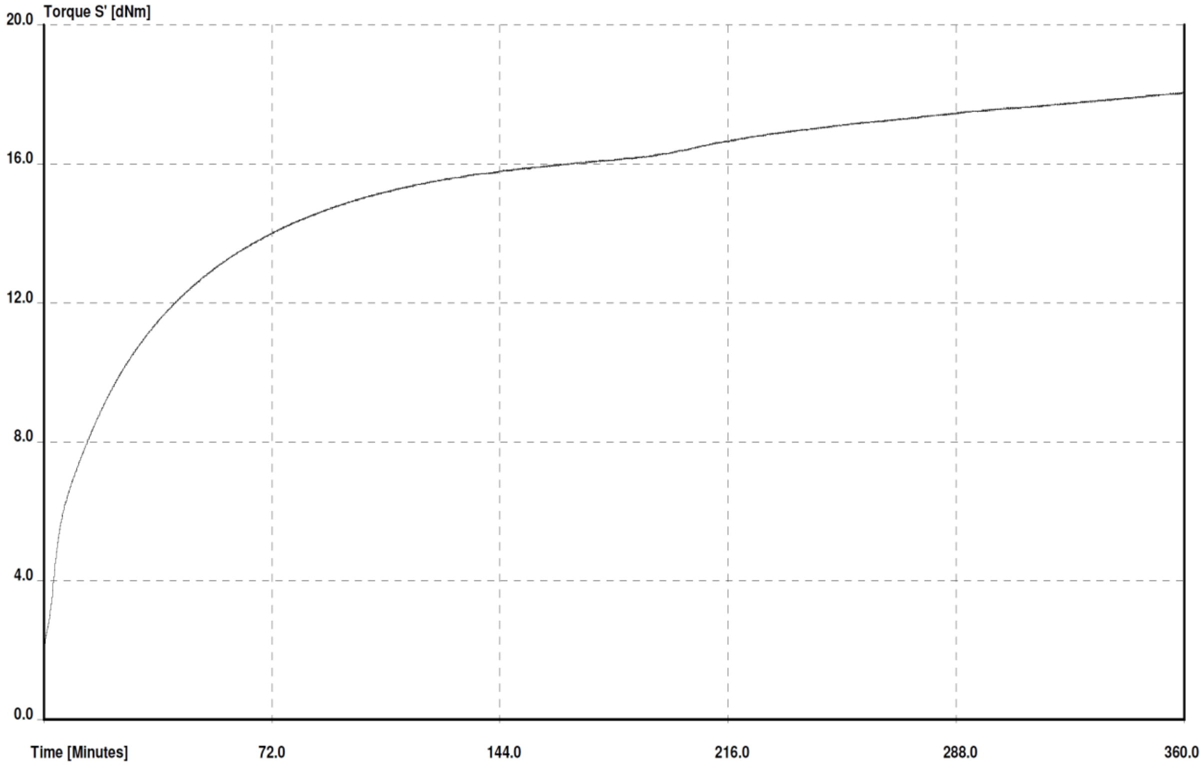


Figure-7: Rheometer Curve generated at 150°C up to 6 hours for EPDM-S

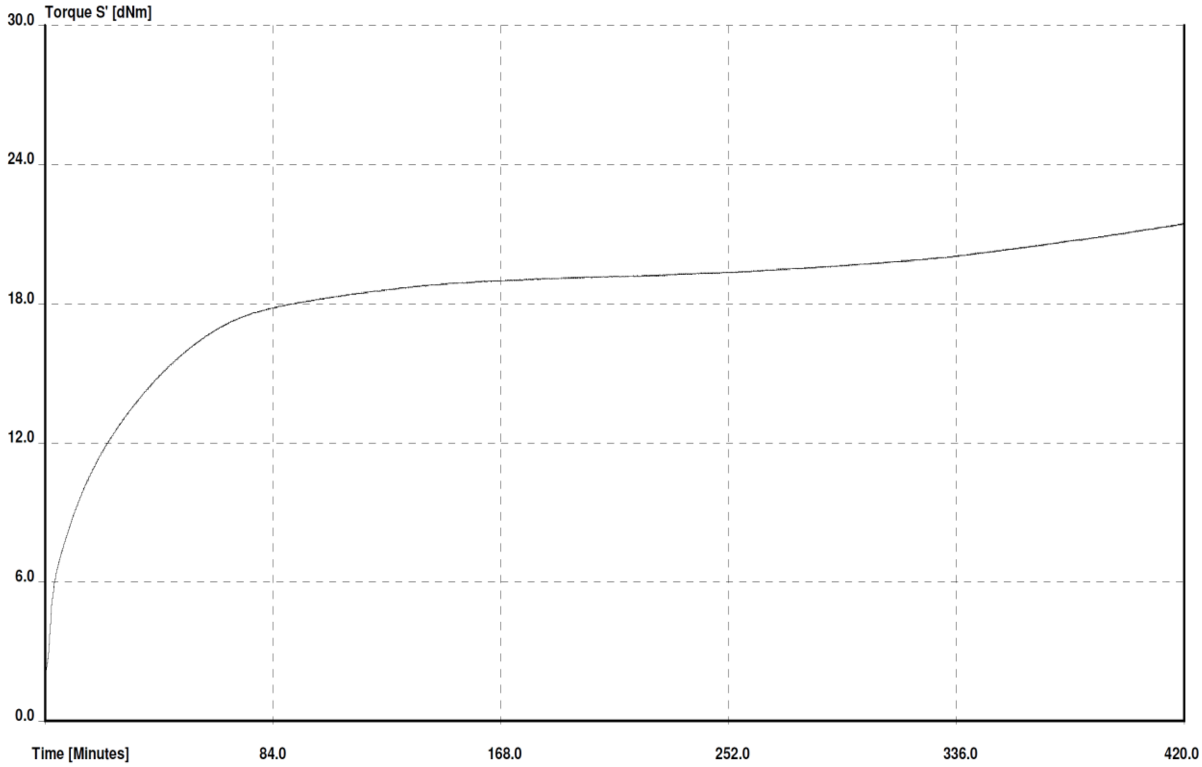


Figure-8: Rheometer Curve generated at 160°C up to 7 hours for EPDM-S

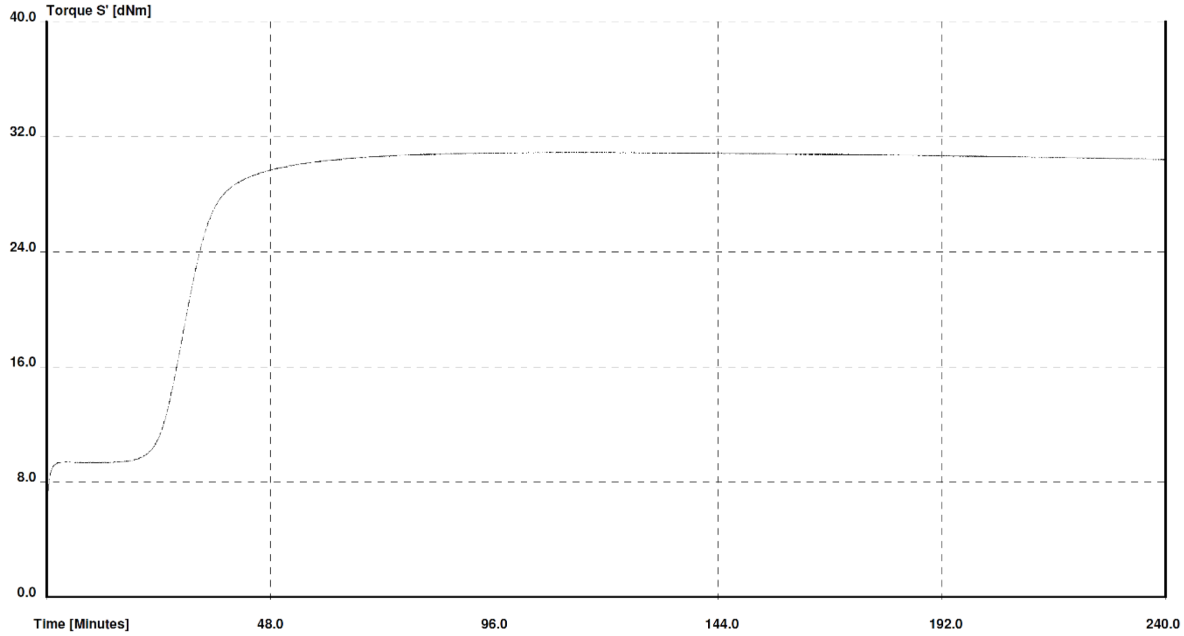


Figure-9: Rheometer Curve generated at 120°C for Nitrile Rubber based insulation

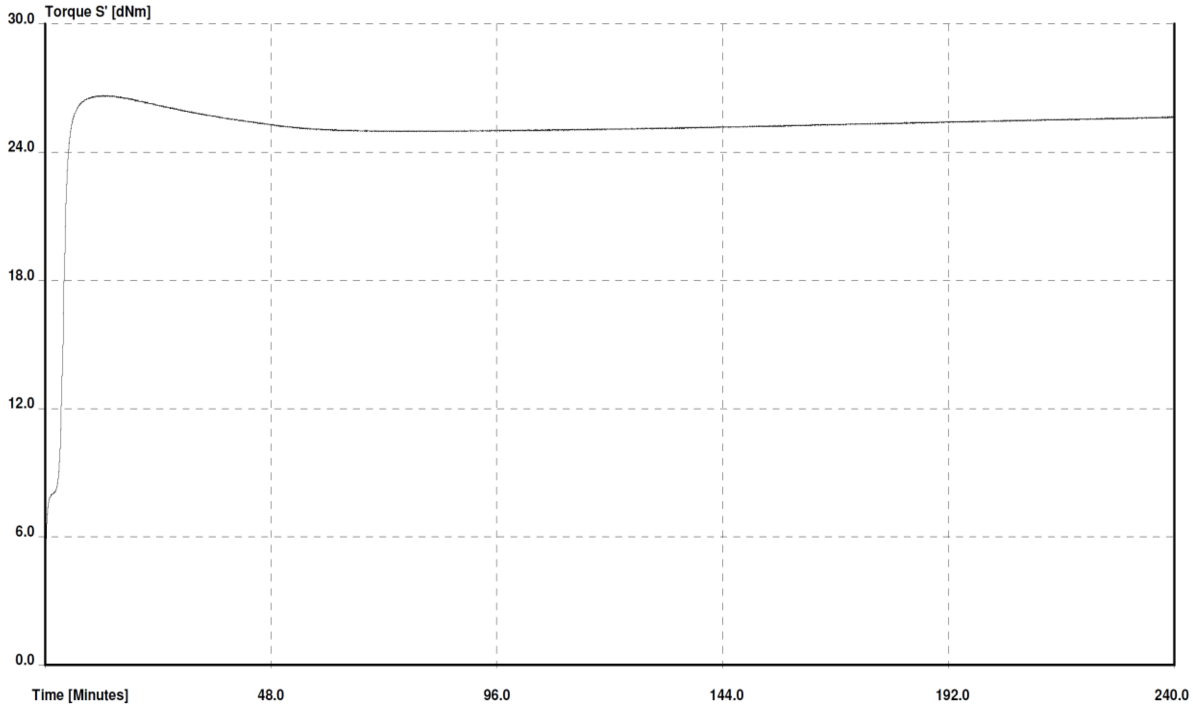


Figure-10: Rheometer Curve generated at 150°C for Nitrile Rubber based insulation

As evident from Figure-9 and 10, Nitrile Rubber based insulation attains completion of cure well within 1 hour both at 120°C and 150°C as the Rheometer curves reach saturation.

But, Rheometer curve of EPDM-S is progressive even at elevated temperature for a longer duration say 160°C for 7 hours, as though curing is incomplete, thereby warranting long cure times even at elevated temperature (160°C). However, long cure time at elevated temperature is not preferable from the manufacturing point of view and given the probability of thermal degradation. Therefore, it was decided to cure the samples at different temperatures for varying durations and subject the same to mechanical testing, DSC, Isothermal TGA and FTIR in order to decide upon the required cure condition.

5.4 EXPERIMENTAL STUDY:

5.4.1 Mechanical Properties Evaluation:

Samples in the form of 150 x 150 mm slabs were placed inside preheated mould. Mould was pre-heated to the given temperature of cure before placing EPDM-S slabs. Samples (inside the mould) were vulcanised in oven at 120°C for a duration of 6 hours and 8 hours. Similarly, samples were vulcanised at 140°C for a duration of 4 hours. At 150°C, samples were vulcanized for a duration of 45 minutes, 3 hours and 6 hours which correspond to 90% of the maximum torque of initial saturation (transient), initial saturation (transient) and additional duration to account for the secondary increase exhibited by the Rheometer curve (Figure- 7, Rheometer curve at 150°C for 6 hours), respectively. Dumbbells were cut from the cured slabs both in warp and weft directions (total 10 Nos; 5 in warp direction and 5 in weft direction from each slab) and tensile testing was carried out as per ASTM standard. Dumbbells were tested using UTM of INSTRON make. Physical properties (Density and hardness) were tested as per ASTM D792 and ASTM D2240.

5.4.2 DSC Study:

Limited literature is available on evaluation of cure behaviour of EPDM by DSC (M.D. Stelescu et al., 2010 and N.C. Restrepo-Zapata et al., 2015). DSC was carried out using DSC instrument of make TA Instruments Discovery DAC employing a heating rate of 10°C/min under Nitrogen environment. Initially unvulcanised rubber compound pertaining to the same batch of EPDM-S was subjected to DSC followed by samples cured at various cured conditions as detailed in Section 5.4.1. The degree of cure was computed based on heat of exotherm obtained from DSC run as follows.

Degree of Cure= $\{\mathbf{1} - (\mathbf{\Delta H\ Residual\ Cure/\Delta H\ Full\ Cure})\}$

5.4.3 Characterization by FTIR spectroscopy:

FTIR spectroscopy was determined using Spectrometer of Agilent make. Uncured EPDM-S and samples cured under different conditions as detailed in Section 5.4.1 were subjected to FTIR Spectroscopy. Peak/band and its relative height obtained at a wave number of 1537cm^{-1} which corresponds to C-S (sulphur crosslink) was monitored and compared.

5.5 RESULTS & DISCUSSION:

5.5.1 Mechanical Properties:

Test results of physical properties (Density and Shore-A hardness) of different cure conditions are given in Table-23 against insulation requirements of large CRMC. Test results of mechanical properties (Tensile strength and % Elongation) for various cure conditions are given in Table-24 against insulation requirements. Achieved tensile strength at various cure conditions are graphically represented in Figure-11 and the achieved % Elongation at various cure conditions are graphically represented in Figure-12.

Table-23: Physical properties achieved of various cure conditions

Properties	Insulation Requirements	Cured @ 120°C		Cured @ 140°C	Cured @ 150°C		
		6 hours	8 hours	4 hours	45 minutes	3 hours	6 hours
Shore-A Hardness	60 minimum	65-69*	70-73	66-71	67-69	75-78	76-79
Density (g/cm^3)	As low as possible	1.06[#]	1.05	1.02	1.05	1.05	1.06

*Values indicate the minimum and maximum of test results

[#]Values indicate the average of test results

Table-24: Mechanical properties achieved of various cure conditions

Properties	Insulation Requirements	Cured @ 120°C		Cured @ 140°C	Cured @ 150°C		
		6 hours	8 hours	4 hours	45 minutes	3 hours	6 hours
Tensile Strength (kg/cm^2)	100 minimum	140 (126-153)[a]	104 (69-145)	85 (66-100)	126 (119-133)	132 (106-154)	101 (65-139)
% Elongation	600 minimum	665 (642-699)	615 (553-674)	573 (528-622)	759 (742-787)	573 (535-629)	492 (412-533)

[a] Values in the parenthesis indicate the minimum and maximum of test results

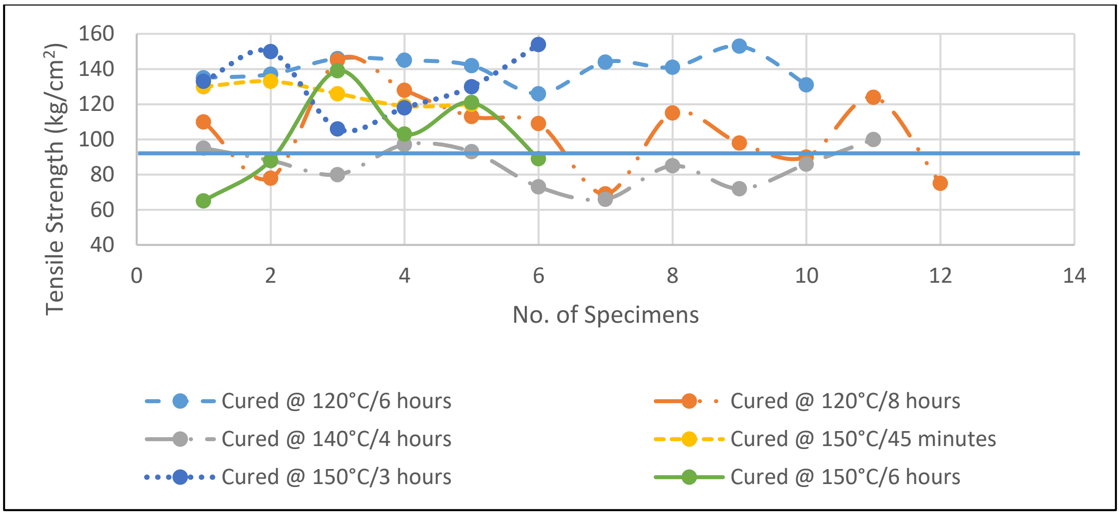


Figure-11: Achieved Tensile Strength at various cure conditions

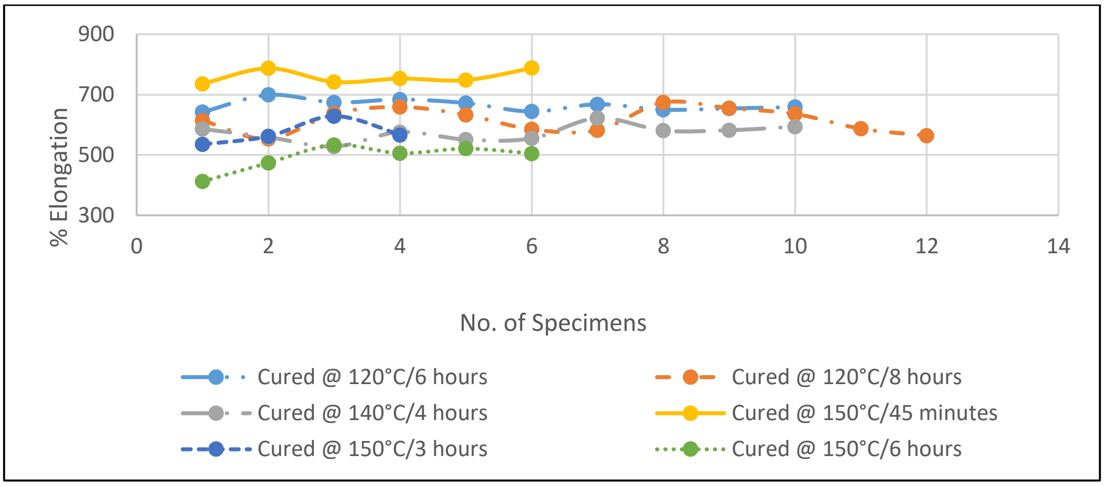


Figure-12: Achieved % Elongation at various cure conditions

The achieved densities are comparable (1.05-1.06 g/cm^3) for all the cure conditions. At each cure condition, Shore-A hardness is found to increase with cure time (for example, Shore-A hardness is 67-69 for 150°/45 minutes, 75-78 for 150°C/3 hours and 76-79 for 150°C for 6 hours).

As evident from Table-24 and Figure-11 and 12, highest tensile strength is achieved in the cure condition of 120°C/6 hours. Among the cure conditions of 150°C, 150°C/ 3 hours gives the highest tensile strength followed by 150°C/45 minutes and 150°C/6 hours gives the least tensile strength. Further, the achieved % elongation is the highest for 150°C/45 minutes. Achieved % elongation is lower than the requirement (600 minimum) in case of 150°C/3 hours, 150°C/6 hours and 140°C/4 hours. In case of 120°C/6 hours, both achieved tensile strength and % Elongation are not only well above the requirement (Tensile strength: 100 kg/cm^2 minimum and % Elongation: 600 minimum) but show least scatter. Large scatter is seen in the achieved mechanical properties of cure conditions 140°C/4 hours, 120°C/ 8 hours and 150°C/6 hours. Even though, the average tensile strength and % elongation, achieved at 120°C/8 hours, just meet the respective requirements, most of the individual values are lower than the respective requirements. Thus, cure conditions viz. 120°C/6 hours and 150°C/45 minutes only meet the insulation specification of CRMC with respect to mechanical properties. 150°C/ 3 hours, even though yielded reasonably good tensile strength, it has shown wide scatter in tensile strength and % elongation. Further, the achieved % elongation, in this case, is less than the requirement. Among the cure conditions of 120°C/6 hours and 150°C/45 minutes, more consistency of achieved mechanical properties is seen in case of 120°C/6 hours. For CRMC manufacturer, curing at 120°C is more preferable, given that glass transition temperature (T_g) of CRMC (made of carbon -Epoxy) is 160°C (The maximum recommended temperature of exposure of CRMC should be 30°C below the T_g i.e. not more than 130°C).

5.5.2 DSC Study:

DSC curves pertaining to the unvulcanised EPDM-S sample and samples cured at 120°C/6 hours, 120°C/8 hours and 140°C/4 hours are given in Figure-13, 14, 15 and 16. DSC curves pertaining to the samples cured at 150°C/45 minutes, 150°C/3 hours and 150°C/6 hours are given in Figure-17, 18 and 19. Degree of cure calculated based on residual heat of exotherm for various cure conditions is given in Table-25.

Table-25: Degree of cure for various cure conditions

Cure Condition	Heat of Exotherm (J/g)	Degree of Cure
Unvulcanised	19.80	-
Cured @ 120°C/6 hours	3.275	0.83
Cured @ 120°C/8 hours	2.010	0.90
Cured @ 140°C/4 hours	1.547	0.92
Cured @ 150°C/45 minutes	1.778	0.91
Cured @ 150°C/3 hours	0.6495	0.97
Cured @ 150°C/6 hours	4.046	**0.80**

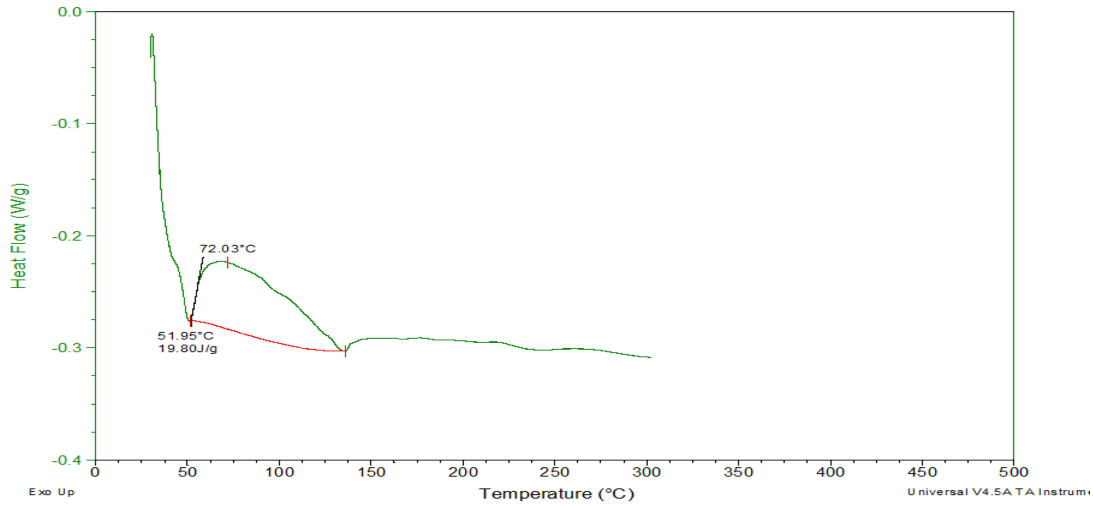


Figure-13: DSC Curve for unvulcanised EPDM-S

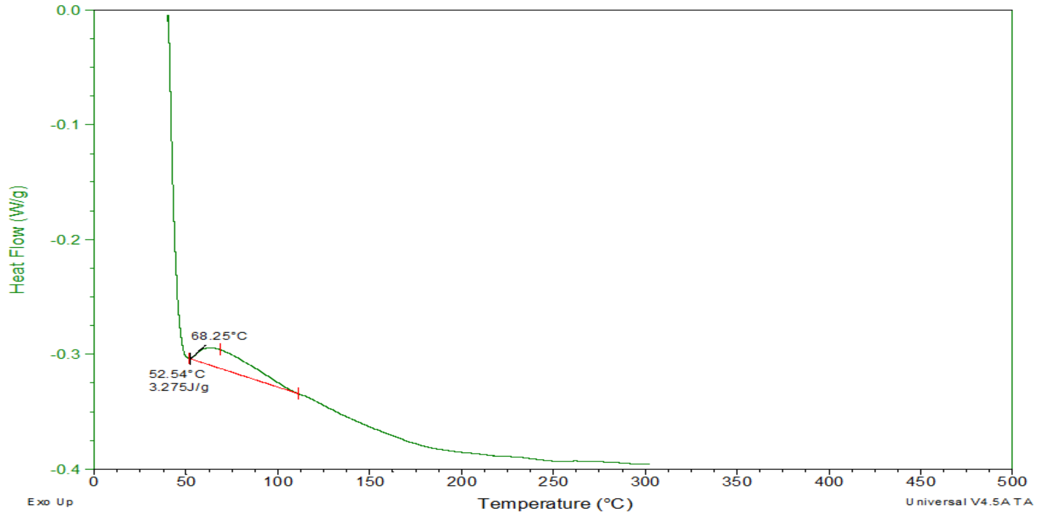


Figure-14: DSC Curve for EPDM-S cured at 120°C/6 hours

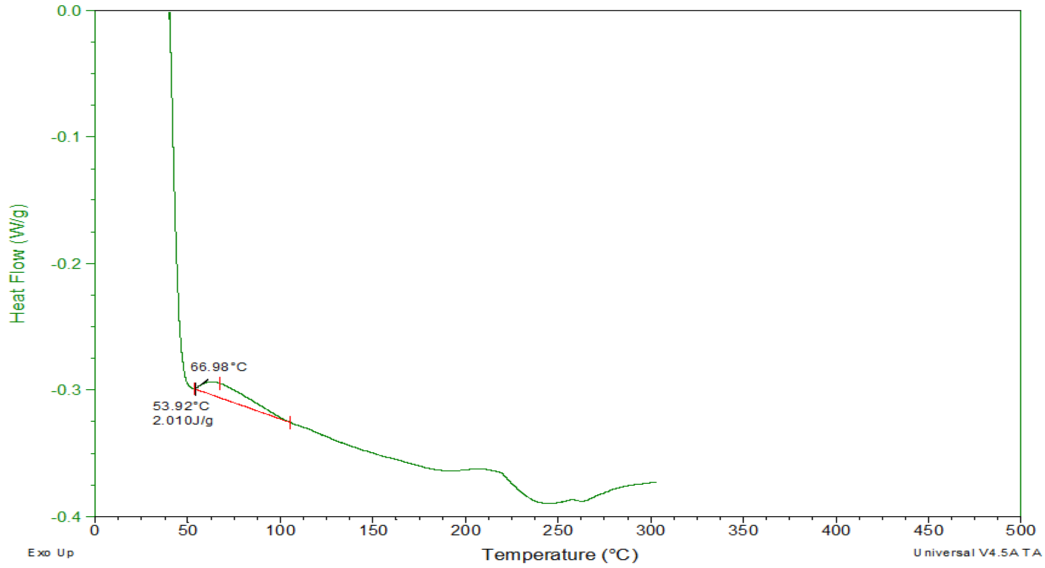


Figure-15: DSC Curve for EPDM-S cured at 120°C/8 hours

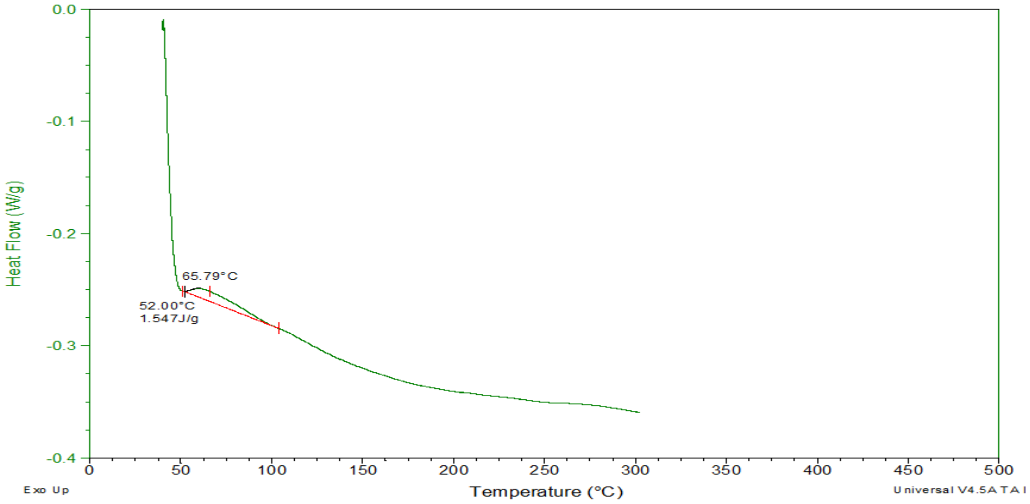


Figure-16: DSC Curve for EPDM-S cured at 140°C/4 hours

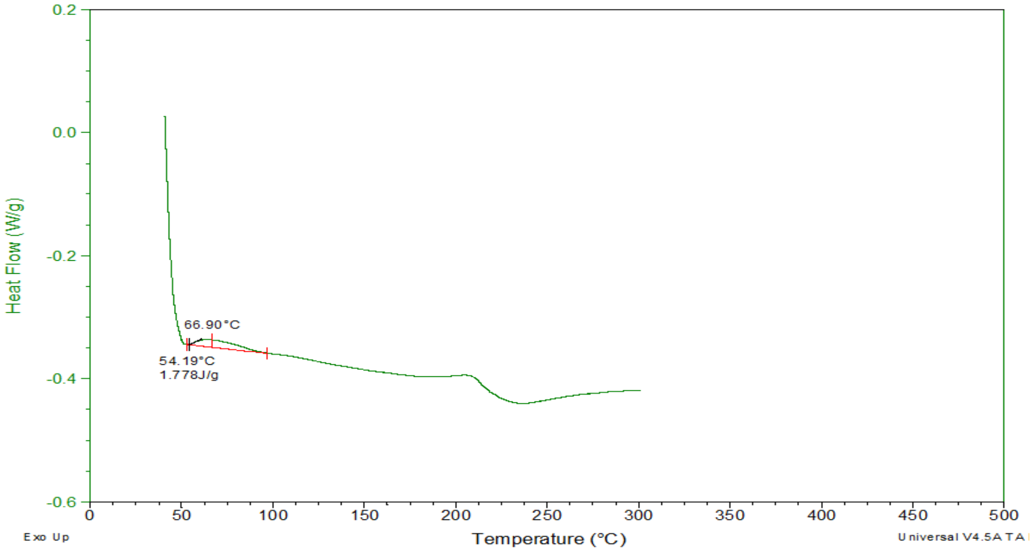


Figure-17: DSC Curve for EPDM-S cured at 150°C/45 minutes

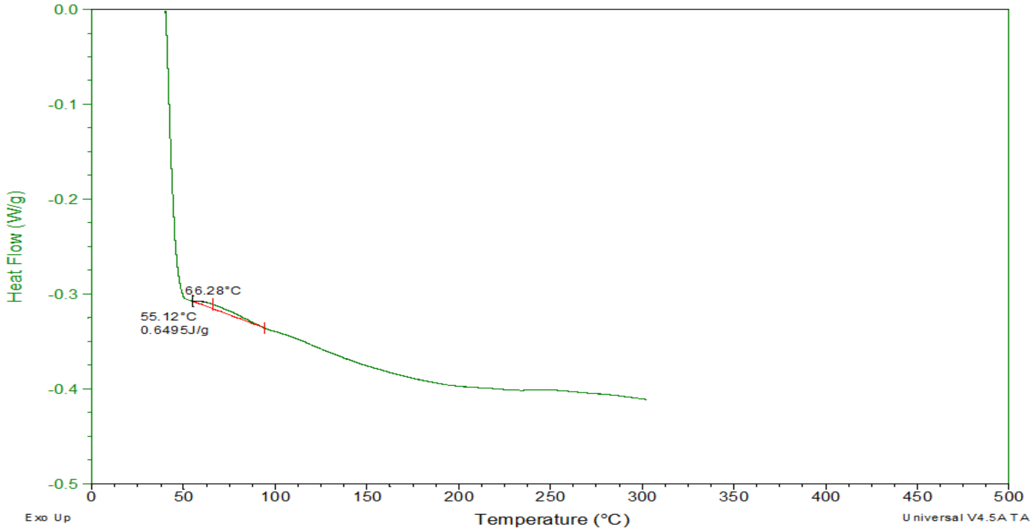


Figure-18: DSC Curve for EPDM-S cured at 150°C/3 hours

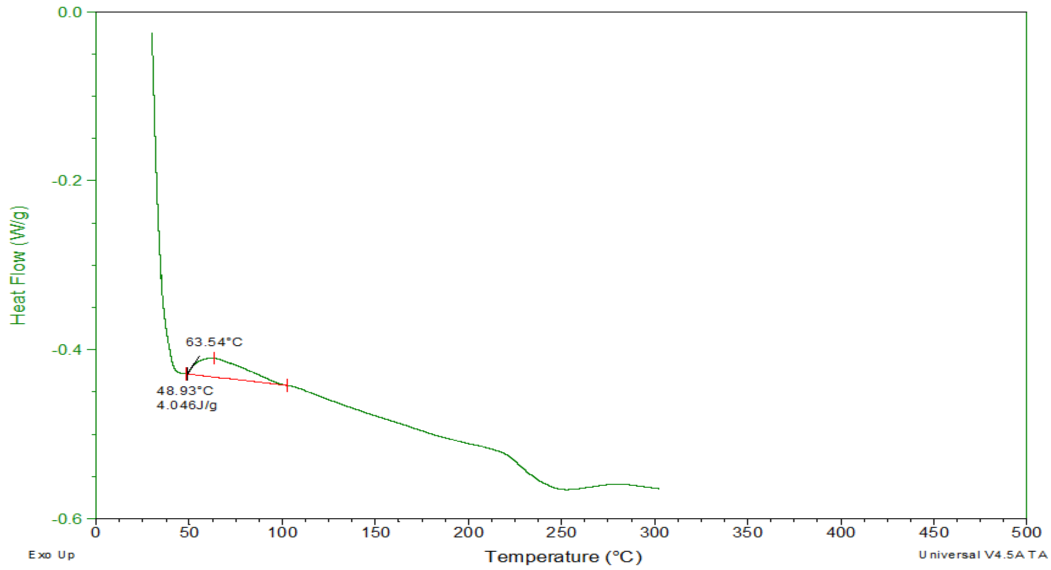


Figure-19: DSC Curve for EPDM-S cured at 150°C/6 hours

The various cure conditions are arranged in the order of increasing degree of cure as follows: 150°C/6 hours < 120°C/6 hours < 120°C/8 hours < 150°C/45 minutes < 140°C/4 hours < 150°C/3 hours.

The findings of DSC are in agreement with those of the Rheometer. As Rheometer curve is progressive at 120°C up to 8 hours, 120°C for 8 hours has shown degree of cure higher than that of 120°C/6 hours. As the Rheometer curve is progressive at 140°C up to 4 hours, the degree of cure at this cure condition is also relatively higher. As evident from the behaviour of Rheometer curve at 150°C (Figure-7), progress in degree of cure is seen reaching a maximum of 0.97 till 3 hours (up to transient saturation). As evident from the secondary increase in the Rheometer curve beyond 3 hours, appreciable increase in the residual heat of exotherm (4.046 J/g) is seen in case of sample cured at 150°/6 hours as compared to 150°C/45 minutes (1.778 J/g) and 150°/3 hours (0.6495 J/g). As evident from Rheometer curve at 150°C (Figure-7), the secondary rise (due to secondary crosslinking) gets initiated after 3 hours. Hence, the sample cured at 150°C for 6 hours, in which the secondary crosslinking has got initiated and progressed to some extent, only shows higher residual exotherm corresponding to the residual secondary crosslinking. Accordingly, the degree of cure, computed in respect of this sample, has got reduced to 0.80.

5.5.3 Isothermal DSC for further investigation

In order to confirm, whether the secondary increase as seen in the Rheometer curve and appreciable increase in the heat of exotherm as seen in DSC of sample cured at 150°C/6 hours is because of additional cross-linking or thermal degradation of insulation, isothermal DSC run was carried out for the unvulcanised EPDM-S at 150°C for 6 hours. The isothermal DSC plot is shown in Figure-20.

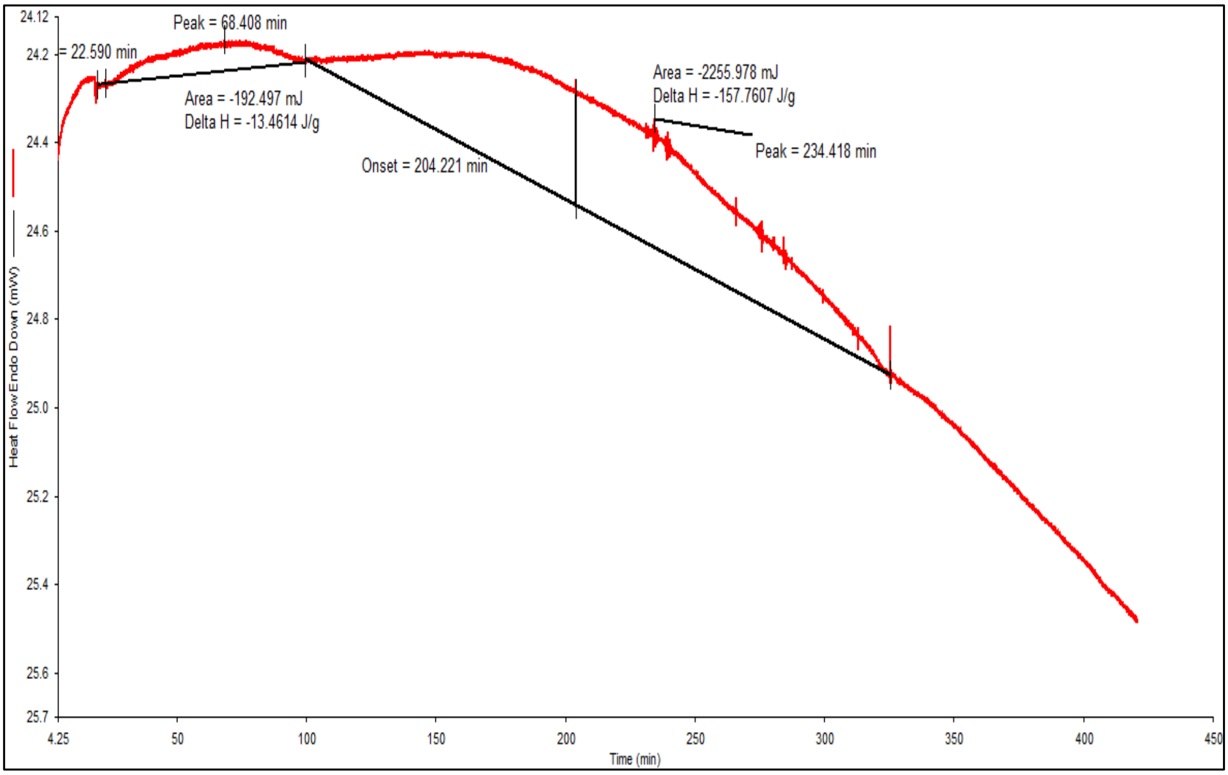


Figure-20: Isothermal DSC Plot of unvulcanised EPDM-S at 150°C/6 hours

Primary and secondary rises seen in the Rheometer curve at 150°C are reflected in terms of two distinct exotherms (first one approximately 25 minutes to 108 minutes giving a heat of exotherm of 13.46 J/g and the second one approximately 108 minutes to 325.6 minutes giving a heat of exotherm of 157.76 J/g). The second exotherm culminates at 325.6 minutes and DSC curve shows clear endothermic shift thereafter. Thus, it is proven based on isothermal DSC that EPDM-S has not undergone any degradation during additional cure beyond 3 hours up to 6 hours at 150°C. However, the crosslinks formed during additional cure are not adding any value to the achieved mechanical properties as the achieved mechanical properties are quite less than the requirement.

5.5.4 Isothermal TGA for additional confirmation

The above findings are further confirmed by Isothermal TGA run carried out at 150°C for 6 hours for unvulcanised EPDM-S. The Isothermal TGA plot thus obtained is given in Figure- 21.

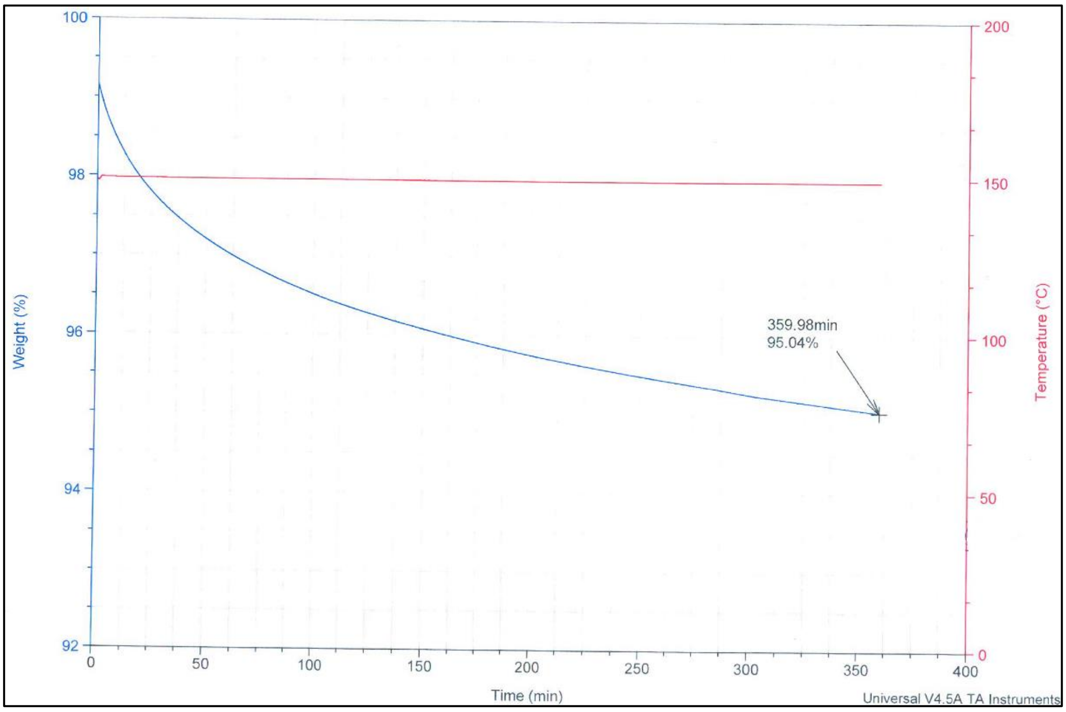


Figure-21: Isothermal TGA plot of unvulcanised EPDM-S at 150°C for 6 hours

As evident from the Figure-21, the maximum weight loss at the end of 6 hours is 5-6 %, which could be attributed to loss of volatiles and by-product formed during the formation of sulphur crosslinks and hence there is no degradation.

5.5.5 Comparison of achieved mechanical properties and degree of cure by DSC

Comparison of Tensile strength, % Elongation and degree of cure at different cure conditions is given in Table-26. As evident from the Table-26, required mechanical properties are achieved at about degree of cure of 0.83 at 120°C and 0.91 at 150°C. Prolonged curing at 120°C up to 8 hours, 140°C up to 4 hours and 150°C up to 3 hours, even though result in further increase in degree of cure, they are not beneficial in terms of achieved mechanical properties.

Table-26: Comparison of Tensile strength and degree of cure at different cure conditions

Cure Condition	Tensile Strength (kg/cm^2)	% Elongation	Degree of Cure
Cured @ 120°C/6 hours	140 (126-153)[a]	665 (642-699)	0.83
Cured @ 120°C/8 hours	104 (69-145)	615 (553-674)	0.90
Cured @ 140°C/4 hours	85 (66-100)	573 (528-622)	0.92
Cured @ 150°C/45 minutes	126 (119-133)	759 (742-787)	0.91
Cured @ 150°C/3 hours	132 (106-154)	573 (535-629)	0.97
Cured @ 150°C/6 hours	101 (65-139)	492 (412-533)	0.80

[a] Values in the parenthesis indicate the minimum and maximum of test results

5.5.6 Characterization by FTIR spectroscopy:

FTIR spectra pertaining to the unvulcanised EPDM-S sample and samples cured at 120°C/6 hours, 120°C/8 hours and 140°C/4 hours are given in Figure-22, 23, 24 and 25 respectively. FTIR spectra pertaining to the samples cured at 150°C/45 minutes, 150°C/3 hours and 150°C/6 hours are given in Figure-26, 27 and 28 respectively.

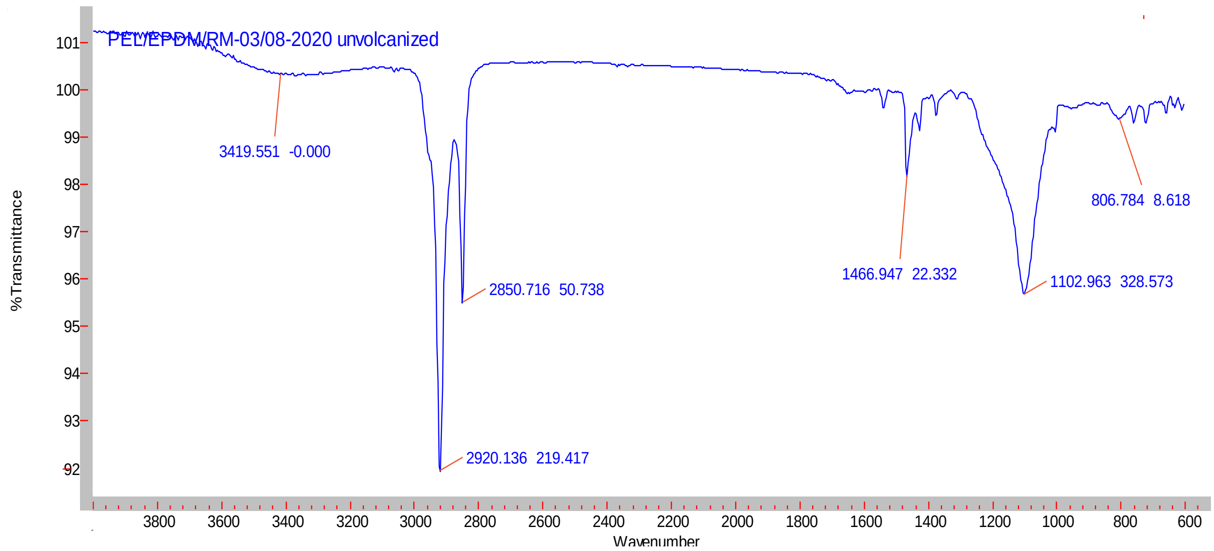


Figure-22: FTIR Spectrum of unvulcanised EPDM-S

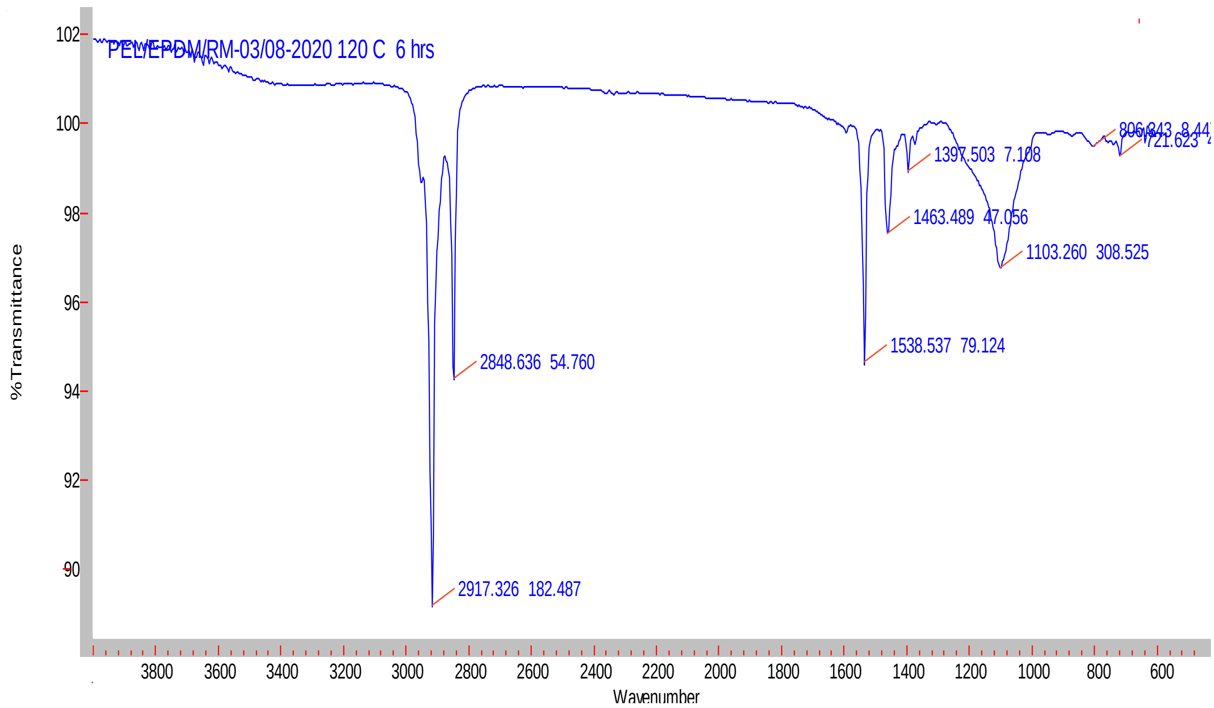


Figure-23: FTIR Spectrum of EPDM-S cured at 120°C/6 hours

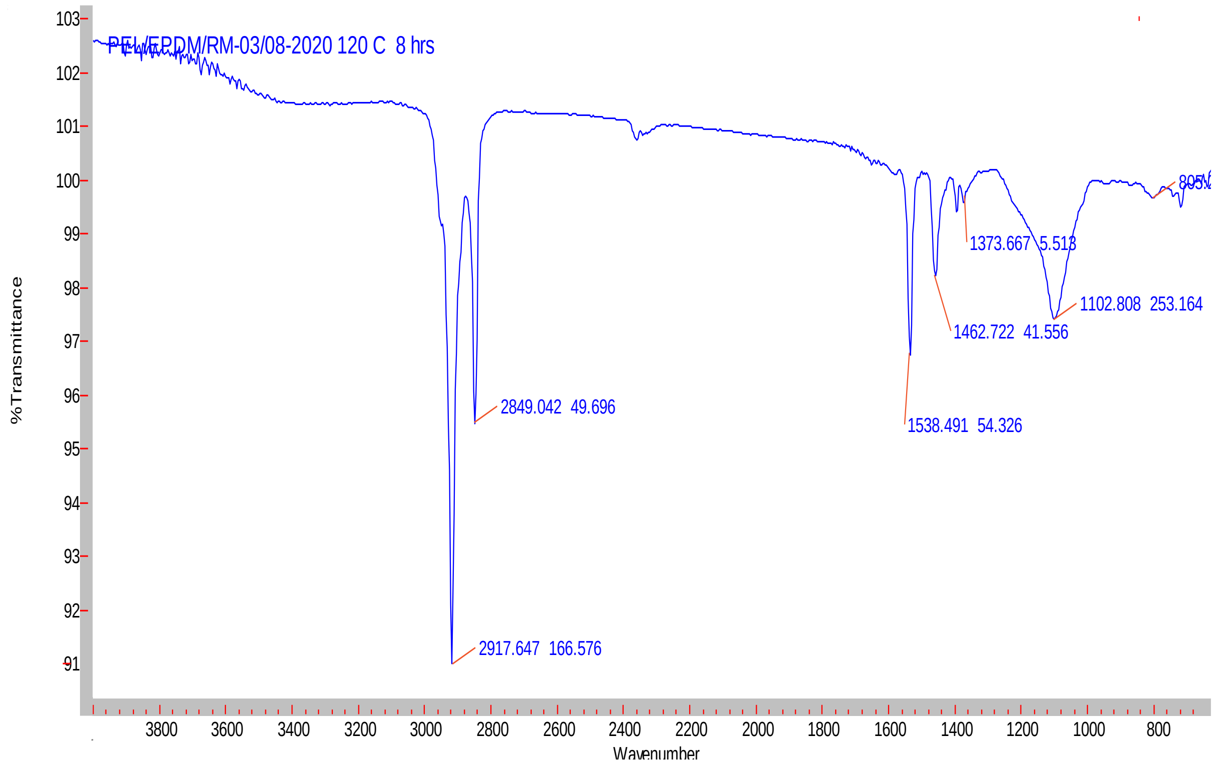


Figure-24: FTIR Spectrum of EPDM-S cured at 120°C/8 hours

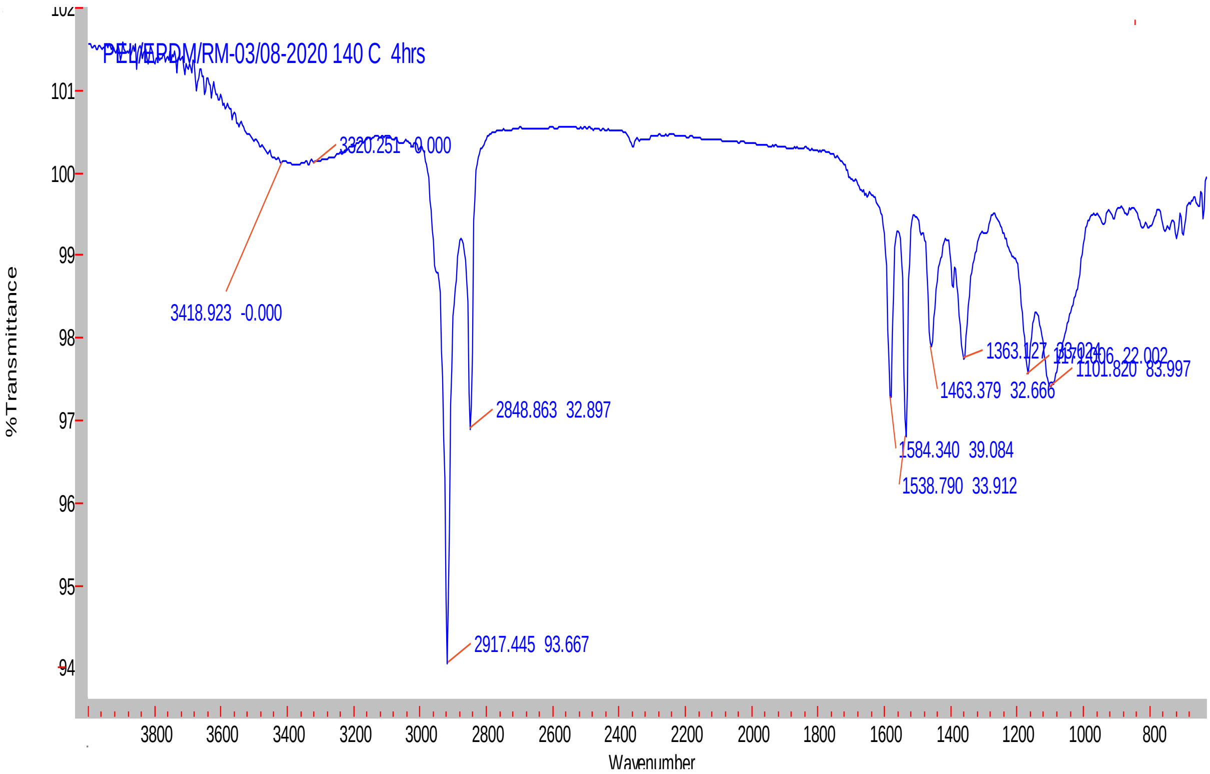


Figure-25: FTIR Spectrum of EPDM-S cured at 140°C/4 hours

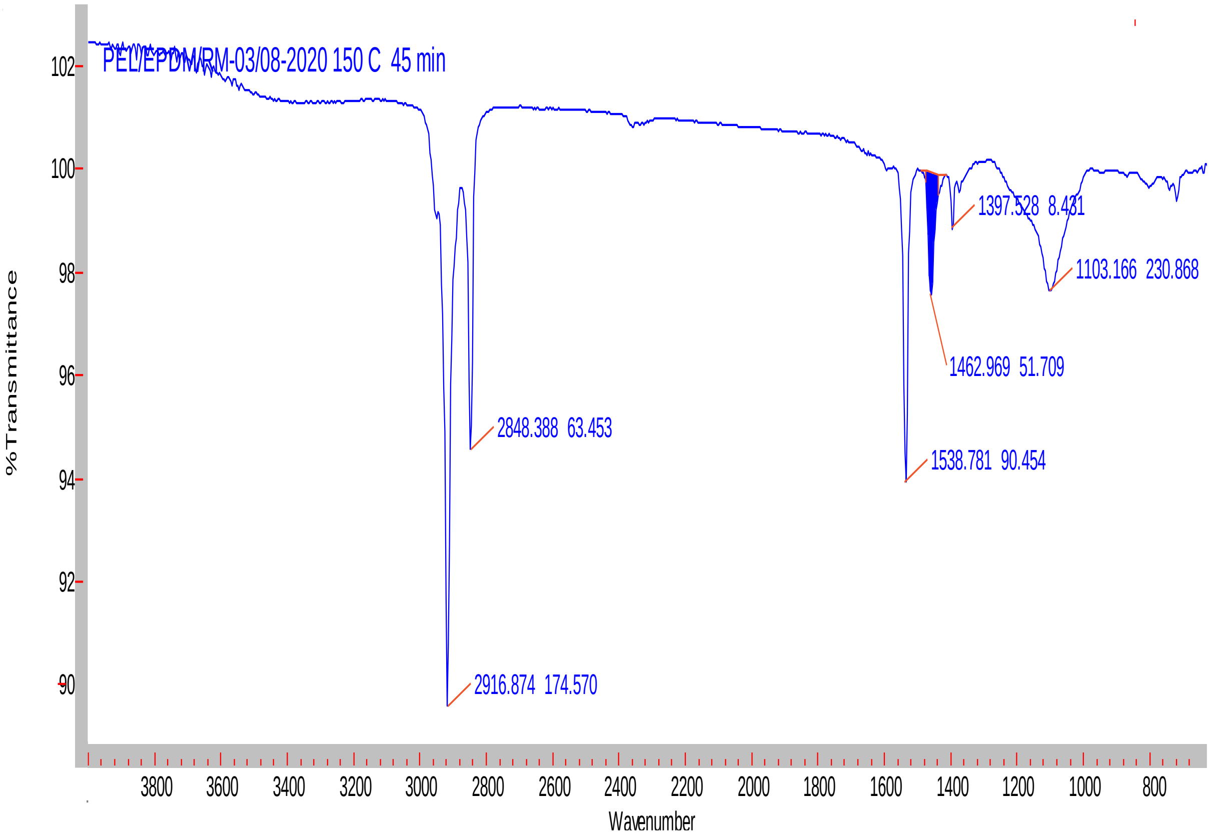


Figure-26: FTIR Spectrum of EPDM-S cured at 150°C/45 minutes

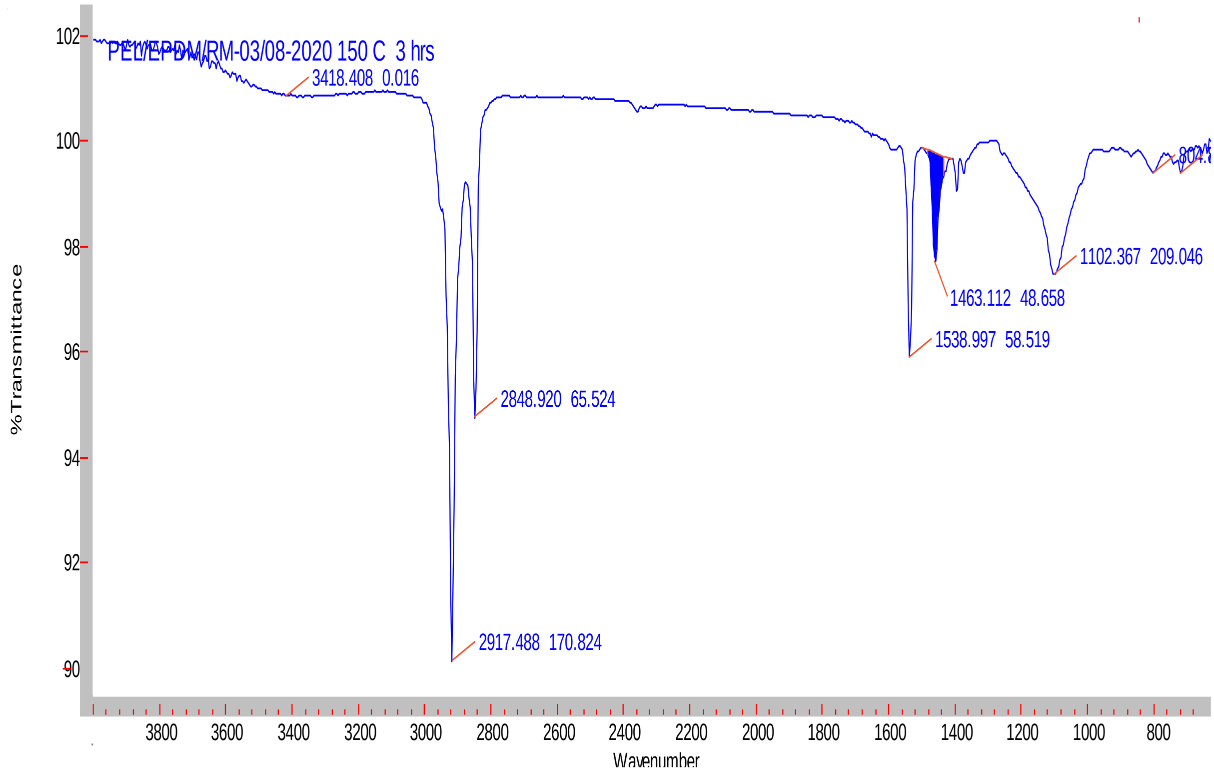


Figure-27: FTIR Spectrum of EPDM-S cured at 150°C/3 hours

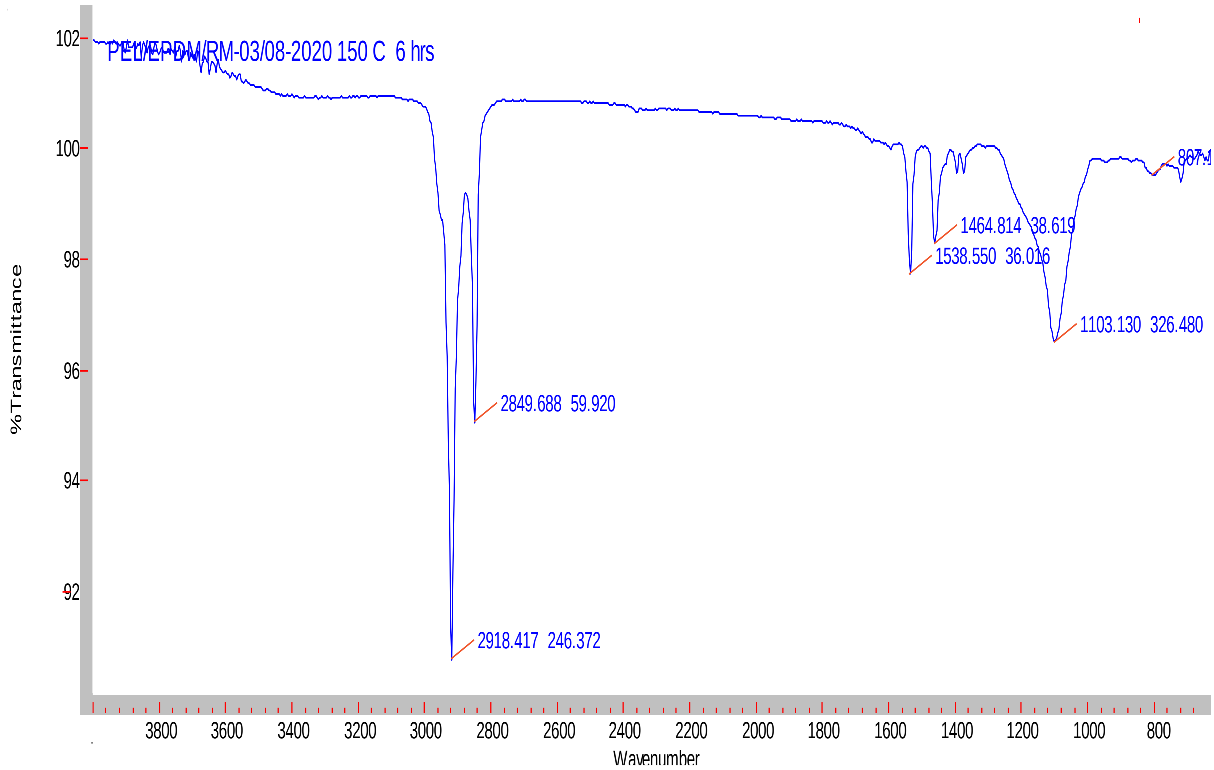


Figure-28: FTIR Spectrum of EPDM-S cured at 150°C/6 hours

The functional groups interpreted from these FTIR spectra are detailed in Table-27.

Table-27: Functional groups interpreted from FTIR spectra

Wavenumber (cm^{-1}) of peaks/bands obtained in Figures 22 to 28	Functional group interpreted
2916-2850	Aliphatic C-H
1680 (seen only in Figure-22 for unvulcanised EPDM-S)	Exo-Cyclic double bond of 5-Ethylidene norbornene
1538	>C-S-
1462-1466	$-CH_2-$
1102-1103	-Si-O-

Table- 27 confirms that, the elastomer is sulphur cured (>C-S-) Ethylene Propylene Diene Terpolymer (Aliphatic C-H, -CH2-) having silica (-Si-O-) as reinforcing filler. Further, the peak/band at 1680 cm^{-1}, which is present only in case of unvulcanised EPDM-S (Figure-22) confirms that the diene present in the terpolymer is 5-Ethylidene norbornene (ENB) and hence EPDM terpolymer has the structural formula as shown in Figure-29.

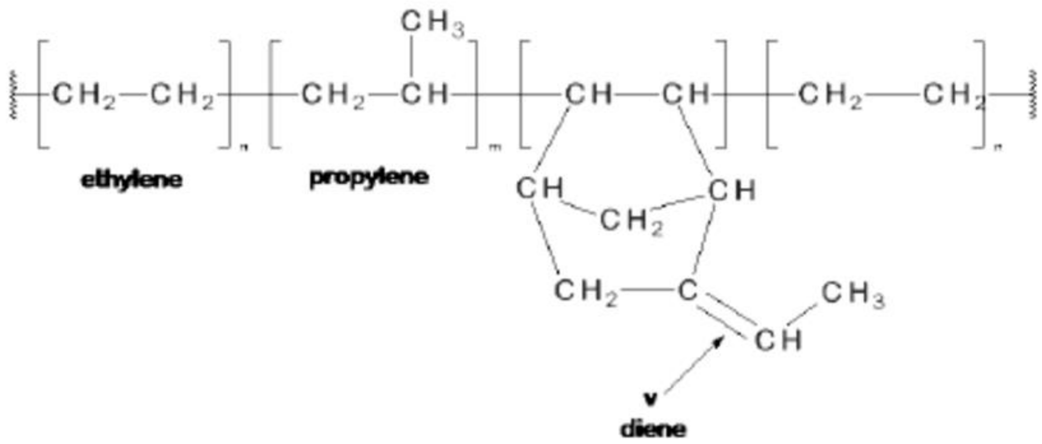


Figure-29: Structural Formula of EPDM Terpolymer as confirmed by FTIR

The disappearance of this peak in the remaining samples (cured at different conditions) confirms that exocyclic double bond of ENB has participated in the crosslinking. It may be noted that, all the samples were subjected to FTIR spectroscopy under identical conditions. Table-28 gives the comparison of % Transmittance at wavenumber of

1538 cm^{-1}, which corresponds to >C-S- bond. The calculated values of % absorbance are also given in Table- 28.

Table-28: Comparison of % Transmittance at 1538 cm^{-1} for various cure conditions

Cure Conditions	% Transmittance	% Absorbance
Unvulcanised	0	0
Cured @ 150°C/6 hours	98.0	2.0
Cured @ 140°C/4 hours	97.0	3.0
Cured @ 120°C/8 hours	96.9	3.1
Cured @ 150°C/3 hours	96.0	4.0
Cured @ 150°C/45 minutes	94.5	5.5
Cured @ 120°C/6 hours	94.0	6.0

From Table-28, it is clear that the >C-S- bond intensity (measure of >C-S- crosslinks) is the highest for EPDM-S cured at 120°C/6 hours followed by that cured at 150°C/45 minutes and the least for 150°C/6 hours. But degree of cure as computed by DSC is 0.83 for sample cured at 120°C/6 hours. This implies that, at each temperature of cure >C-S- bond intensity increases with degree of cure till the latter reaches a threshold value, which seems to be 0.83 at 120°C and 0.91 at 150°C. Further curing beyond these levels might result in undesirable crosslinking reactions, which are not beneficial to achieve the required mechanical properties. Thus, based on FTIR spectroscopic characterization, 120°C/6 hours and 150°C/45 minutes seem to be preferable cure conditions. Findings of section-5.5.1 (results of mechanical properties) corroborate the same.

5.6 FINDINGS:

Based on Rheometer study, mechanical properties evaluation, DSC analysis, Isothermal TGA and FTIR spectroscopy, findings concerning the cure behaviour of EPDM-S are summarized as follows:

- Unsaturation being present in the side chain, EPDM-S exhibits slow curing as compared to proven Nitrile rubber based insulation, which is also sulphur cured. Therefore, the Rheometer curves are progressive even at 160°C for duration as long as 7 hours.

- Even though, prolonged curing at a given temperature (say 120°C, 140°C and 150°C) in order to achieve highest possible degree of cure, does not lead to degradation (as confirmed by Isothermal DSC and TGA runs), it does not yield desirable mechanical properties as required by insulation of large CRMC.
- FTIR spectroscopy measures crosslink density in terms of C-S bond intensity. Endeavour to increase the degree of cure beyond a threshold value, by prolonged exposure at a given temperature, does not lead to increase in C-S bond intensity. Rather it leads to undesirable cross linking reaction affecting the achieved mechanical properties.
- Therefore, finding an optimum cure condition by striking a balance between achieved mechanical properties, degree of cure and C-S bond intensity seems to be the practical way. The optimum cure conditions, for the requirements of insulation of large CRMC, are found to be 120°C/6 hours (degree of cure 0.83) and 150°C/45 minutes (degree of cure 0.91), which have given the maximum % absorbance (highest C-S bond intensity) and maximum Tensile strength and % Elongation. Owing to T_g constraints of CRMC, 120°C/6 hours is preferred for the curing of EPDM-S.

5.7 Outcome of Study on Cure Behaviour of EPDM-S insulation :

Sulphur curing of EPDM based insulation is not as simple as that of Nitrile rubber based insulation. Novel approach to arrive at the optimum cure condition (120°C/6 hours), has been demonstrated in this Chapter (Chapter-5), through extensive study. Even though, the optimum cure condition arrived at, is specific to the insulation requirements of large CRMC, it is believed that the approach would be applicable to EPDM-S having other end applications too. Validity of the cure condition/cycle has been adequately explained in terms of mechanical properties and instrumental techniques. Further, this Chapter renders scope for further study/research to understand the undesirable crosslinking reactions occurring beyond the threshold value of degree of cure at various cure temperatures. There exists scope to carry out study to reduce the curing time further from the existing cure time of 6 hours at 120°C.

CHAPTER 6

EVALUATION OF EPDM-S INSULATION AGAINST NITRILE RUBBER BASED INSULATION FOR REQUIREMENTS OF LARGE COMPOSITE ROCKET MOTOR CASING

EVALUATION OF EPDM-S INSULATION AGAINST NITRILE RUBBER BASED INSULATION FOR REQUIREMENTS OF LARGE COMPOSITE ROCKET MOTOR CASING

6.1 Introduction:

Even though literature available on EPDM is abundant, the data on physical, mechanical, thermal, interface properties and ablative performance as specifically required for the design and acceptance of internal insulation of large Composite Rocket Motor Casing is scant. This gave the primary impetus to take up this experimental work. Further, the scatter in the achieved mechanical properties of EPDM-S insulation of 4 kg trial discussed in Chapter-4, raised scepticism over the uniformity in distribution of Kevlar on EPDM matrix. Understanding the influence of Kevlar on the overall achieved properties of insulation, thus happened to be yet another necessity. Keeping in view of the above, this comparative characterization study was undertaken, wherein, the formulation given in Table-3 of Chapter-4 (which was validated through 4 kg trial), was taken as basis. 10 kg batch of EPDM-S insulation was made by adhering to the formulation given in Table-3 of Chapter-4 fully, which is herein after called EPDM with Kevlar. Another 10 kg insulation was made by replacing 35 phr of silica and 9 phr of Kevlar Pulp (RHENOGRAN P91-40/EPDM) in Formulation given in Table-3 of Chapter-4 by 44 phr of silica alone, which is hereinafter called EPDM without Kevlar. Insulations based on EPDM with Kevlar and EPDM without Kevlar were characterized in comparison with proven Nitrile Rubber based insulation for the requirements of large CRMC. Comparative characterization thus carried out, is discussed in this Chapter.

6.2 Experimental study:

6.2.1 Formulation used for characterization and details of sheet drawn:

EPDM-S insulation containing Kevlar and precipitated silica (hereinafter called EPDM with Kevlar) and EPDM-S insulation containing precipitated silica alone (hereinafter called EPDM without Kevlar) prepared as per the base line formulation given in Table-29, which was solely based on formulation given in Table-3 of Chapter-4, validated through 4 kg trial. EPDM (TER-4038, Make- Versalis, Italy), liquid EPDM (Trilene-77) and other ingredients (all of the same batch/lot) as given in Table-3 and section 4.2 of Chapter-4, were used in both the formulations.

Table-29: Formulation of EPDM with Kevlar and EPDM without Kevlar

Ingredients	Parts Per Hundred Rubber (PHR)	
	EPDM with Kevlar	EPDM without Kevlar
EPDM TER-4038 +Liquid EPDM (Trilene-77)	100	100
Kevlar Pulp (RHENOGRAN P91-40/EPDM)	9	0
Precipitated Silica (Ultrasil VN-3)	35	44
Zinc Oxide + Stearic acid	6	6
Sulphur + TMTD + MBTS	3.5	3.5
Rubber Oil-501 + Tackifier + Polyethylene glycol (PEG-400)	22	22
Titanium dioxide + Antimony trioxide + TDQ	3	3
Total	178.5	178.5

Ten kg each of EPDM with Kevlar and EPDM without Kevlar was produced as per the mixing/compounding process detailed in Table-18 and Table-19 of Section 4.3 of Chapter-4. Only difference in mixing of EPDM without Kevlar with respect to the above established compounding process is that first activity in premixing (Table-18 of Chapter-4) was not warranted as there is no Kevlar Pulp. Accordingly, activity-3 of premixing (Table-18 of Chapter-4) in case of EPDM without Kevlar becomes cross mixing of EPDM and liquid EPDM alone and activity-4 of premixing (Table-18 of Chapter-4) in case of EPDM without Kevlar becomes EPDM-liquid EPDM blend +TDQ (i.e. addition and mixing of TDQ with EPDM-liquid EPDM blend). Further, extra time gained by doing away with activity-1 of premixing (Table-18 of Chapter-4) was given to activity-5 of premixing (Table-18 of Chapter-4) i.e. addition and mixing of precipitated silica such that total premixing time was almost the same in case of both EPDM with Kevlar and EPDM without Kevlar. Final mixing process was exactly the same as detailed in Table-19 of Chapter-4, for both EPDM with Kevlar and EPDM without Kevlar.

The baseline formulation of nitrile rubber based insulation containing precipitated silica as reinforcing filler, which is proven as insulator for large CRMC, is given in Table-30. Ten kg of Nitrile rubber insulation produced using the formulation as given in Table-30, was used as a reference to evaluate the performance of above EPDM insulations (EPDM with Kevlar and EPDM without Kevlar) with respect to insulation requirements of large CRMC.

Table-30: Formulation of Nitrile Rubber based insulation

Ingredients	Parts Per Hundred Rubber (PHR)
NBR-Perbunan 3445	100
Precipitated Silica (Ultrasil VN-3)	50
Sulphur + Activators + Accelerators	9.25
Tackifier + Process Aid	22

Sheets of approximately 6 meter length, 660 mm width and 2 mm thickness were drawn from each of 10 kg insulations thus made for EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber. Lay out of sheets, thus drawn, is given in Figure-30, which depicts the various zones and the locational details of samples drawn for physical, mechanical, thermal and erosion (ablative) resistance properties.

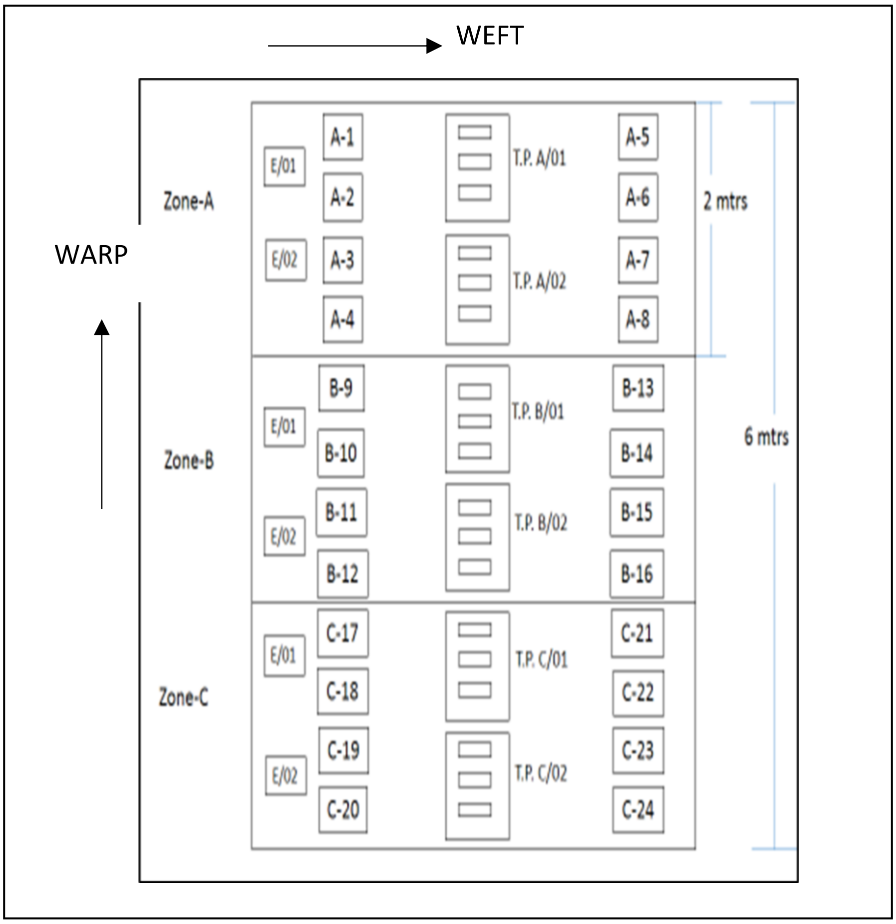


Figure-30: Sheet Lay-out giving details of sample locations

Details of Samples/Specimens drawn for evaluation of various properties are given in Table-31. As established based on detailed study on cure behaviour, described in Chapter-5, samples/specimens of EPDM with Kevlar were cured at 120°C for 6 hours. Given that all ingredients including curative, activators and accelerators but Kevlar is the same for both EPDM with Kevlar and EPDM without Kevlar, the cure behaviour of EPDM without Kevlar was expected to be no different from that of EPDM with Kevlar. Hence, samples/specimens of EPDM without Kevlar, too, were cured at 120°C/6 hours. It may be noted that the achieved mechanical properties (discussed in the subsequent section) of samples, drawn from various locations of the sheet (Figure-30) drawn from EPDM without Kevlar, were well within the requirements, thereby validated the cure condition of 120°C/6 hours. Whereas, the samples/specimens pertaining to Nitrile Rubber insulation were cured at 120°C for 4 hours, which is the proven cure condition for this insulation, which has been validated in several static tests and flight tests of CRMC.

Table-31: Details of Samples/Specimens for various properties

Location (Fig-30)	**EPDM with Kevlar/EPDM without Kevlar and Nitrile Rubber insulation**	**Cure Condition**
Zone A	A-2 (Warp), A-6 (Weft), for Mechanical Properties	120°C/6 hours for EPDM with Kevlar and EPDM without Kevlar; 120°C/4 hours for Nitrile Rubber insulation
	T.P. A/02 (6mm thick) for Thermal Properties	
	E/02 (for Erosion Rate)	
Zone B	B-10(Warp), B-14 (Weft), for Mechanical Properties	120°C/6 hours for EPDM with Kevlar and EPDM without Kevlar; 120°C/4 hours for Nitrile Rubber insulation
	T.P. B/02 (6mm thick), for Thermal Properties	
	E/02 (for Erosion Rate)	
Zone C	C-18(Warp), C-22 (Weft), for Mechanical Properties	120°C/6 hours for EPDM with Kevlar and EPDM without Kevlar;
	T.P. C/02 (6mm thick), for Thermal Properties	
	E/02 (for Erosion Rate)	

Samples of Sheet Lay-out (Figure-30) other than those detailed in Table-31 were cured at various other conditions viz. 120°C / 8 hours and 140°C/4 hours for EPDM with Kevlar and EPDM without Kevlar. However, owing to the fact that 120°C/6 hours is found to be the optimum cure condition based on extensive cure study described in Chapter-5 and keeping prime focus on the objectives of the present research, data generated on the properties evaluated of samples cured at conditions other than 120°C/6 hours are neither presented nor discussed in this Chapter. Specimens/samples, as detailed in Zone- A and Zone-B of Table-31only, were cured at 120°C/4 hours in case of Nitrile Rubber insulation.

6.2.2 Physical and Mechanical Properties:

Slabs from various zones (Zone-A, B and C) as detailed in Table-31, were prepared as per the procedure described in Section-4.5 of Chapter-4 for each of EPDM with Kevlar, EPDM without Kevlar and Nitrile Rubber insulation. From each zone, out of the two slabs cured for each of the insulations, one slab was used for the evaluation of mechanical properties in the warp direction and the other one was used for the evaluation of mechanical properties in the weft direction. Physical properties viz. Shore A hardness and density were evaluated as per ASTM D 2240 and ASTM D 792 respectively. Mechanical properties viz. Tensile strength and % Elongation were evaluated as per ASTM D 412 using UTM of INSTRON make employing long travel extensometer for the accurate measurement of % Elongation.

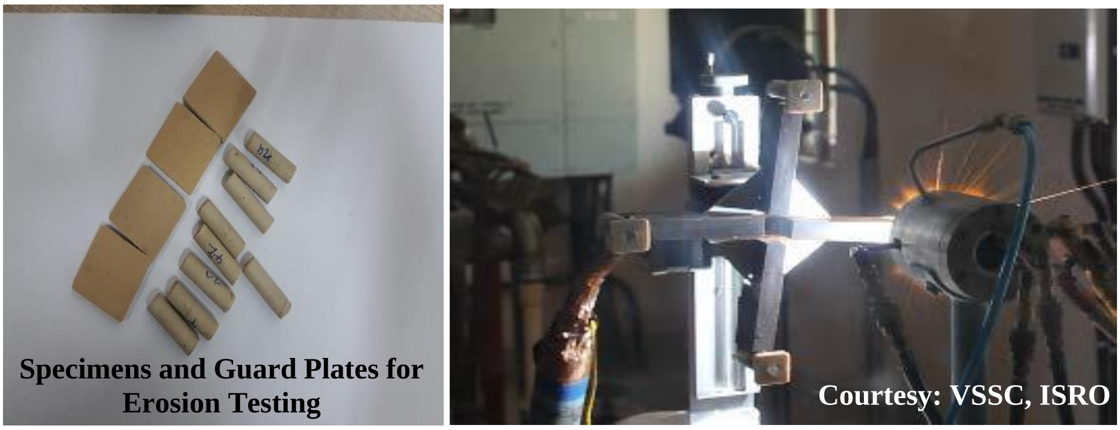
6.2.3 Thermal Properties:

Specimens for Thermal conductivity, Specific heat and Coefficient of thermal expansion (Figure-31 and 32) were made as per ASTM E 1530, ASTM E 1269 and ASTM E 831 respectively for EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulations from the respective 6 mm thick slabs made as per the procedure detailed in Section 4.6 of Chapter-4. Thermal conductivity, Specific heat and Coefficient of thermal expansion were evaluated using Guarded Heat Flow Meter, Differential Scanning Calorimeter of make TA Instruments Discovery DAC and Thermo Mechanical Analyser of make TA Instruments Q400 respectively, available at ISRO, VSSC, Thiruvananthapuram. As required by insulation designer, Thermal conductivity and specific heat were evaluated at 80° C for all the 3 types of insulation.

Figure-31 and 32: Specimens for Thermal Properties

6.2.4 Ablative Properties:

Cylindrical specimens of diameter 10 mm and length 25 mm, as depicted in Figure-33, were moulded at 120°C/6 hours for EPDM with Kevlar and EPDM without Kevlar and at 120°C/4 hours for Nitrile Rubber insulation using specially designed moulds for testing of erosion rate. Ablative performance of all the three rubbers was evaluated by measuring Erosion rate of representative cylindrical specimens (made by drawing sample from various zones as detailed in Figure-30 and Table-31) using Plasma Arc Jet facility available at ISRO, VSSC, Thiruvananthapuram, by simulating a heat flux of 300W/cm^2. Figure-33 also depicts erosion testing with Plasma Arc Jet Facility.



Specimens and Guard Plates for Erosion Testing

Courtesy: VSSC, ISRO

Figure-33: Specimens for Erosion Rate **Erosion Testing in progress**

The erosion rate in mm/sec was determined as follows:

$$\text{Erosion Rate} = \frac{Initial\ Thickness - Final\ Thickness\ after\ erosion}{Time\ of\ Exposure}$$

Heat of ablation was also derived from the above test as follows:

$$\text{Heat of Ablation} = \frac{Q.A.t}{m1 - m2}$$

Q = Heat Flux (300 W/cm^2)

A = Cross-section area of specimen

t = time of exposure

m_1-m_2 = Weight loss during testing

6.2.5 Water absorption behaviour:

Both precipitated Silica and Kevlar are hydrophilic in nature (Herring et al., (1989)). Insulation is expected to have as low a tendency to absorb moisture/ water as possible. This is because, the absorbed water will instantly react with isocyanate based curing agent of bonding agent between insulation and propellant and will result in de-bond between insulation and propellant. Further, the effect of absorbed water on the mechanical, thermal and ablative properties of insulation rubber are not quite understood from the literature. Therefore, water absorption study was carried out on the representative specimens (76.2 mm long, 25.4 mm wide and 2 mm thick) of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulations as per ASTM D 570. In order to understand the influence of absorbed water on the Tensile strength and % Elongation, dumbbells (as per ASTM D 412) cut from the cured slabs of EPDM with Kevlar and EPDM without Kevlar, were conditioned, tested for initial tensile properties as conditioned and immersed along with other specimens of water absorption under identical conditions in 1 litre beaker containing distilled water. Weights of specimens were recorded initially after 24 hours of immersion, thereafter after every 1 week until water absorption reached saturation. On attaining saturation, dumbbells representative of EPDM with Kevlar and without Kevlar too were removed, their surfaces were wiped with dry cloth and subjected to tensile testing as per ASTM D 412.

6.2.6 Drying Behaviour:

The specimens (described in section 6.2.5) representative of all the three insulations (after being saturated with water) were subjected to drying in calibrated oven at 105°C. Specimens were drawn at regular interval and weights were recorded upon drying, till the weight of each specimen matched the respective original conditioned weight. Specimens of EPDM with Kevlar and EPDM without Kevlar (as saturated with water and as completely dried after water absorption study) were subjected to TGA till degradation using TGA of make TA Instruments Q600 SDT.

6.2.7 Thermal Analysis by DSC and TGA:

Samples representative of all the three rubbers were subjected to DSC (Differential Scanning Calorimetry) using DSC instrument of make TA Instruments Discovery DAC and TGA (Thermo Gravimetric Analysis) using TGA of make TA Instruments Q600 SDT employing a heating rate of 10°C/min.

6.2.8 Interface Properties:

It is understood from the literature that EPDM is non-polar and Kevlar improves the interfacial bonding strength to some extent (Jia X et al., (2013) and Muraleekrishnan R et al., (2000)). In order to check if EPDM based insulation will exhibit required interfacial bonding strength (measured in terms of peel strength) with various interfaces encountered during insulation lining of large CRMC, peel strength for each interface was evaluated using UTM of INSTRON make for EPDM without Kevlar and the results were compared with that of Nitrile rubber. Various interfaces encountered during insulation lining of large CRMC and the subsequent propellant casting are Carbon-Epoxy composite to unvulcanised (uncured) insulation, unvulcanised insulation to unvulcanised insulation, vulcanised (cured) insulation to unvulcanised insulation and vulcanised insulation to HTPB based composite solid propellant. Based on experimental trials, bonding agent for each interface was finalized for EPDM without Kevlar. Whereas, Nitrile Rubber insulation being proven one, established bonding agents are available for each interface. Preparation and testing of interface specimens pertaining to few interfaces are shown in Figure-34 for EPDM without Kevlar.

Figure-34: Preparation and Testing of Peel Specimens for various interfaces

6.3 Results and Discussion:

6.3.1 Physical and Mechanical Properties:

Test results for physical and mechanical properties, obtained in case of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulations are given in Table-32, against the insulation requirements of large CRMC.

Table-32: Physical and Mechanical Properties in comparison

Properties	Insulation Requirements	EPDM With Kevlar	EPDM without Kevlar	Nitrile Rubber Based Insulation
Shore A Hardness	60 min	62-70	68-72	70-76
Density (g/cm^3)	As low as possible	1.03 (1.02-1.04)*	1.08 (1.06-1.09)	1.19 (1.18-1.19)
Tensile strength (kg/cm^2)				
Warp	100 min	145 (103-175)	207 (163-225)	255 (221-276)
Weft	100 min	104 (92-124)	200 (155-223)	253 (228-275)
% Elongation				
Warp	600 min	618 (545-669)	682 (593-722)	715 (660 -793)
Weft	600 min	604 (574-635)	659 (610-700)	707 (659-760)

*values in the parenthesis indicate the minimum and maximum of test results

The achieved values for tensile strength (Warp and Weft direction) in case of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulations are graphically represented in Figure- 35, 36 and 37 respectively. The achieved values of % Elongation (Warp and Weft directions) in case of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulations are graphically represented in Figure- 38, 39 and 40 respectively. It may be noted that in each of Figure-35, 36, 37, 38, 39 and 40, Slab-1 warp represents A-2 of Figure-30, Slab-1 weft represents A-6 of Figure-30, Slab-2 warp represents B-10 of Figure-30, Slab-2 weft represents B-14 of Figure-30, Slab-3 warp represents C-18 of Figure-30 and Slab-3 weft represents C-22 of Figure-30.

As evident from Table-32 and Figures- 35 to 40, the achieved average tensile strength and % Elongation of both EPDM with Kevlar and EPDM without Kevlar are well above the minimum required value of 100 kg/cm^2 and 600 minimum respectively. However, few individual values of tensile strength and % Elongation in case of EPDM with Kevlar are lower than the respective specified limits. The maximum value of Tensile strength and % Elongation of EPDM without Kevlar are higher than those of EPDM with Kevlar.

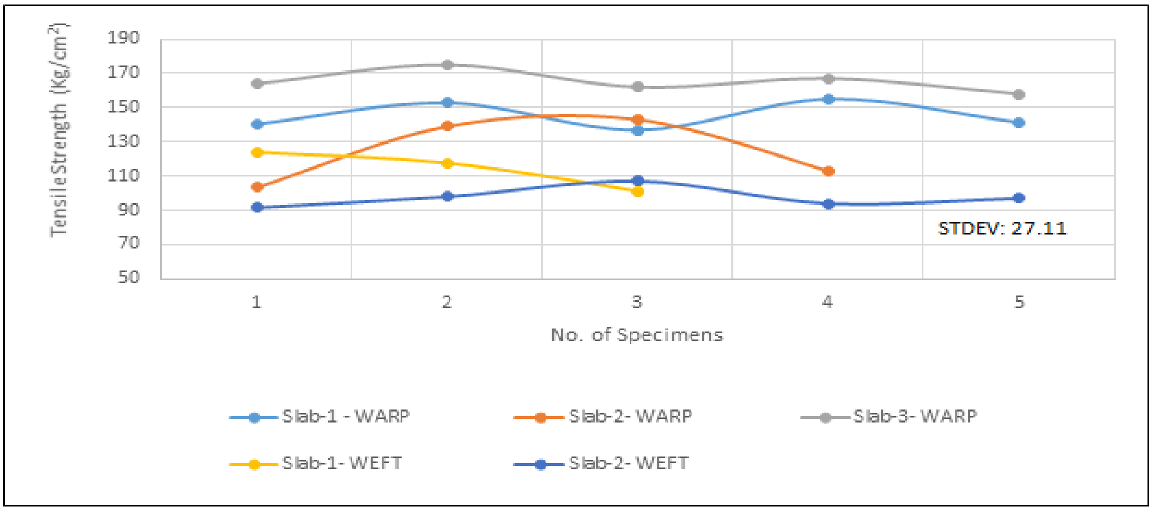


Figure-35: Tensile strength in warp and weft direction of EPDM with Kevlar

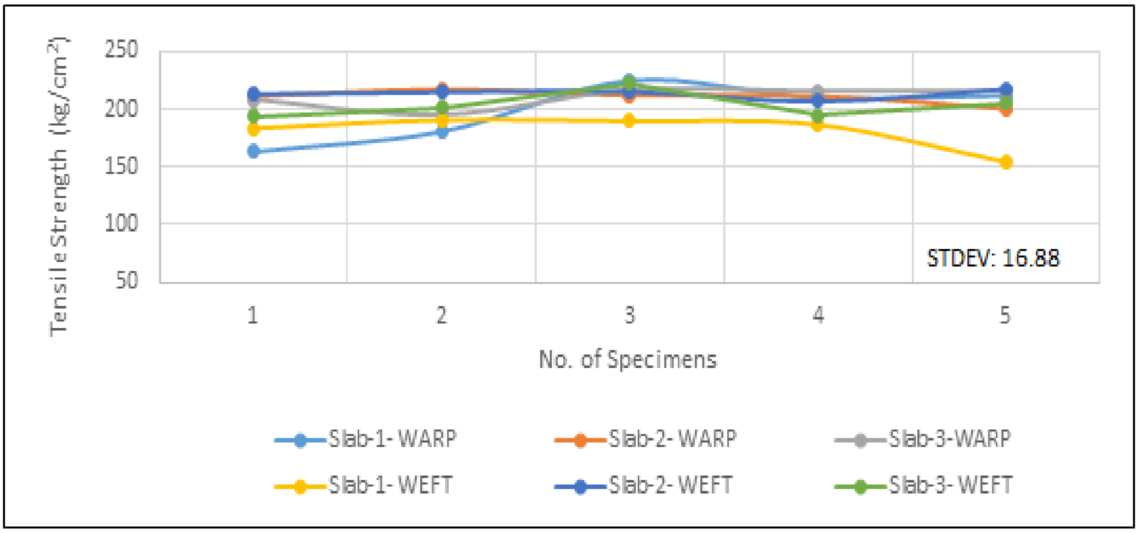


Figure-36: Tensile strength in warp and weft direction of EPDM without Kevlar

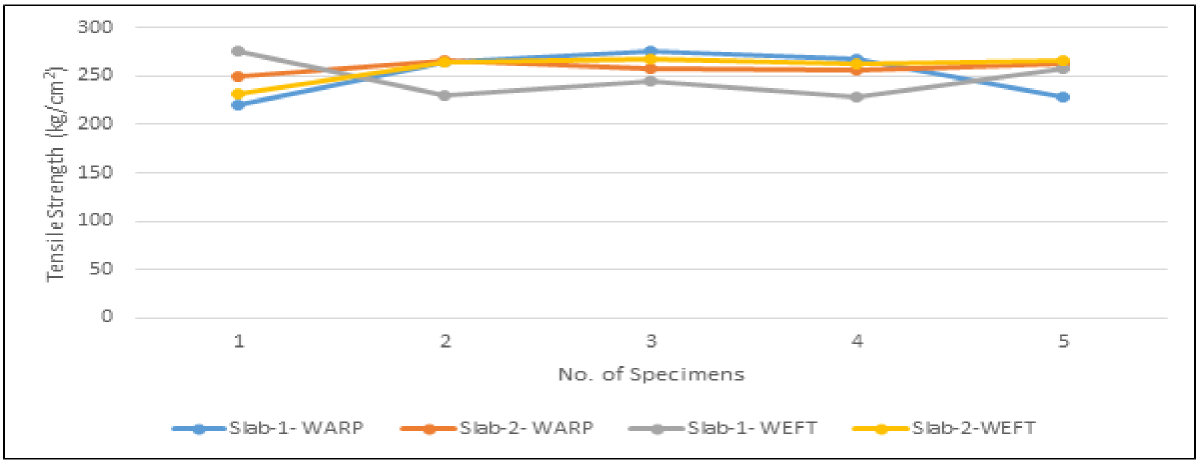


Fig-37: Tensile strength in warp and weft direction of Nitrile rubber based insulation

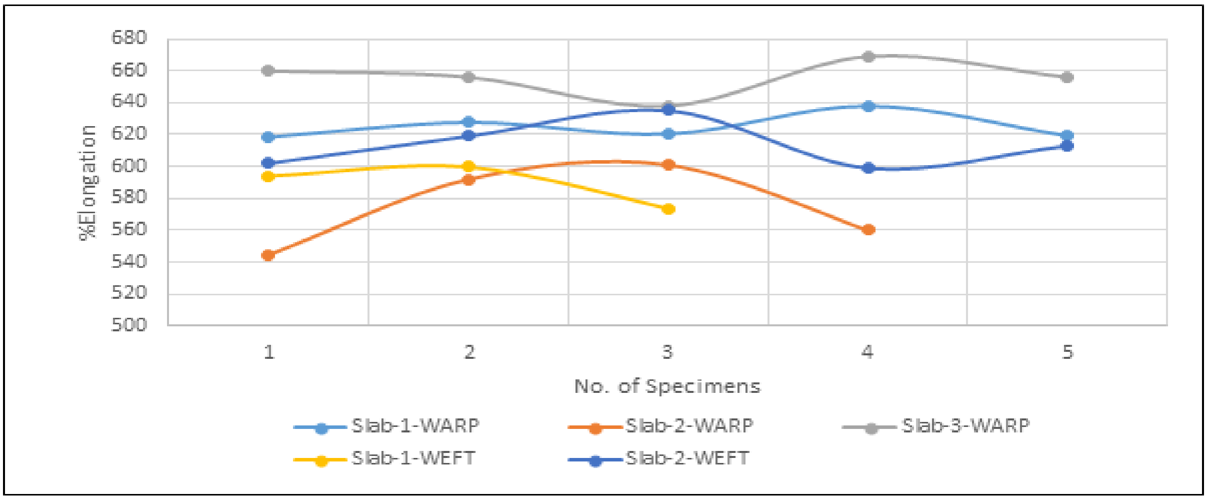


Figure-38: % Elongation in warp & weft direction of EPDM with Kevlar

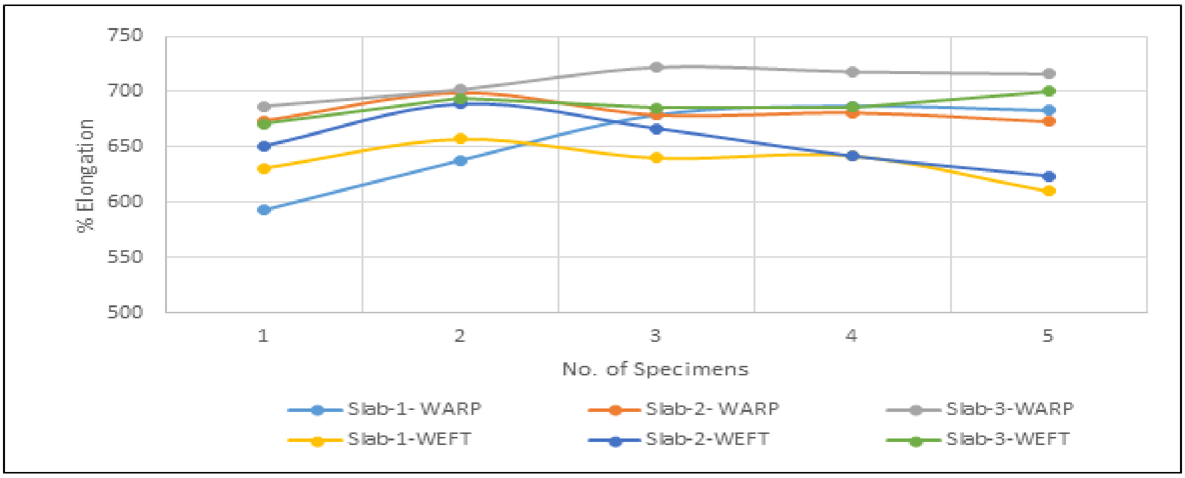


Figure-39: % Elongation in warp & weft direction of EPDM without Kevlar

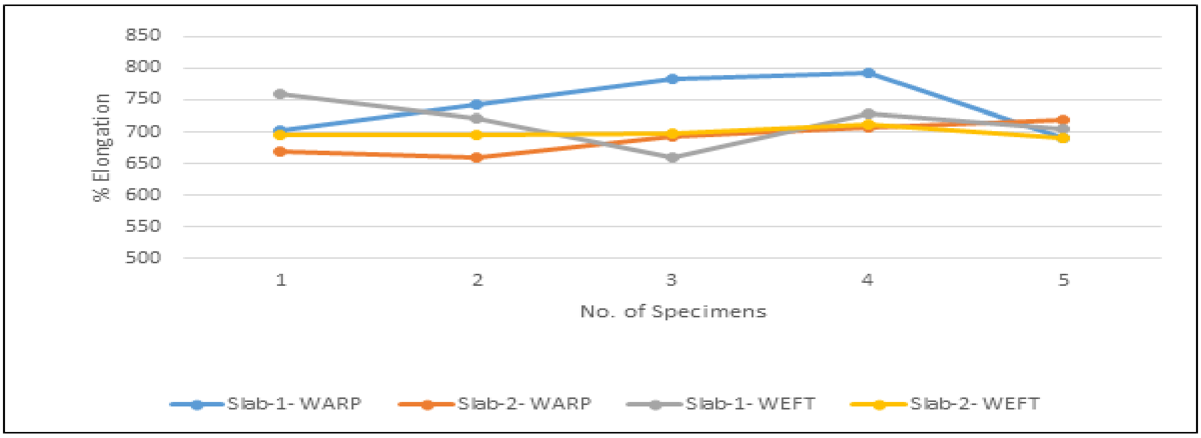


Figure-40: % Elongation in warp & weft direction of Nitrile Rubber based Insulation

The scatter in mechanical properties are wider in case of EPDM with Kevlar than EPDM without Kevlar. The achieved values of Tensile Strength and % Elongation in case of Nitrile rubber based insulation (evaluated as reference) are higher than those of both EPDM with Kevlar and EPDM without Kevlar. In terms of scatter in the achieved values of mechanical properties, EPDM without Kevlar compares well (less scatter) with Nitrile rubber based insulation as both of them contain only precipitated silica as reinforcing filler. Whereas, EPDM with Kevlar shows more scatter (probably due to non-uniform distribution/ orientation of Kevlar filler in the EPDM matrix).

Kevlar being incorporated as Rhenogran (which is nothing but 40% aramid fibre (KEVLAR) pulp pre-dispersed in 60% EPDM polymeric binder with dispersing agent), EPDM with Kevlar gives smooth surface finish which is comparable to that of Nitrile rubber based insulation. But, surface finish of EPDM without Kevlar is not as smooth as that of EPDM with Kevlar and Nitrile rubber based insulation. The measured value of specific gravity is the least for EPDM with Kevlar (1.03 g/cm^3), followed by EPDM without Kevlar (1.08 g/cm^3) and the highest for Nitrile rubber based insulation (1.19 g/cm^3).

6.3.2 Thermal properties:

Test results of thermal properties in comparison with insulation requirements are given in Table-33.

Table-33: Thermal Properties in comparison

Properties	**Insulation Requirement**	**Test Result**		
		EPDM with Kevlar	**EPDM without Kevlar**	**Nitrile Rubber based insulation**
Thermal conductivity, at 80°C, Cal/cm. sec.°C (Max)	$6.5x10^{-4}$	$5.5x10^{-4}$ ($5.4-5.5x10^{-4}$)	$6.1x10^{-4}$ ($6.1-6.3x10^{-4}$)	$6.2x10^{-4}$ ($6.0-6.4x10^{-4}$)
Specific heat at 80°C Cal/g.°C (Min)	0.35	0.44 (0.44-0.45)	0.45 (0.45-0.46)	0.43 (0.41-0.45)
Coefficient of linear thermal expansion °C^{-1} (Max)	$3.0x10^{-4}$	$3.1x10^{-4}$	$3.02x10^{-4}$ ($2.9-3.1x10^{-4}$)	$2.02x10^{-4}$ ($1.7-2.3x10^{-4}$)

As evident from Table-33, Thermal conductivity is the least for EPDM with Kevlar (5.4 -5.5x10^{-4} cal/cm. sec °C) and comparable for both EPDM without Kevlar and Nitrile based insulations. In case of EPDM with Kevlar, Kevlar plays a vital role in reducing the Thermal conductivity appreciably. Therefore, in terms of Thermal conductivity, Kevlar seems to be more beneficial than silica (Thermal conductivity of Kevlar is lower (0.022-0.023 W/m.°K) than silica (1.4 W/m.°K)). Achieved values of specific heat capacity are comparable for all the three rubbers. Coefficient of thermal expansion values are comparable for both EPDM with Kevlar and EPDM without Kevlar, but they are higher than that of Nitrile rubber based insulation. Higher coefficient of thermal expansion for both the EPDM based insulations could be attributed to the flexibility of base rubber in their formulation i.e. EPDM TER 4038, which is more flexible than Purbunan 3445 (Nitrile rubber).

6.3.3 Ablative Properties:

Achieved values of erosion rate and heat of ablation of EPDM with Kevlar and EPDM without Kevlar in comparison with Nitrile rubber based insulation are given in Table-34.

Table-34: Erosion Rate and Heat of Ablation in comparison

Properties	Insulation Requirement	Test Result		
		EPDM with Kevlar	EPDM without Kevlar	Nitrile Rubber based insulation
Erosion Rate (mm/Sec) Max.	0.20	0.12	0.14	0.15
Heat of Ablation (MJ/kg)	As high as possible	19.60	18.27	16.99

The ablative performance of EPDM without Kevlar is comparable to Nitrile rubber based insulation. EPDM with Kevlar shows the best ablative performance as its achieved erosion rate is the least (0.12 mm/sec). Further, the lower specific gravity is found to augment heat of ablation of both the EPDM rubber based insulations. Insulation material is expected to have heat of ablation as high as possible. Thus, in terms of ablative performance, EPDM with Kevlar seems to be the best and both EPDM with Kevlar and EPDM without Kevlar are better than Nitrile rubber based insulation.

6.3.4 Water absorption behaviour:

Data generated of water absorption behaviour (% water absorbed as a function of time of immersion in distilled water) for EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulation are given in Table-35, Table-36 and Table-37 respectively. Water absorption behaviour (% water absorption vs. time) of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulation are graphically represented in Figure-41, Figure-42 and Figure-43 respectively.

Table-35: % Water absorption w.r.to Time for EPDM with Kevlar

Specimen ID	% Water content												
	24 hours	Week-1	Week-2	Week-3	Week-4	Week-5	Week-6	Week-7	Week-8	Week -9	Week-10	Week-11	Week-12
1	1.08	3.77	5.55	6.92	7.94	8.74	9.14	9.17	9.42	9.58	9.74	9.90	9.97
2	1.11	3.92	5.76	7.40	8.45	9.24	9.64	9.95	10.25	10.46	10.55	10.65	10.73
3	1.08	4.03	5.82	7.29	8.37	9.38	9.92	9.97	10.21	10.47	10.77	11.07	11.11
4	1.09	3.89	5.64	7.15	8.16	8.79	9.36	9.65	9.82	9.92	10.27	10.56	10.47
5	1.04	3.73	5.40	6.88	7.81	8.35	8.74	8.82	8.84	8.92	9.20	9.48	9.56

Table-36: % Water absorption w.r.to Time for EPDM without Kevlar

Specimen ID	% Water content					
	24 hrs	Week -1	Week -2	Week -3	Week -4	Week -5
1	1.04	3.56	4.98	5.37	5.54	5.80
2	0.99	3.60	5.17	5.56	6.06	6.04
3	1.12	3.80	5.22	5.47	5.64	5.69
4	1.08	3.75	4.88	5.46	5.69	5.65
5	1.04	3.54	4.90	5.42	5.73	5.78

Table-37: % Water absorption w.r.to Time for Nitrile Rubber insulation

Specimen ID	% Water content				
	24 hrs	Week -1	Week -2	Week -3	Week -4
1	1.49	4.71	7.64	7.41	7.71
2	1.48	4.77	7.52	7.25	7.63
3	1.49	4.72	7.49	7.27	7.59

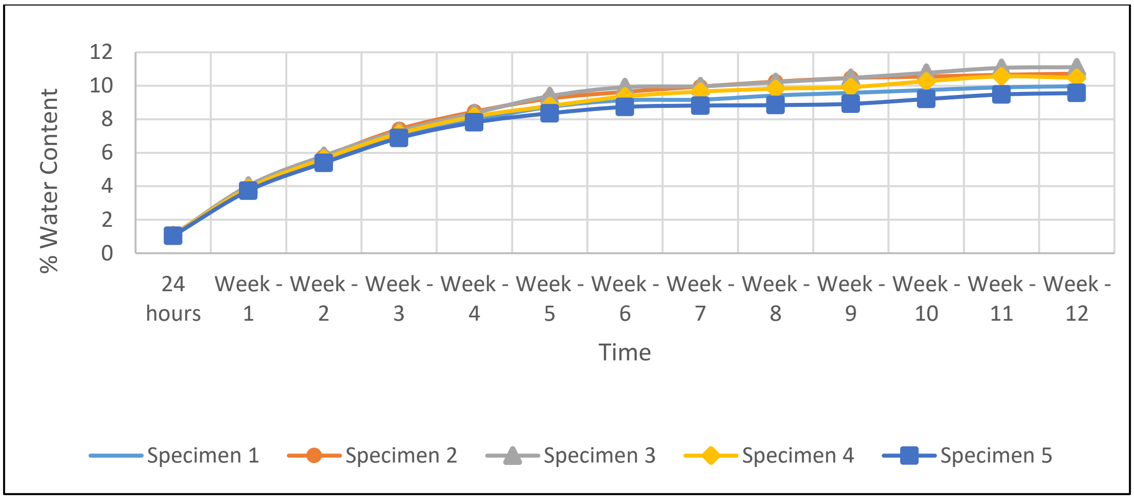


Figure 41: % Water absorption of EPDM with Kevlar as a function of time

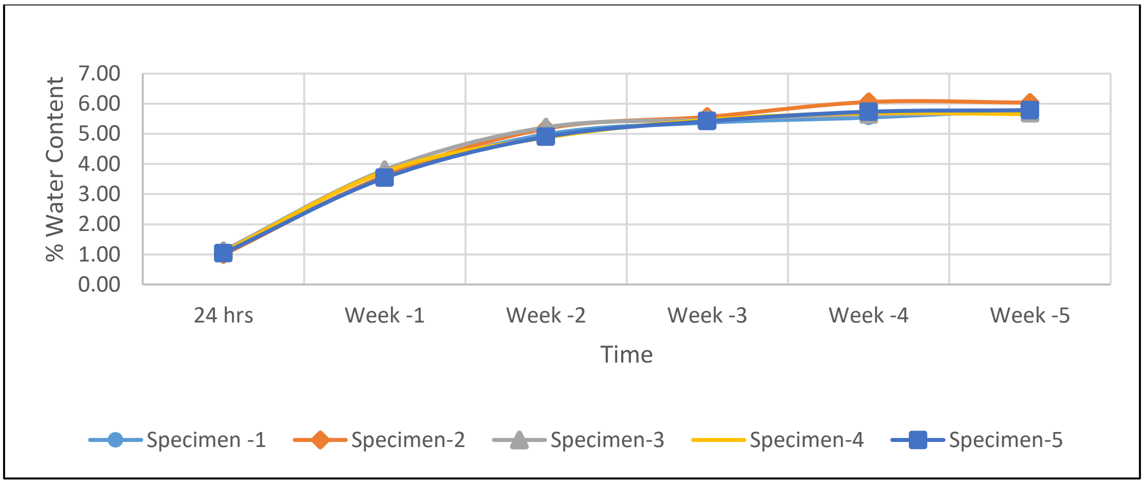


Figure 42: % Water absorption of EPDM without Kevlar as a function of time

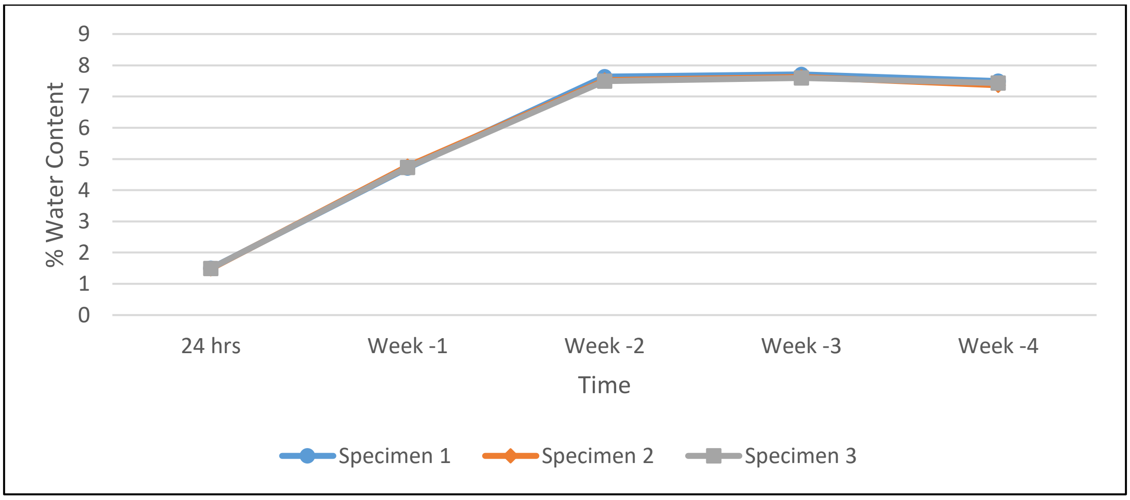


Figure 43: % Water absorption of Nitrile rubber insulation as a function of time

Water absorption behaviour of all the three types of insulation are represented collectively in Figure-44, by plotting the average of % water absorbed by all the specimens of each type at given point of time say after 24 hours, 1 week , 2 week etc.

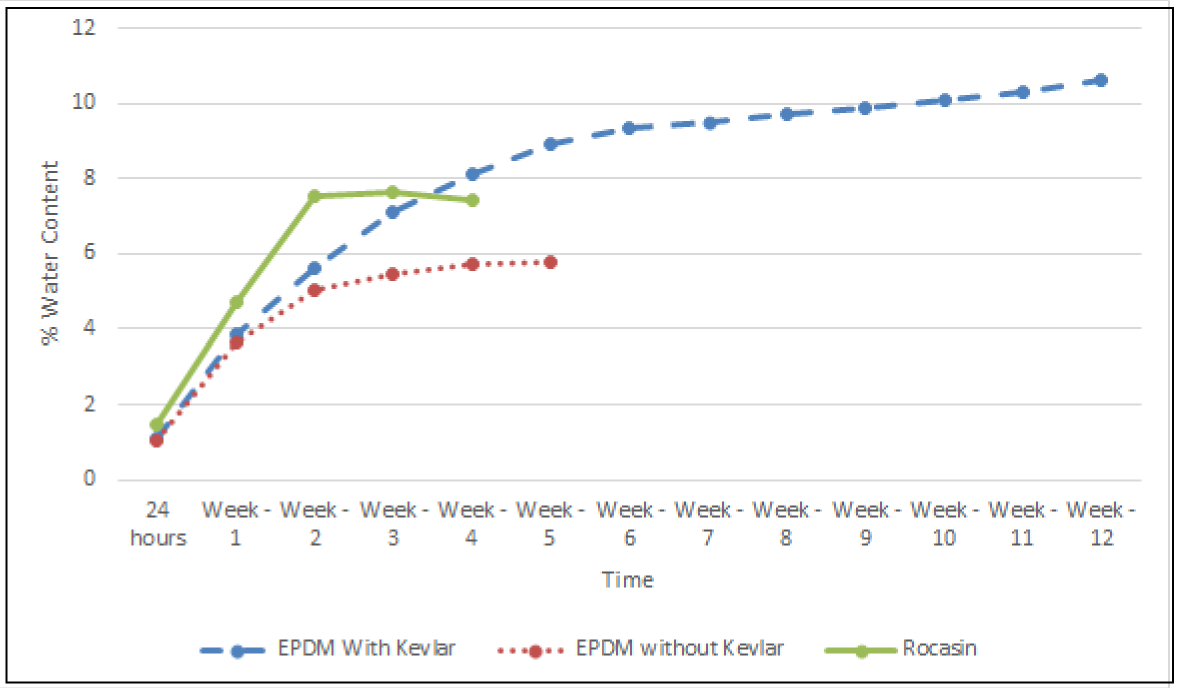


Figure 44: **% Water absorption of EPDM with Kevlar, EPDM without Kevlar and Nitrile Rubber insulation (abbreviated as Rocasin in Figure) as a function of time**

The influence of absorbed water over Tensile strength and % Elongation of EPDM with Kevlar and EPDM without Kevlar is given in Table- 38.

Table-38: Influence of absorbed water over Tensile strength and % Elongation

Category	Avg. Initial Tensile Strength	Avg. Tensile strength as Saturated with water	% Change in Tensile Strength	Avg. Initial % Elongation	Avg. % Elongation as Saturated with water	% Change in Elongation
EPDM with Kevlar	14.29	13.37	-6.43	625.4	627.5	+0.34
EPDM without Kevlar	18.59	18.43	-0.86	720.5	747.5	+3.75

As evident from Table-35 to 37 and Figure-41 to 44, initial tendency to absorb water up to 24 hours is almost the same for EPDM with Kevlar and EPDM without Kevlar.

Longer time taken for saturation by EPDM with Kevlar (12 weeks as against 5 weeks in case of EPDM without Kevlar) and higher % of water absorption in case of EPDM with Kevlar i.e. 10.63 % against 5.79 % in case of EPDM without Kevlar, corroborate that Kevlar is more hygroscopic and increases the absorbed water content of EPDM.

As evident from Table-35 to 37 and Figure-41 to 44, % water absorption (on saturation) of Nitrile rubber based insulation is higher than that of EPDM without Kevlar but lower than that of EPDM with Kevlar. Precipitated Silica is a common reinforcing filler (50 PHR in case of Nitrile, 35 PHR in case of EPDM with Kevlar and 44 PHR in case of EPDM without Kevlar) in all the three rubbers. Therefore, the above finding could be attributed to high content of precipitated silica in Nitrile rubber based insulation as compared to EPDM without Kevlar. Further, non-polar nature of EPDM as reported in the literature (Bhuvaneswari CM et al., (2008)) might also account for lower water absorption by EPDM without Kevlar. Thus, in terms of water absorption behaviour, EPDM without Kevlar is more preferable than EPDM with Kevlar and proven Nitrile based insulation. As evident from Table-38, the absorbed water has no significant influence on the mechanical properties (Tensile Strength and % Elongation) as % change in Tensile Strength and Elongation are not significant.

6.3.5 Drying Behaviour:

Plots of % water retained versus time obtained during drying of saturated (with water) specimens of EPDM with Kevlar, EPDM without Kevlar and Nitrile Rubber based insulation at 105°C, are given in Figure-45, Figure-46 and Figure-47 respectively.

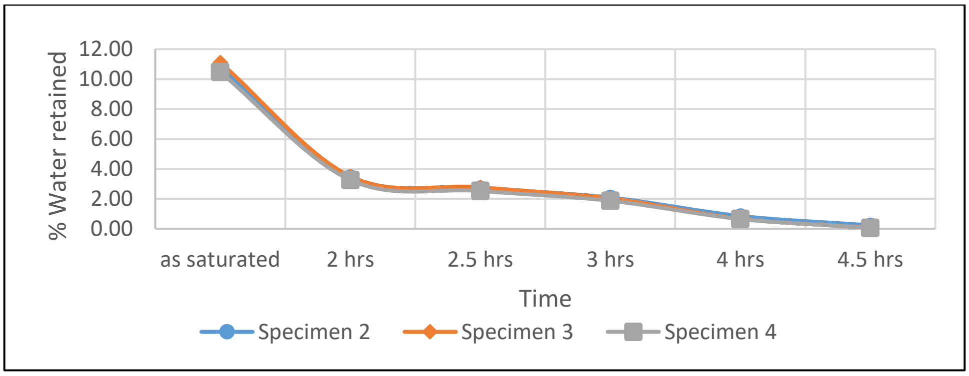


Figure 45: % Residual Water content of EPDM with Kevlar as a function of drying time at 105°C

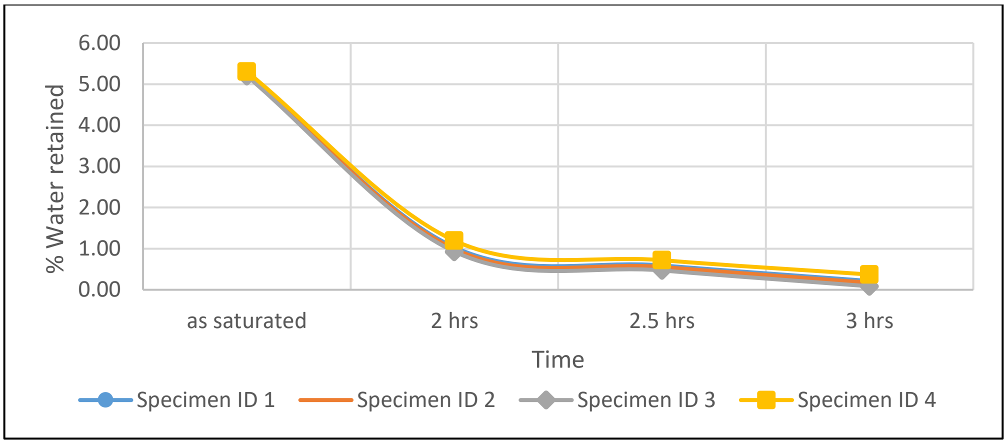


Figure 46: % Residual Water content of EPDM without Kevlar as a function of drying time at 105°C

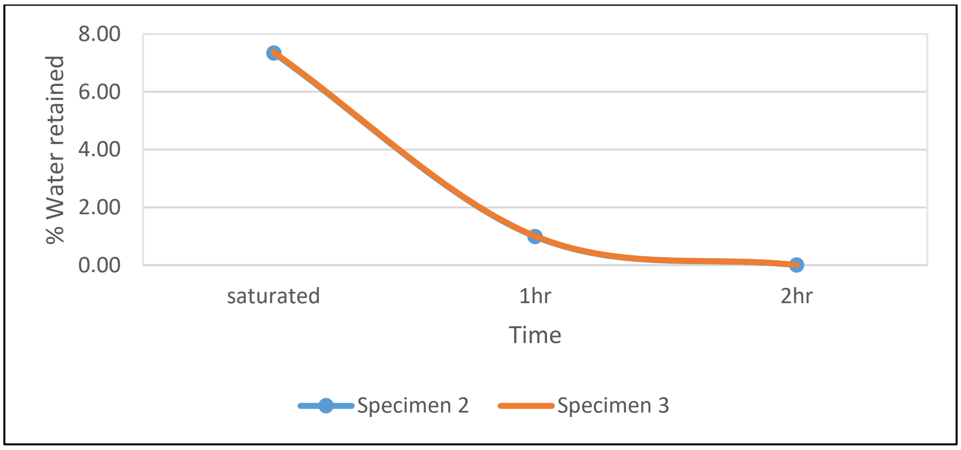


Figure 47: % Residual Water content of Nitrile Rubber insulation as a function of drying time at 105°C

Based on this study, it is found that minimum time required, for complete drying of absorbed water at 105°C, is 4.5 hours, 3 hours and 2 hours for 2 mm thick specimen of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber respectively. Thus time required for complete removal of water (complete drying) is the longest for EPDM with Kevlar, followed by EPDM without Kevlar and the least for Nitrile rubber based insulation.

TGA (Thermo Gravimetric Analysis) curves pertaining to EPDM with Kevlar as completely saturated with water and after complete drying at 105°C are given in Figure-48. TGA curves pertaining to EPDM without Kevlar as completely saturated with water and after complete drying at 105°C are given in Figure-49.

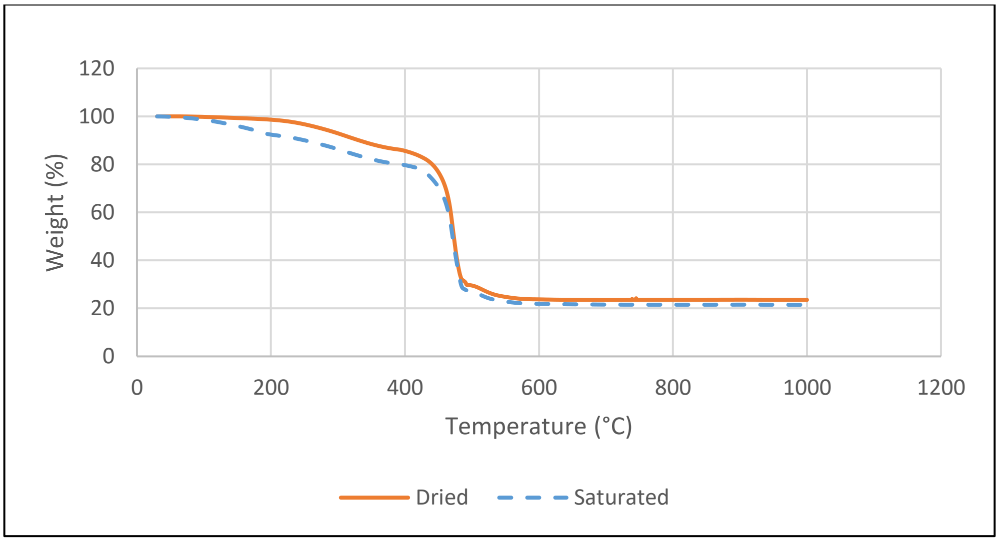


Figure 48: TGA Curve for EPDM with Kevlar as saturated with Water & after complete drying

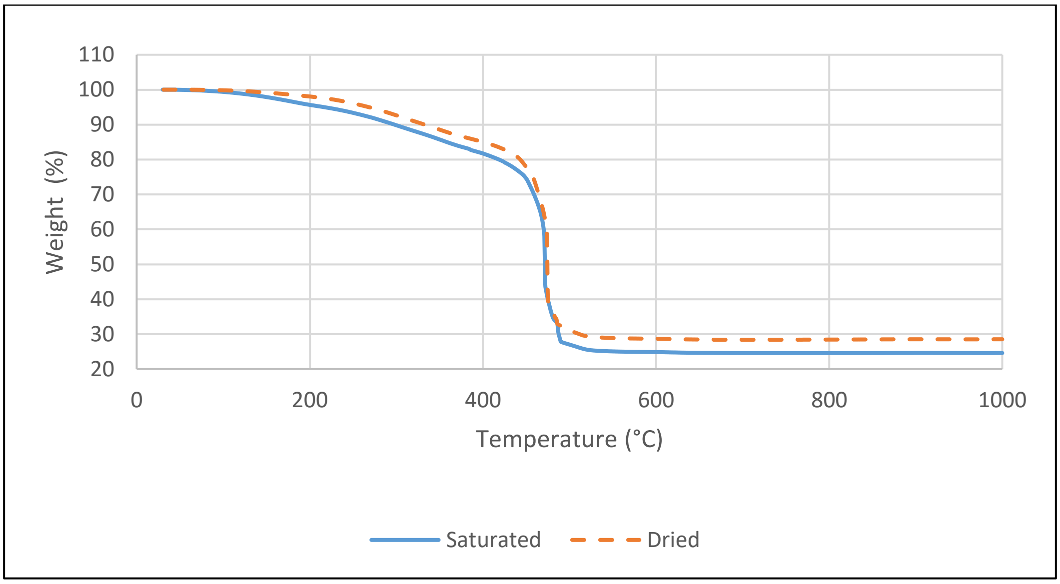


Figure 49: TGA Curve for EPDM without Kevlar as saturated with Water & after complete drying

As evident from Figure-48 and 49, absorbed moisture is found to have no appreciable effect on the degradation behaviour of EPDM with Kevlar and EPDM without Kevlar. Difference in % weight loss at 400°C between saturated and dried specimens of each of EPDM with and without Kevlar could be attributed to the respective % water absorbed (which is 10.63% in case of EPDM with Kevlar and 5.79% in case of EPDM without Kevlar).

6.3.6 Thermal Analysis by DSC and TGA:

The DSC (Differential Scanning Calorimetry) plots of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber are given in Figure-50. TGA plots of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber are given in Figure -51.

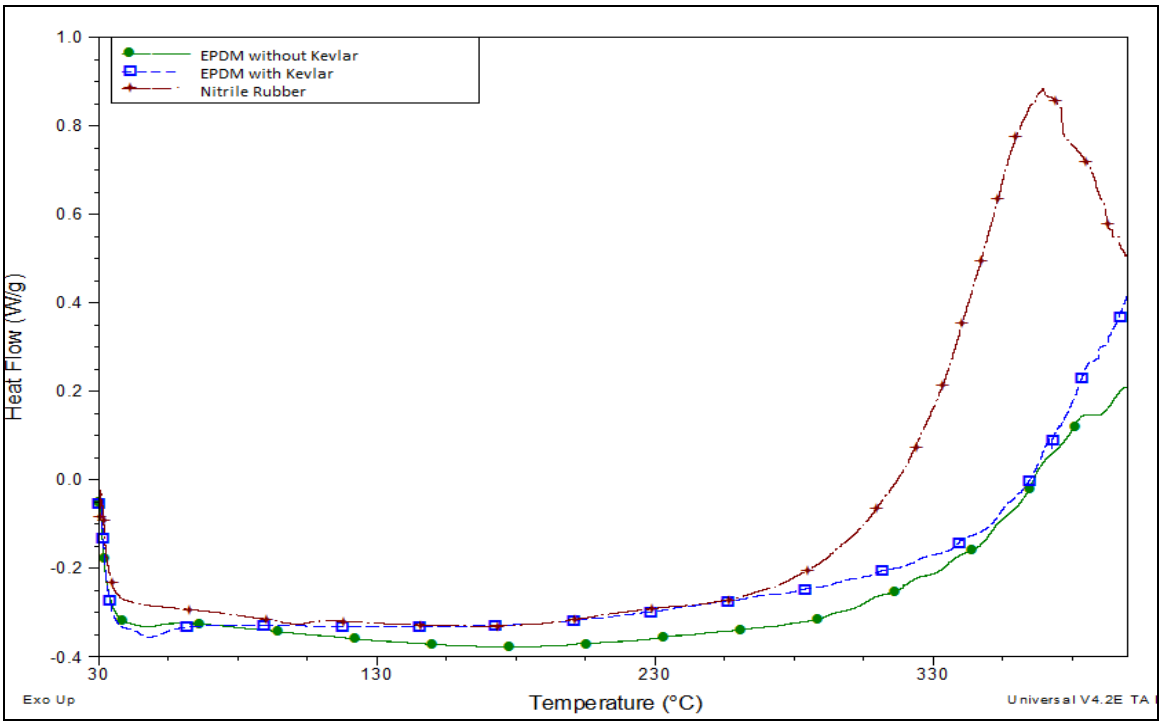


Figure 50: DSC Curve for EPDM with Kevlar, EPDM without Kevlar & Nitrile Rubber Insulation

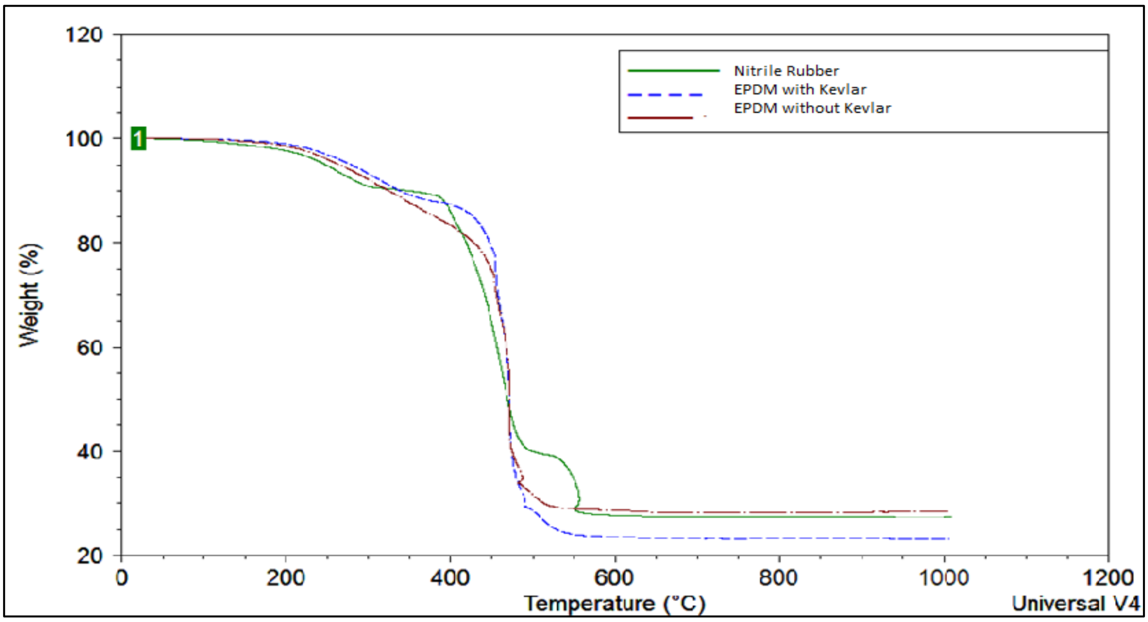


Figure 51: TGA Curve for EPDM with Kevlar, EPDM without Kevlar & Nitrile Rubber insulation

As evident from Figure-50 and 51, degradation occurs at relatively high temperature in case of EPDM with and without Kevlar as compared to Nitrile rubber (about 365°C against 300°C for Nitrile). This proves adequately that EPDM as an elastomer (irrespective of the filler used) has better thermal stability than Nitrile rubber. It may be noted that EPDM without Kevlar has 44 PHR of precipitated silica as compared to EPDM with Kevlar, which has 35 PHR of Precipitated Silica and 9 PHR of Kevlar in the form of Rhenogran (Refer Table-29 and Table-30).

Lower residual weight at 1000°C in case of EPDM with Kevlar as compared to EPDM without Kevlar and Nitrile Rubber could be attributed to the total decomposition of Kevlar even below 600°C. Thus, silica besides being a reinforcing filler has much better and higher ablative characteristic than Kevlar. Thus, EPDM without Kevlar seems to be better than EPDM with Kevlar in terms of weight retention at elevated temperature.

Further, glass transition temperature (T_g) as determined by DSC of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber are -47°C, -43°C and -25°C respectively. The lower T_g of EPDM with Kevlar and without Kevlar, further proves that EPDM will have better low temperature flexibility than Nitrile rubber.

6.3.7 Interface Properties:

The results of peel strength, for EPDM without Kevlar, are given in Table- 39, in comparison with those of Nitrile rubber based insulation. Figure-52 gives the comparison of Peel Strength between EPDM without Kevlar and Nitrile Rubber based insulation for various interfaces encountered during insulation lining of CRMC. As evident from Table- 39 and Figure-52, the peel strength of EPDM without Kevlar evaluated for each interface exceeded the respective minimum required value and the values are well comparable to those of Nitrile rubber based insulation also. Significant finding is that bonding agent for Nitrile rubber based insulation to HTPB based propellant works well with EPDM to HTPB based propellant too. As EPDM without Kevlar itself offered the required interfacial bonding strength, there is adequate confidence that interfacial bonding strength of EPDM with Kevlar would be some order higher.

Table-39: Achieved Peel Strength for various interfaces (EPDM without Kevlar vs. Nitrile Rubber based insulation)

Interface details	Bonding agent used	Achieved Peel strength (kg-f/cm)	Peel strength requirement (kg-f/cm)
Carbon Epoxy composite – unvulcanised EPDM without Kevlar	Chemlok 205 + Chemlok 238 + solution of EPDM without Kevlar	8.61 (8.57-8.65)	5.0 minimum
Carbon Epoxy composite – unvulcanised Nitrile Rubber	Chemlok 205 + solution of Nitrile Rubber	10.69 (9.63-11.75)	
Vulcanised Nitrile Rubber – Unvulcanised EPDM without Kevlar	Chemlok 205 + Chemlok 238 + solution of EPDM without Kevlar	6.26 (5.47-7.31)	5.0 minimum
Vulcanised Nitrile Rubber – Unvulcanised Nitrile Rubber	Chemlok 205 + solution of Nitrile Rubber + Desmodur Solution	5.10 (4.89-5.40)	
Unvulcanised EPDM without Kevlar - Unvulcanised EPDM without Kevlar	Solution of EPDM without Kevlar	5.74 (5.36-6.09)	5.0 minimum
Unvulcanised Nitrile rubber - Unvulcanised Nitrile Rubber	Solution of Nitrile Rubber	5.85 (5.47-6.23)	
Vulcanised EPDM without Kevlar to HTPB based Propellant	bonding agent is based on HTPB and contains fillers (Carbon Black), catalyst (V_2O_5) & curatives (TDI)	1.57	0.6 minimum
Vulcanised Nitrile rubber to HTPB based Propellant		1.54	

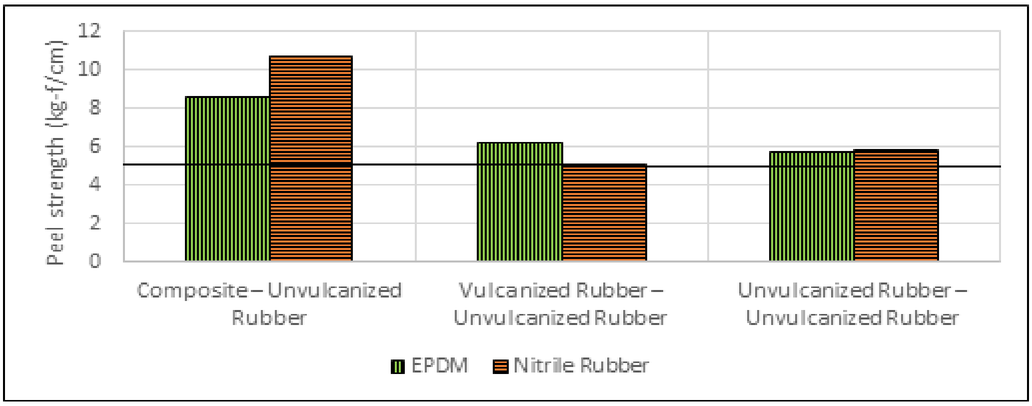


Figure 52: Peel Strength Comparison between EPDM without Kevlar and Nitrile Rubber insulation for various Interfaces

6.4 Summary of Findings:

It is found based on the comparative characterization study that EPDM with Kevlar offers lowest specific gravity (Section 6.3.1), lowest thermal conductivity (Section 6.3.2) and highest ablative performance (Section 6.3.3) out of all the three insulations. The surface finish of EPDM with Kevlar is as smooth as that of nitrile rubber based insulation and better than that of EPDM without Kevlar (Section 6.3.1). Specific heat capacity of EPDM with Kevlar is comparable to that of EPDM without Kevlar and Nitrile rubber based insulation (Section 6.3.2). But EPDM with Kevlar shows widest scatter in mechanical properties (Section 6.3.1), highest tendency to absorb water (Section 6.3.4), requires longest time to dry moisture (Section 6.3.5) and exhibits highest weight loss at elevated temperature (600°C) (Section 6.3.6) among all the three insulations, due to the presence of Kevlar as reinforcing filler.

The above short comings of EPDM with Kevlar are overcome to a large extent by EPDM without Kevlar, as it shows less scatter in mechanical properties (Section 6.3.1), less tendency to absorb moisture (Section 6.3.4), less time to drive moisture (Section 6.3.5) and less weight loss at elevated temperature (Section 6.3.6). In terms of specific gravity, thermal conductivity and tendency to absorb moisture, EPDM without Kevlar is even better than proven nitrile rubber based insulation (Section 6.3.1, Section 6.3.2 and Section 6.3.4). In terms of scatter in mechanical properties, specific heat, ablative performance and interface properties, EPDM without Kevlar compares well with the proven Nitrile rubber based insulation (Section 6.3.1, Section 6.3.2, Section 6.3.3 and 6.3.7). Glass Transition Temperature (T_g) of both EPDM with Kevlar and EPDM without Kevlar are less than that of nitrile rubber based insulation and confirms that EPDM based insulation is more preferable for low temperature application as it offers better flexibility.

It is found that initial decomposition temperature of both EPDM with Kevlar and EPDM without Kevlar are higher than (365°C) that of Nitrile rubber based insulation (300°C) (Section 6.3.6). EPDM without Kevlar despite overcoming the limitations of EPDM with Kevlar, has slightly higher specific gravity and slightly lower ablative performance than EPDM with Kevlar but its specific gravity is still lower than that of Nitrile rubber based insulation and its ablative performance is well comparable to that of Nitrile rubber based insulation (Section 6.3.1 and Section 6.3.3).

6.5 Additional Characterization to corroborate Findings:

6.5.1 Characterization by Scanning Electron Microscopy (SEM):

SEM images were captured using table top SEM of SEC Korea make (Model No. SNE 4500 M Plus). SEM images of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber based insulation are given in Figure- 53, Figure-54 and Figure-55 respectively.

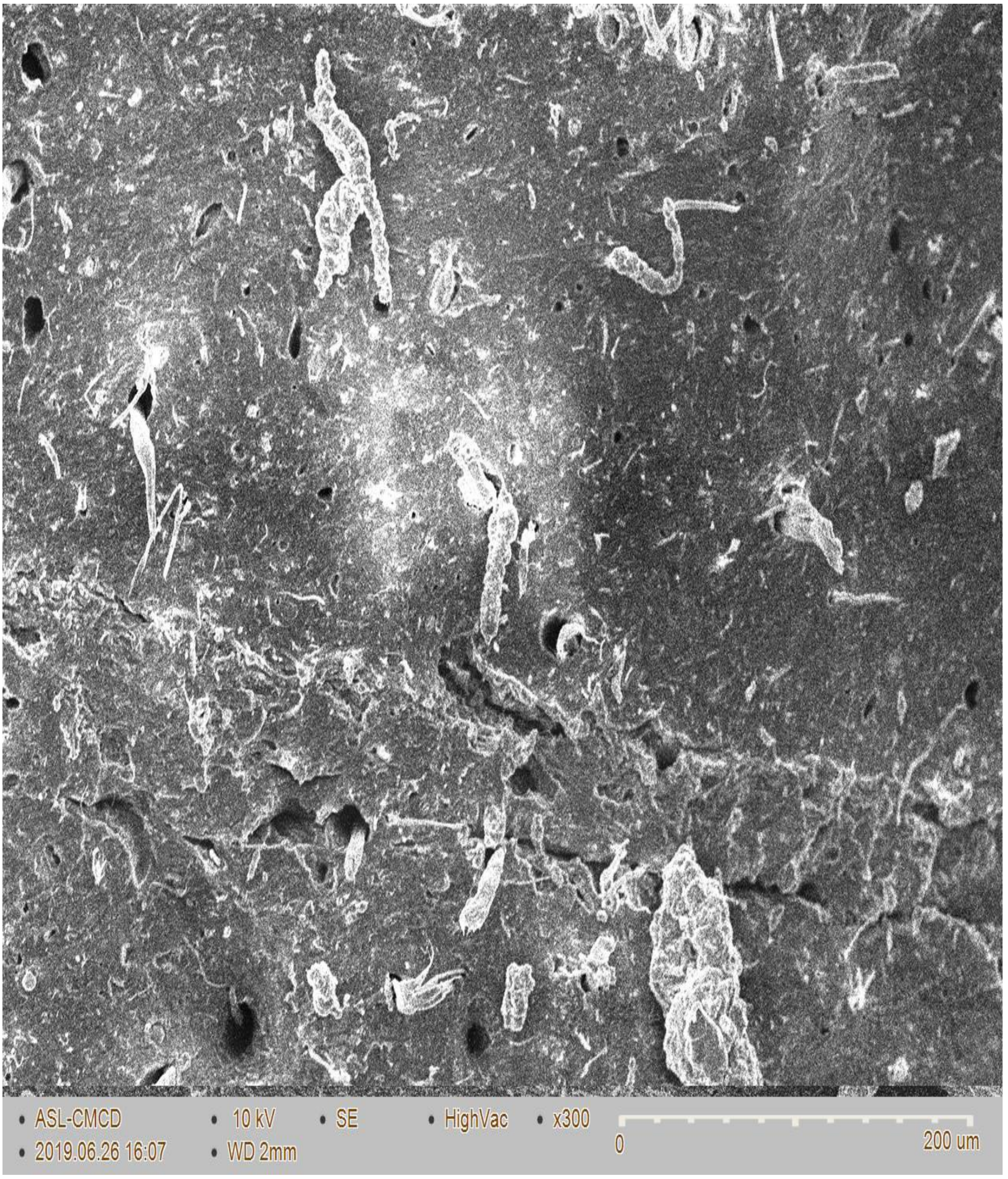


Figure-53: SEM image of EPDM with Kevlar

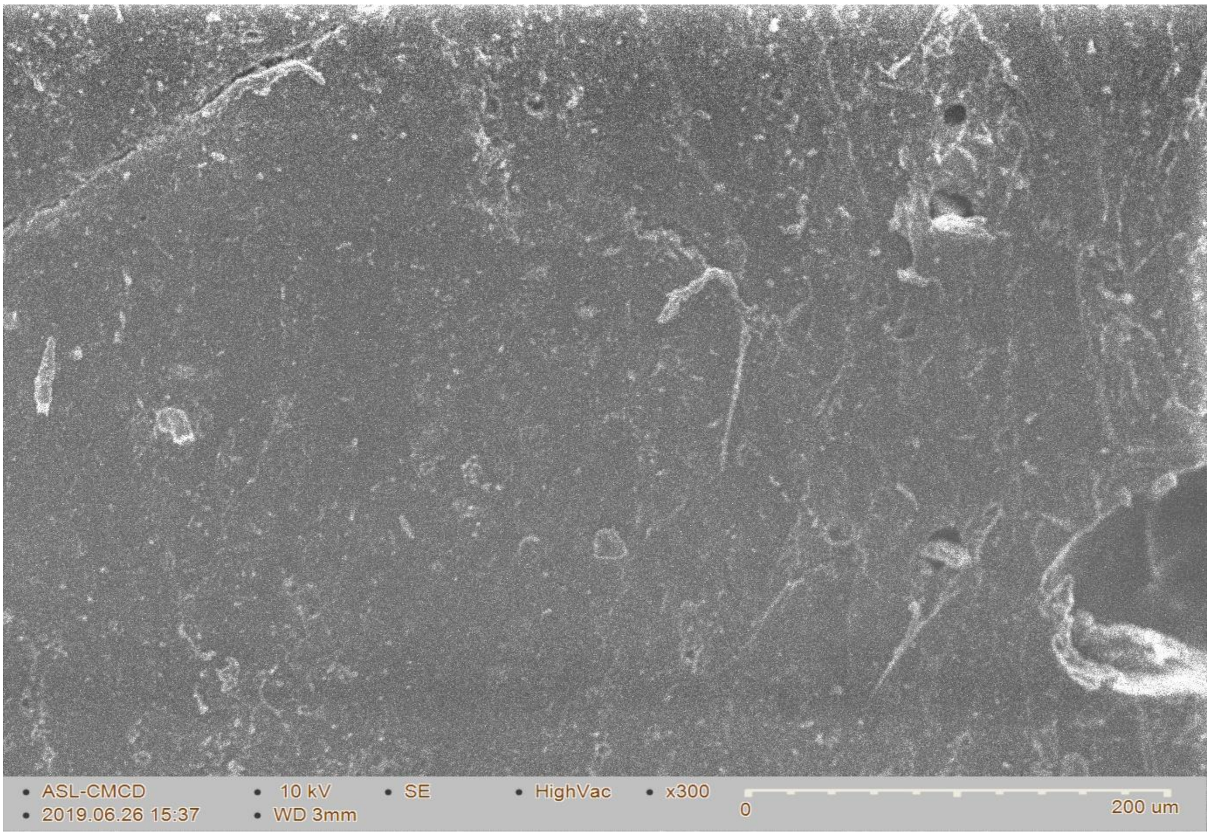


Figure-54: SEM image of EPDM without Kevlar

Figure-55: SEM image of Nitrile Rubber based insulation

As evident from SEM images (Figure-53 and 54), filler distribution is more orderly in case of EPDM without Kevlar (precipitated silica is the only filler) than EPDM with Kevlar, in which the distribution of fibrous filler (Kevlar) is not uniform. This probably explains the wide scatter in mechanical properties observed in case of EPDM with Kevlar as discussed in Section 6.3.1. As evident from Figure- 55, SEM image of Nitrile rubber based insulation (which too has only precipitated silica as filler), the filler distribution is quite orderly and explains the less scatter in the achieved mechanical properties of Nitrile rubber based insulation as discussed in Section 6.3.1.

6.5.2 Characterization by FTIR Spectroscopy:

FTIR spectroscopy was carried out for all the three rubbers using FTIR Spectrometer of Agilent make operated in ATR mode in the range of 4000-600 cm^{-1}. FTIR spectra of EPDM with Kevlar, EPDM without Kevlar and Nitrile rubber are given in Figure- 56, Figure-57 and Figure-58 respectively. The bands obtained at various wavenumbers and the functional groups assigned based on interpretations for EPDM with Kevlar (Figure-56), EPDM without Kevlar (Figure-57) and Nitrile Rubber (Figure-58) based insulations are summarized in Table-40, Table-41 and Table-42 respectively.

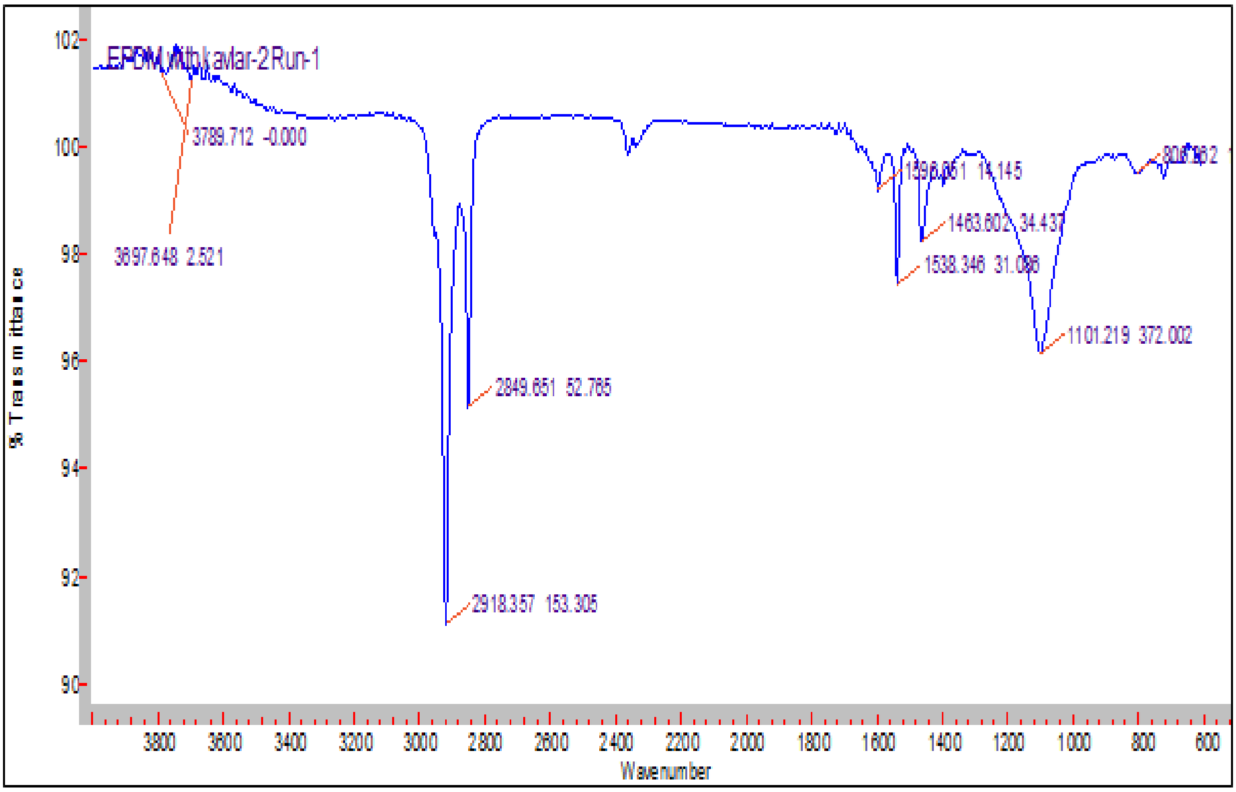


Figure-56: FTIR Spectrum of EPDM with Kevlar

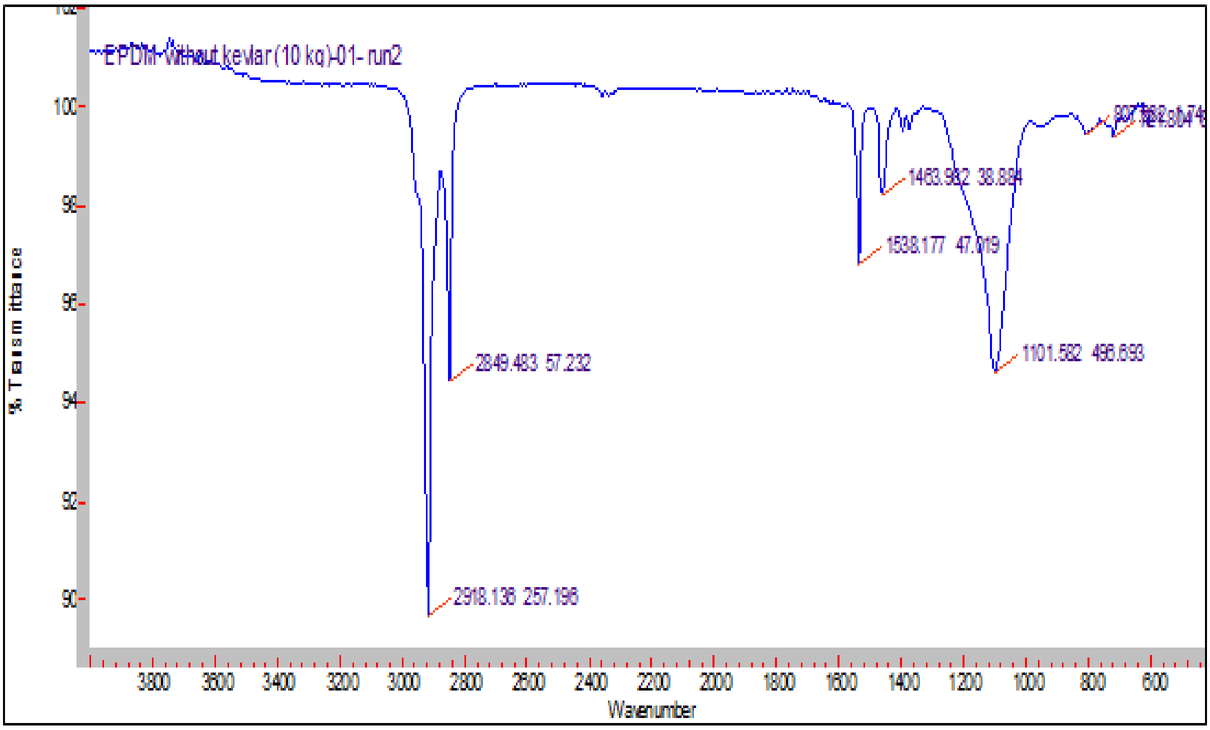


Figure-57: FTIR Spectrum of EPDM without Kevlar

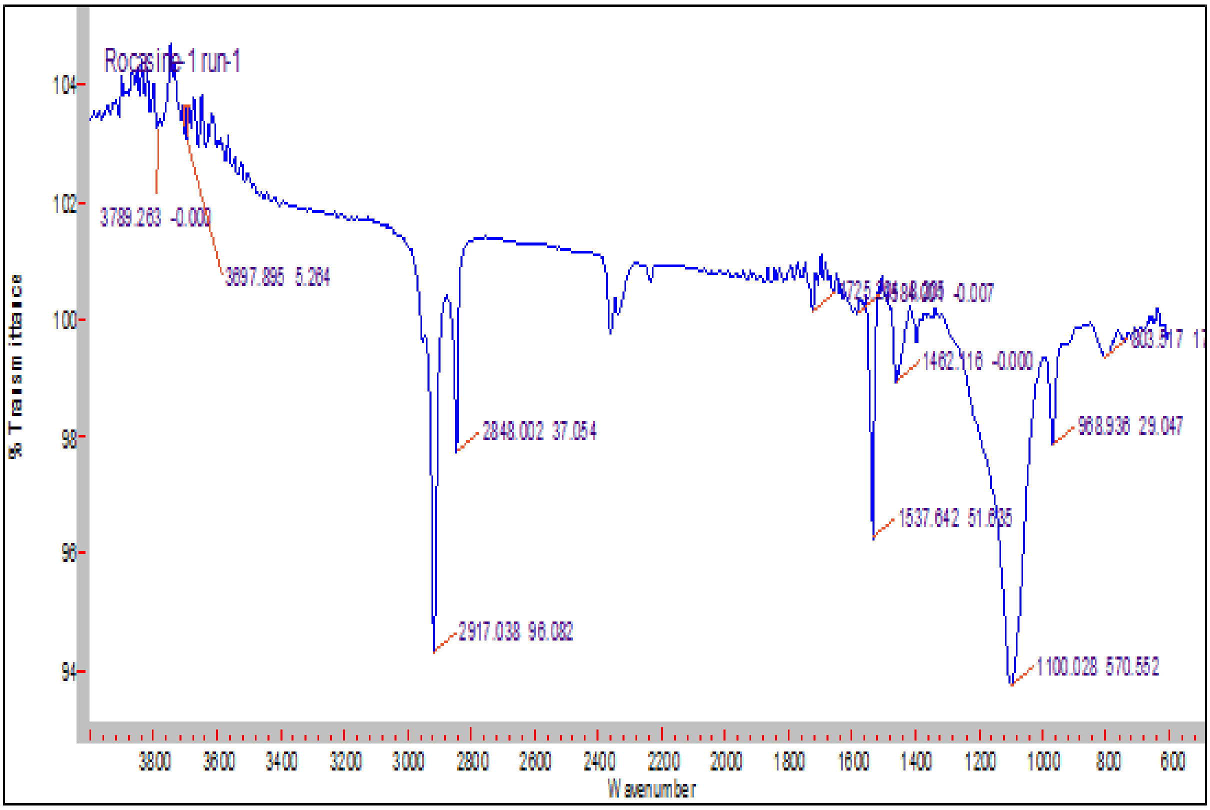


Figure-58: FTIR Spectrum of Nitrile Rubber based insulation

Table-40: Functional Groups interpreted from FTIR spectrum of EPDM with Kevlar

Wavenumber (cm^{-1})	Functional Group interpreted
3789-3697	-N-H (Amine, Amide) or –OH Alcohol or Phenol or acid
2918 and 2849	Aliphatic C-H
1538	>C-S-
1463	$-CH_2-$
1101	-Si-O-

Table-41: Functional Groups interpreted from FTIR spectrum of EPDM without Kevlar

Wavenumber (cm^{-1})	Functional Group interpreted
2918 and 2849	Aliphatic C-H
1538	>C-S-
1463	$-CH_2-$
1101	-Si-O-

Table-42: Functional Groups interpreted from FTIR spectrum of Nitrile Rubber based insulation

Wavenumber (cm^{-1})	Functional Group interpreted
3789-3697	-N-H (Amine, Amide) or –OH, Alcohol or Phenol or acid
2917and 2847	Aliphatic C-H
2240	-CN
1537	>C-S-
1462	$-CH_2-$
1101	-Si-O-
968	-CH=CH- (trans)

As evident from Table- 40 and 41, except for the band obtained at wavenumber of 3789-3697 cm^{-1}, spectra of both EPDM with Kevlar and EPDM without Kevlar are comparable and confirm that both are EPDM (Ethylene Propylene Diene Terpolymer) rubbers. Additional band obtained in wavenumber range of 3789-3697 cm^{-1} in case of EPDM with Kevlar, could be attributed to the amide group of Kevlar filler (p-phenylene terephthalamide). Further as evident from Table-40, 41 and 42, the presence of band at a wavenumber of 1538-1537 cm^{-1} (which correspond to C-S bond) in case of all the 3 rubbers confirm beyond doubt that all are sulphur cured.

The common presence of band at wavenumber of 1101 cm^{-1} in all the 3 rubbers (which correspond to Si-O) confirms the presence of silica as reinforcing filler in all the 3 rubbers. Based on the relative height of this peak/band, it can be interpreted that Silica % (SiO_2 %) is the highest in Nitrile rubber based insulation, followed by EPDM without Kevlar and the least in case of EPDM with Kevlar. Thus FTIR spectra clearly demarcate the % of silica in all the three rubbers. It may be noted that by formulation, % Silica in Nitrile Rubber, EPDM without Kevlar and EPDM with Kevlar are 27.59, 24.65, and 19.61 respectively (Table-29 and Table-30).

Height of peak/band at wavenumber of 1537 cm^{-1} is almost the same for EPDM with Kevlar and EPDM without Kevlar but the same is higher in case of Nitrile rubber based insulation. This implies that C-S bond intensity (i.e. sulphur crosslink) is more in case of Nitrile rubber based insulation as compared to EPDM with Kevlar and EPDM without Kevlar probably due to the difference in reactivity arising because of the presence of unsaturation in the side chain in case of EPDM as compared to main chain unsaturation in case of Nitrile rubber. Thus FTIR spectra explain why the achieved mechanical properties (Tensile strength and % Elongation) of Nitrile rubber based insulation are higher than those of EPDM with Kevlar and EPDM without Kevlar (Section 6.3.1).

Presence of additional bands at 2240 cm^{-1} and 968 cm^{-1} (Table-42) confirms the presence of –CN (acrylonitrile) and -CH=CH- (butadiene) and thus proves that the base rubber is copolymer of acrylonitrile-butadiene in case of Nitrile rubber based insulation. Band at 3789-3697 cm^{-1} in case of Nitrile Rubber based insulation could be attributed to Dioctyl Phthalate as plasticizer in the formulation.

6.6 Conclusion:

- EPDM insulation based on two formulations (EPDM with Kevlar and EPDM without Kevlar) were evaluated for the insulation requirements of large CRMC and the results were compared with the proven Nitrile rubber based insulation.
- Both EPDM with Kevlar and EPDM without Kevlar are found to be advantageous over proven Nitrile Rubber based insulation due to lower specific gravity, better ablative performance, lower glass transition temperature (and hence better low temperature flexibility) and higher initial decomposition temperature.
- Higher tendency to absorb moisture, larger scatter in mechanical properties and higher weight loss at elevated temperature are the shortcomings of EPDM with Kevlar, which are overcome by EPDM without Kevlar.
- Chapter-6 opens the scope for further research to tailor the formulation in order to reap the full benefits of EPDM without Kevlar while keeping the specific gravity as low as possible and ablative performance as high as possible.

CHAPTER 7

LIMITED ACCELERATED AGEING STUDY TO PREDICT THE LIFE OF SULPHUR CURED EPDM INSULATION

Limited Accelerated Ageing Study to predict the life of Sulphur cured EPDM insulation

7.1 Introduction:

EPDM Rubber based insulation, due to the presence of unsaturation in the side chain, is expected to have higher ageing resistance and hence longer service life as compared to Nitrile Rubber based insulation. This Chapter aims to predict the life of EPDM-S in order to give adequate confidence as to whether EPDM-S insulation will have longer life than Nitrile Rubber based insulation. Based on accelerated ageing study carried out earlier as per ISO 11346, Nitrile Rubber based insulation was predicted to have life of 15 years at ambient condition and the same has been validated through Natural ageing (Courtesy: ELD/HTCC of ASL/DRDO). Therefore, prime objective of this Chapter is to carry out accelerated ageing for EPDM-S insulation at 90°C (which is recommended for Nitrile Rubber based insulation) so as to confirm if EPDM-S insulation will have life of more than 15 years at ambient condition.

7.2 Experimental details:

EPDM-S insulation with Kevlar and Silica as reinforcing filler i.e. EPDM with Kevlar realized as per formulation given in Table-29 of Section 6.2.1 of Chapter-6, was used for the accelerated ageing study. 150 mm x 150 mm x 2 mm thick slabs of insulation cured at 120°C/6 hours (proven cure cycle based on Chapter 5) were used for the study. Dumbbells cut from the cured slabs were tested for initial mechanical properties. Remaining dumbbells were placed inside calibrated Hot air oven at 90°C as depicted in Figure-59. Dumbbells were drawn after 28 days of ageing at 90°C and subjected to evaluation of mechanical properties.

Figure-59: Hot air oven ageing in progress at 90°C

Ageing coefficient was calculated as follows:

$$Ageing\ Coefficient = \frac{\%\ Elongation\ after\ ageing}{\%\ Elongation\ before\ ageing}$$

7.3 Test Results and Discussion:

Test Results of Accelerated ageing are given in Table-43.

Table-43: Test Results of Hot Air Oven Ageing at 90°C

Sample Details	Mechanical Properties		% Change in U.T.S	% Change in Elongation	Ageing coefficient (0.6 min)
	Tensile strength MPa	% Elongation			
Initial	11.85* (11.1 – 13.0)	564.80 (563.0-569.0)	------	------	------
28 days	9.56 (6.5 – 12.1)	359.39 (268.1-410.2)	-19.33	-36.37	0.636

*Value in the parenthesis indicates minimum and maximum of test result

As evident from Table-43, upon ageing both Tensile strength and % Elongation decreases for EPDM-S insulation (EPDM with Kevlar). % Change in Tensile strength after 28 days of ageing at 90°C is -19.33, which is well within the generally accepted limit of -25 maximum. Change in percentage Elongation after 28 days of ageing at 90°C is -36.37, which too is well within the generally accepted limit of -40 maximum. That, change in percentage elongation after ageing 28 days of ageing at 90°C is within acceptability limit, is supported by Ageing Coefficient, computed based on test results. Ageing Coefficient obtained after 28 days of ageing at 90°C is 0.636, which is above the minimum required value of 0.6 minimum. As per the empirical relation based on extensive Accelerated Ageing study (Courtesy: HAL document), 1 week at 90°C is equal to 5 years life at ambient condition. Therefore, as EPDM-S insulation has withstood 90°C for 28 days, cured EPDM-S insulation will have an assured life of 20 years at ambient temperature.

7.4 Conclusion:

Based on Limited Accelerated Hot Air Oven Ageing Study, there is adequate confidence to say that EPDM-S insulation will have an assured life of 20 years, which is higher than that of Nitrile Rubber based insulation, whose life, based on accelerated ageing study, has been predicted to be 15 years. Thus Chapter-7 has corroborated the finding of the literature that EPDM Rubber based insulation will have better ageing resistance and longer life than Nitrile Rubber based insulation.

CHAPTER 8

CONCLUSIONS

8.1 Concluding Remarks of Present Research:

The research work entitled ***"Study on Sulphur Cured Ethylene Propylene Diene terpolymer based insulation for large Composite Rocket Motor Casing "*** has successfully validated the potential formulation using Kevlar and Silica as reinforcing fillers for the requirements of CRMC. It has successfully demonstrated novel methodology to optimize the cure condition for sulphur cured EPDM insulation. Further, extensive characterization of sulphur cured EPDM insulation with Kevlar and Sulphur as reinforcing fillers (EPDM with Kevlar) and sulphur cured EPDM insulation with only silica as reinforcing filler (EPDM without Kevlar) have been extensively characterized in comparison with proven Nitrile Rubber based insulation for various requirements of CRMC insulation. Comparative characterization thus carried out brought out the relative advantages and disadvantages of EPDM with Kevlar and EPDM without Kevlar against the insulation requirements of CRMC and generated valuable data which instilled confidence to adopt EPDM based insulation for large CRMC. Limited accelerated ageing study carried out as a part of present research has given adequate confidence that sulphur cured EPDM insulation will have an assured life of 20 years, which is more than that of proven Nitrile Rubber based insulation. Thus, present research has bridged the gap between literature and data actually required of adopting more advantageous EPDM insulation for large CRMC.

Further, the objectives finalized in Section 3.1 of Chapter-3 have been fulfilled completely. In Chapter-4, available potential formulation has been successfully validated for the requirements of insulation for large CRMC. Thus, objective 3.1.1 has been fulfilled in Chapter-4.

Chapter-5 presents the detailed study on cure behaviour of EPDM-S insulation based on EPDM with Kevlar and demonstrated the Novel Methodology to find out optimum cure condition. Thus, objective 3.1.2 has been fulfilled in Chapter-5. Applicability of optimum cure condition finalized for EPDM with Kevlar, to EPDM without Kevlar, has been proven in Chapter-5, as all the achieved mechanical properties of EPDM without Kevlar, cured at the optimum cure condition of 120°C / 6 hours, are well above the minimum required values for insulation of large CRMC.

Chapter-6 presents the extensive characterization carried out for EPDM-S insulation with Kevlar and Silica as reinforcing fillers (EPDM with Kevlar) and EPDM-S insulation with only Silica as reinforcing filler (EPDM without Kevlar) in comparison with proven Nitrile

Rubber based insulation for various requirements which are over and above those specified in Table-1 of Chapter-1. Study on water absorption behaviour, drying behaviour and characterization by SEM and FTIR Spectroscopy covered in Chapter-6, brought in extraordinary enlightenment over the relative advantages and disadvantages of EPDM with Kevlar and EPDM without Kevlar. Chapter-6 further gives comprehensive review of performance of EPDM with Kevlar and EPDM without Kevlar with respect to Nitrile Rubber based insulation and instilled data based confidence to the Propulsion designers to consider EPDM-S insulation for large CRMC. Thus, objectives 3.1.3 and 3.1.4 have been fulfilled in Chapter-6.

Limited Accelerated Hot Air Oven Ageing Study, summarized in Chapter-7, gives an assurance that EPDM-S insulation will have an assured life of 20 years, which is higher than that of Nitrile Rubber based insulation. Objective 3.1.5 has been fulfilled in Chapter-7. Outcome of this research, [which has been published in Polymers for Advanced Technologies and Polymer Composites (both of Wiley & Sons)], has led to successful implementation of EPDM-S insulation based on EPDM with Kevlar, in large CRMCs of strategic systems.

CHAPTER 9

SCOPE FOR FUTURE RESEARCH

9.1 SCOPE FOR FUTURE RESEARCH:

9.1.1 There is ample scope to carry out further work based on study on cure behaviour, demonstrated in Chapter-5, to optimize the cure condition at 120°C to a duration which is less than 6 hours.

9.1.2 As evident from the findings of Chapter-6, EPDM without Kevlar offers several advantages over EPDM with Kevlar. But density of EPDM without Kevlar is higher than that of EPDM with Kevlar. Therefore, in order to reap the full benefits of EPDM without Kevlar, filler optimization (precipitated silica) study in EPDM without Kevlar is an inevitable need of the hour. Filler optimization study would bring down the density to much lower than 1.0 g/cm^3 and improve the performance of strategic system as there will be appreciable weight reduction. It would pave way for invention of low density insulation based on sulphur curing and conventional silica filler, as well. It may be noted that prevailing low density EPDM insulation are based on specialty fillers viz. glass microspheres, nano-silica etc. whose batch to batch quality consistency and commercial availability in large scale in order to meet the production requirements of reliable insulation for large CRMC are quite uncertain.

9.1.3 No major work has been initiated towards peroxide cured EPDM insulation, even though, reasonable literature is available on peroxide curing of EPDM for various other applications, whose requirements are not as critical as those of insulation for large CRMC. As evident from literature, peroxide curing further improves the thermal stability and ageing resistance of EPDM insulation, undergoes no deterioration upon little prolonged exposure at the temperature of cure. It further offers compatibility with any type of propellant viz. composite, double-base, new generation NEPE based propellant etc. Therefore, peroxide cured EPDM insulation will be a work horse for large CRMC and opens the gate way for future research.

9.1.4 Peroxide cured EPDM insulation once established, would necessitate filler optimization study in order to reduce its density, thereby improve the performance of large CRMC on which it is laid as an insulation. Thus, filler optimization study leading to low density peroxide cured insulation would be yet another area for future research.

References

1. Abhijit Mukhopadhyay et al., SEM study of worn surface morphology of an indigenous EPDM rubber, Polymer Testing. 2016; 52:167-173.
2. AM El-Dakhakhny et al., Effects of aramid fibers and colloidal particle fillers in composite ethylene propylene diene monomer rubber thermal insulators for rocket motor insulation, Journal of Composite Materials. 2018; 52(15):1989-1995.
3. Audrey Favre et al., Comparative study of fiber-reinforced elastomer composites subjected to accelerated aging in water, Journal of Elastomers and Plastics, First Published May 29, 2014 Research Article, https://doi.org/10.1177/0095244314534102.
4. Bhuvaneswari C M et al., Ethylene-propylene Diene Rubber as a Futuristic Elastomer for Insulation of Solid Rocket Motors, Defence Science Journal, 2006;56(3):309-320.
5. Bhuvaneswari C M et al., Filled Ethylene-propylene Diene Terpolymer Elastomer as Thermal Insulator for Case-bonded Solid Rocket Motors, Defence science Journal. 2008; 58(1):94-102.
6. Blackley D.C., Synthetic Rubbers: Their chemistry and technology. Applied Science Publishers ltd, Essex; 1983. 213-34p.
7. Blow, C.M., Raw Polymeric Materials, In Rubber Chemistry and Technology, Butterworths, London; 1971. 102-03p.
8. Botros S H et al., Compatibility and Thermal Stability of EPDM-NBR Elastomer Blends, Journal of Elastomers and Plastics. 2005; 37(4):299-317.
9. Brydson, J.A., Rubber chemistry. Applied Science Publishers, London, 1978. 462p.
10. Çavdar S et al., Comparative study on mechanical, thermal, viscoelastic and rheological properties of vulcanised EPDM rubber, Plastics, Rubber and Composites: Macromolecular Engineering. 2010; 39(6):277-282.
11. Chakraborty S et al., Application of FTIR in characterization of acrylonitrile-butadiene rubber (Nitrile rubber), Polymer Testing. 2007; 26:38–41.
12. El-Dakhakhny A. M et al., Comparative Study Between Different Fillers used as Reinforcements of Rubber Thermal Insulators, 16th International Conference on Aerospace Sciences and Aviation Technology, ASAT - 16 – May 26 - 28, 2015.
13. Gueguen V et al., Thermal oxidation of EPDM terpolymer and vulcanisate, Polymer Degradation and Stability. 1994; 43(2):217-223.
14. Guillot et al., Novel EPDM Rocket Motor Insulation, International Patent WO 00/43445. 27 July 2000.

15. Gunasekaran S et al., FTIR spectra and mechanical strength analysis of some selected rubber derivatives, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2007; 68(2):323-330.
16. Herring et al., Elastomeric insulation materials for rocket motors. US Patent No. 4,501,841. 26 February 1985.
17. Herring et al., Elastomeric insulating materials for rocket motors. Hercules Inc, USA Patent No. 4, 878, 431, dated 7 November 1989. 18 p.
18. Jabez I K L et al., Oscillatory disc rheometer: An important quality assurance tool to assess the shear modulus of natural rubber in flex seals of large rocket motor, Journal of Elastomers and Plastics, 2016; 49(8): 650-664.
19. Jamal Gul et al., Kevlar Filled Ethylene-Propylene Diene Ter-Monomer Based Internal Thermal Insulation for Space Vehicles, Paper number IAC-12.C2.8.11. 12890, 63rd International Astronautical Congress 2012 (IAC 2012).
20. Jiang Li et al., Ablation and erosion characteristics of EPDM composites under SRM operating conditions, Composite Part A: Appl. Sci. and Manufacturing. 2018; 109:392-401.
21. Kesiya George et al., Nanosilica filled EPDM/Kevlar fiber hybrid nanocomposites: Mechanical and thermal properties, Materials Today: Proceedings, Available online 3 April 2020.
22. Kumar A et al., Ageing of elastomers: a molecular approach based on Rheological characterization, Polymer Degradation and Stability. 2004; 85(2):751-757.
23. Larry D et al., Asbestos Free Insulation Development for the Space Shuttle Solid Propellant Rocket Motor (RSRM), Thiokol Propulsion, P.O. Box 707, Brigham City, Utah, NASA Document.
24. Macro Rallini et al., Thermal and ablation properties of EPDM based heat shielding materials modified with density reduced filler, Composite Part A: Appl. Sci. and Manufacturing. 2018; 112:71-80.
25. Macro Rallini et al., Boron based fillers as char enhancer of EPDM based heat shielding materials for SRMs: A comparative analysis, Composite Structures. 2018; 198:73-83.
26. Mahmoud Emad Awad et al., Effect of Insulation Layer Composite and Water Adsorption on Bonding Performance in Heat Barriers, Advanced Journal of Chemistry-Section A, 2020, 3(3), 370-377.
27. Maria Daniela Stelescu et al., Use of Differential Scanning Calorimetry (DSC) in the Characterization of EPDM/PP Blends, Int J Thermophys, 2010; 31:2264–2274.

28. Maurizio Natali et al., EPDM based heat shielding materials for Solid Rocket Motors: A comparative study of different fibrous reinforcements, Polymer Degradation and Stability. 2013; 98(11):2131-2139.
29. Mohamad I et al., Vulcanization Kinetics and Mechanical Properties of Ethylene Propylene Diene Monomer Thermal Insulation, Bulletin of Chemical Reaction Engineering and Catalysis. 2015; 10(2):104-110.
30. Muraleekrishnan R et al., In HEMCE. Development of EPDM rubber-based low-density insulator for solid propellant rocket motors. In Proceedings of the 3rd International Conference, 6-8 December 2000, Thiruvananthapuram. pp. 265-68.
31. Nanying Ning et al., Enhanced thermo-oxidative aging resistance of EPDM at high temperature by using synergistic antioxidants, Polymer Degradation and Stability. 2014; 102:1-8.
32. Nora Catalina Restrepo ‐ Zapata et al., Vulcanization of EPDM rubber compounds with and without blowing agents: Identification of reaction events and TTT ‐ diagram using DSC data, POLYM. ENG. SCI, 2015; 55:2073–2088.
33. Pervez T et al., Comparison between fresh and exposed swelling elastomer, Journal of Elastomers and Plastics. 2012; 44(3)237-250.
34. Quanlin Zhao et al., Aging of ethylene–propylene–diene monomer (EPDM) in artificial weathering environment, Polymer Degradation and Stability. 2007; 92(10):1841-1846.
35. Raa Khimi S et al., A New Method to Predict Optimum Cure Time of Rubber Compound Using Dynamic Mechanical Analysis, J. Appl. Polym. Sci., 2014; 131:40008.
36. Rosca I D et al., Study of process of cure of EPDM rubbers in moving die rheometer, Journal of Plastics, Rubbers and Composites : Macromolecular Engineering:2001:30(6):275-281.
37. Saha Deuri A et al., Ageing of rocket insulator compound based on EPDM, Polymer Degradation and Stability. 1986; 16(3):221-239.
38. Saha Deuri A et al., Thermal and ablative properties of rocket insulator compound based on EPDM, Polymer Degradation and Stability, 1988:21(1):21-28.
39. Sangita Singh et al., Development of polyimide-nanosilica insulator compound: Influence of polyimide-nanosilica loading on thermal ablation and mechanical properties, Composite Part A: Appl. Sci. and Manufacturing. 2013; 44:8-15.
40. Santanu Datta et al., Reinforcement of EPDM-based ionic thermoplastic elastomer by precipitated silica filler, Polymer. 1996; 37(12):2581 2585.

41. Suresh Kumar M S et al., Studies on the properties of EPDM–CSE blend containing HTPB for case bonded solid rocket motor insulation, Polymers for Advanced Technologies. 2008; 19(2):144-150.
42. Tohid Farajpour et al., Effect of borax on the thermal and mechanical properties of ethylenepropylene-diene terpolymer rubber-based heat insulator, Journal of Applied Polymer Science. 2015; 132(19):41936.
43. TA 389, Characterization of the Degree of Cure of Thermosetting resins by DSC
44. Vinicius Pistor et al., Degradation kinetics of ethylene propylene diene terpolymer residues devulcanized by microwaves, Journal of Elastomers and Plastics. 2014; 46(1):69-83.
45. Vojislav Jovanovic et al., Composite based on carbon black reinforced NBR/EPDM rubber blends, Composite Part B: Engineering. 2013; 45:333-340.
46. Xiaolong Jia et al., Enhancement of ablative and interfacial bonding properties of EPDM composites by incorporating epoxy phenolic resin, Composite Part B: Engineering. 2013; 54:234-240.
47. Yiwen Guan et al., Ablation characteristics and reaction mechanism of insulation materials under slag deposition condition, Acta Astronautica, 2017; 136:80-89.

Publications in Present Work

1. Isaac Kingstone Lesley Jabez, Urmila Das, Ramalingam Manivannan and Sarat Babu Anne, Cure behavior of ethylene propylene diene terpolymer insulation for large composite rocket motor casing, Polymer Composites, 2021; 42:3996-4004, DOI: 10.1002/pc.26111. **(Impact factor: 3.171; ISSN: 0272-8397; E-ISSN: 1548-0599; United States)**
2. I. Kingstone Lesley Jabez, Urmila Das, Manivannan Ramalingam and Sarath Babu Anne, Evaluation of Ethylene Propylene Diene Terpolymer based insulation against Nitrile rubber based insulation for Large Composite Rocket Motor Casing, Polymers Advanced Technologies, 2021; 32: 111-122 **(Impact factor: 3.665; ISSN: 1042-7147; E-ISSN: 1099-1581; England)**
3. I. Kingstone Lesley Jabez, Urmila Das, R. Manivannan, and Sarat Babu Anne, Influence of HTPB prepolymer on achieved properties of composite solid propellant, High Performance Polymers, 2019; 31 (9-10): 1162-1172 **(Impact factor: 2.161**; **ISSN: 0954-0083; E-ISSN: 1361-6412; England)**