

# Spectroscopic, Dielectric, Thermal and Hardness studies on uncured and cured Hydrogenated Nitrile Butadiene Rubber and Chlorosulphonated monomer

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**Abstract:** The enormous increase in the commercial demand for the rubber and the probability of the continuance of this increase in view of the great variety of purposes to which the material can be applied, demands a thorough understanding of its structure, composition and physical/mechanical properties. Hydrogenated Nitrile Butadiene rubber (HNBR) and Chlorosulphonated monomer (CSM) were investigated in the uncured and the cured form for systematic characterization by employing important experimental techniques. The effect of reinforcement and vulcanization on the properties of these rubber materials were comparatively studied with that of the uncured ones. The complete vibrational band assignment was made available for the rubber materials from FTIR spectra. The dielectric measurements were carried out for the cured and uncured rubber materials in the microwave frequency region by utilizing X-band and K-band microwave test benches. Further, thermal behavior of the rubber materials was studied from Thermogravimetric Analysis (TGA). The thermal stability was studied from TGA curves and the activation energy for the degradation of rubber materials was calculated using Murray-White and Coats-Redfern plot. Further, the hardness of rubber materials in the raw and cured state were determined using Shore A durometer.

**Keywords:** reinforcement; vulcanization; FTIR; dielectric measurements; Activation energy; hardness.

## 1 Introduction

The development of the rubber industry has now reached a stage at which more exact methods of determining the chemical composition and physical properties of rubber materials are required. This will facilitate the design and manufacture of rubber products economically i.e. goods with low cost and high performance. Hence, the present work deals with the characterization of uncured and cured Hydrogenated Nitrile Butadiene rubber (HNBR) and Chlorosulphonated monomer (CSM). Vulcanization refers to a specific curing process of rubber involving high heat and the addition of sulphur. Vulcanization is the treatment of rubber to give it certain qualities, e.g., strength, elasticity and resistance to solvents and to render it impervious to moderate heat and cold. It is a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulphur atoms. For many uses, even vulcanized rubbers do not exhibit satisfactory tensile strength, stiffness, abrasion resistance and tear resistance. Therefore, the rubber has

to be compounded with reinforcing fillers before vulcanization in order to obtain vulcanizates with adequate mechanical properties known as reinforcement. Filler can act to shield a rubber compound from abrasive contact with another surface. In addition to the physical properties, filler can also enhance resistance to creep, cold flow, hysteresis and heat-build-up. Though non-black fillers like silica, clay, metallic oxides and calcium carbonate are used today, carbon black is the most important rubber filler. N. Rattanasom et al have studied reinforcement of NR with silica/carbon black hybrid filler at various ratios in order to determine the optimum silica/carbon black ratio [1]. R. S. Stearns and B. L. Johnson reported the interaction between carbon black and polymer in cured elastomers [2]. J. C. Kenny et al have reported structural investigations on Carbon black filled natural rubber [3]. K. A. Mazich et al have investigated the dynamic mechanical, thermal and physical properties of Elastomer blends and their effect with carbon black [4]. Thus the scientific community's efforts have led to intense research on vulcanization and reinforcement of rubber materials.

## 2 Experimental Methods

The rubber materials viz., Hydrogenated Nitrile Butadiene Rubber (HNBR) and Chlorosulphonated monomer (CSM) were procured from Industrial Rubber Products (IRP), Chennai, India for systematic characterization. Carbon black was used as the reinforcing filler and sulphur was used as the principle-vulcanizing agent for the two rubber materials in the industrial lab. After proper mastication, the rubber material was passed through the rolls of the roll mill equipment. The combined cure package comprises the cure agent sulphur together with accelerators like Dibenzothiazyl disulfide (MBTS) and Tetra Methylthiuram Disulfide (TMTD), activators like zinc oxide and stearic acid and antidegradants according to the desired formulations as presented in Table 1. Antidegradants are used to prevent degradation by heat, oxygen and ozone. The composites were vulcanized at 160°C under a pressure of about 45 kg/cm<sup>2</sup>. The time of vulcanization was 30 minutes. The reinforced rubber materials were obtained by mixing carbon black filler to the vulcanizates in the roll mill equipment. The carbon black filler content was 50 Phr (Phr-parts hundred in rubber). After the rubber, filler, sulphur and organic accelerator were mixed, the compound was placed in molds and subjected to heat and pressure. The rubber article was intended to adopt the shape of the mold. The samples were obtained in the form of slabs with thickness about 8 ± 0.5 mm. Infrared spectroscopic analysis of uncured and cured rubber materials have been carried out with Bruker IFS 66V spectrophotometer at Indian Institute of Technology (IIT), SAIF, Chennai, India. The FTIR spectra have been recorded in the range 4000 - 400 cm<sup>-1</sup> and the frequencies of all the sharp bands are accurate to ± 1 cm<sup>-1</sup> [5]. The resonant cavity and waveguide method has been employed here to study the dielectric behavior of rubber samples using the X-band and K-band microwave test benches [6]. The K band mainly comprises of a Gunn oscillator and a rectangular waveguide of dimension 1.1cm x 0.4cm in the dominant TE<sub>1,0</sub> mode. The X band consists of a Klystron oscillator and a rectangular waveguide of dimension 2.2cm x 1cm. All the samples were shaped to the dimensions of the waveguide and intercepted in the path of the microwave ensuring that there is no air gap between the dielectric sample and the inner walls of the rectangular waveguide. The measurements of the standing wave have been repeated for all the four faces of the shaped rubber samples.

**Table 1 Formulations used in the preparation of rubber materials<sup>a</sup>**

Ingredients	HNBR	CSM
HNBR	100	-
CSM	-	100
ZnO <sup>b</sup>	5	5
Stearic acid	2	2
MBTS <sup>c</sup>	1.5	1.5
TMTD <sup>d</sup>	0.5	0.5
Sulphur	2.5	2.5

a-In phr: parts per hundred parts by weight of rubber

b- zinc oxide c- Dibenzothiazyl disulfide d- Tetra Methylthiuram Disulfide

Thermal analysis is a high-resolution technique in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme [7].

Thermogravimetric Analysis was carried out in a high-resolution thermobalance (NETZSCH STA 409C/CD instrument) at Indian Institute of Technology (I.I.T), Chennai, India. 6mg of rubber sample was heated from room temperature to 1400°C with a continuous circulation of nitrogen gas inside the sample and reference chamber. The heating rate was 20°C/min but when a loss of weight was detected for the sample, the heating rate slowed down in response to mass and the system tried to keep it at the lowest value (0.01°C/min) until the end of weight loss. The hardness of uncured and cured HNBR and CSM was measured using Shore A durometer. The durometer is an International Standard instrument used to measure the hardness of rubber or rubber-like materials. Durometers measure hardness by the penetration of an indenter into the rubber sample [8]. The instrument is a spring loaded indentation device, in which values are obtained as a function of the viscoelastic property of the material. The calibrated reading is expressed in a number value. Samples used were approximately 6mm thick with a surface area sufficient to permit at least 3 test points 5mm apart, 13mm from any edge.

### 3 Results and Discussion

#### 3.1 FTIR Spectroscopy

The chemical composition of the polymeric materials was more accurately characterized by IR spectroscopy. The FTIR spectra of Hydrogenated Nitrile Butadiene Rubber and Chlorosulphonated monomer in the raw (uncured) and cured state are given in Figs. 1 and 2. The spectra are nearly identical and confirm that the polymeric units are the same for the elastomers in the raw and cured state except for minor differences [9]. A quantitative analysis of structure and confirmation of polymer chains requires the assignment of absorption bands and qualitative measurement of their intensities. The assignments of the fundamental frequencies have been made on the basis of magnitude and relative intensities of the observed bands [10, 11]. The vibrational band assignments of the rubber materials have been made in correlation with molecular composition and with their indices of stereo regularity. The frequencies of the elastomers with their relative intensities and probable assignments are summarized in Tables 2-5.

On comparison of raw and vulcanized states of the rubber materials, it can be stated that the difference is in their rate of absorption only. The process of vulcanization is considered to introduce cross-links between the polymer molecules due to addition of sulphur. Since the infrared spectrum of an elastomer is determined almost entirely by the small recurring structural units and not by the gross size or configuration, the net result of vulcanization, consisting mainly of changes which involve relatively few of the recurring polymer units, does not alter the rubber spectrum to any appreciable extent. As the spectrum of each elastomer is unique and experimentally reproducible; this serves as a basis for characterization of the elastomer content of commercial rubber products.

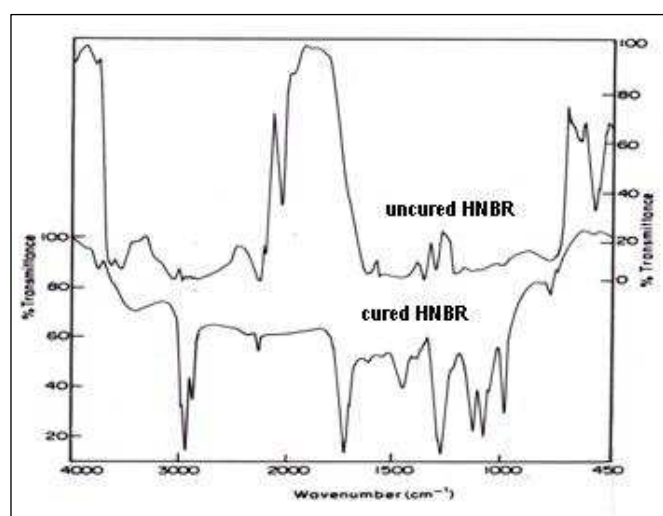


Fig. 1 FTIR Spectra of uncured HNBR and cured HNBR

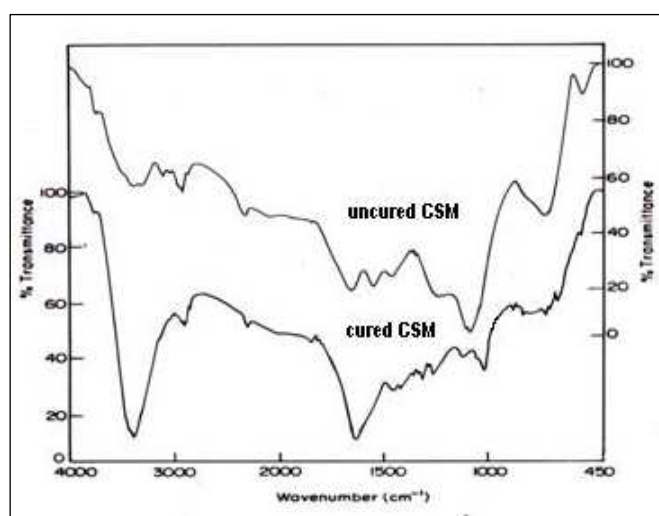


Fig. 2 FTIR Spectra of uncured CSM and cured CSM

**Table 2 FTIR assignment of uncured HNBR**

Frequency ( cm <sup>-1</sup> )		Assignment
FTIR	Intensit	
3040	vs <sup>e</sup>	C-H asymmetric stretching
2972	vs	CH <sub>2</sub> asymmetric stretching
2821	vs	CH <sub>2</sub> symmetric stretching
2240	vs	C≡N stretching
1620	vs	C=C stretching
1560	vs	CH <sub>2</sub> asymmetric bending
1454	vs	CH <sub>2</sub> scissoring
1345	vs	CH <sub>2</sub> wagging
1210	vs	CCH asymmetric bending
1120	vs	CCH symmetric bending / CH <sub>2</sub>
975	vs	C-C stretching
755	vs	CH <sub>2</sub> rocking
545	ms <sup>f</sup>	C-C deformation

e- very strong f- medium strong

**Table 3 FTIR assignment of uncured CSM**

Frequency ( cm <sup>-1</sup> )		Assignment
FTIR	Intensity	
3090	w <sup>g</sup>	C-H asymmetric stretching
2960	mw <sup>h</sup>	C-H symmetric stretching
2917	mw	CH <sub>2</sub> asymmetric stretching
2880	mw	CH <sub>2</sub> symmetric stretching
1646	vs	C=C stretching
1541	vs	CH <sub>2</sub> asymmetric bending
1455	s <sup>i</sup>	CH <sub>2</sub> scissoring
1330	ms	SO <sub>2</sub> asymmetric stretching / CH <sub>2</sub> wagging
1235	vs	CCH asymmetric bending
1122	vs	SO <sub>2</sub> symmetric stretching / CCH symmetric bending
1083	vs	C-C stretching
720	m <sup>j</sup>	C-Cl stretching / C-S-O symmetric bending / CH <sub>2</sub> rocking
602	vw <sup>k</sup>	C-S stretching / In-plane SO <sub>2</sub> bending
540	vw	C-C deformation / SO <sub>2</sub> rocking

g- weak h- medium weak i- strong j- medium k- very weak

**Table 4 FTIR assignment of cured HNBR**

Frequency ( cm <sup>-1</sup> )		Assignment
FTIR	Intensity	
3040	w	C-H asymmetric stretching
2965	s	C-H symmetric stretching
2924	vs	CH <sub>2</sub> asymmetric stretching
2857	s	CH <sub>2</sub> symmetric stretching
2236	m	C ≡ N stretching
1610	m	C = C stretching
1545	m	CH <sub>2</sub> asymmetric deformation

1456	ms	CH <sub>2</sub> scissoring
1360	m	CH <sub>2</sub> wagging
1271	vs	CCH asymmetric bending
1121	s	CCH symmetric bending/CH <sub>2</sub> twisting
1072	vs	C-C stretching
742	w	CH <sub>2</sub> rocking
540	vw	C-C deformation

**Table 5 FTIR assignment of cured CSM**

Frequency (cm <sup>-1</sup> )		Assignment
FTIR	Intensity	
3010	m	C-H asymmetric stretching
2950	m	C-H symmetric stretching
2929	m	CH <sub>2</sub> asymmetric stretching
2880	m	CH <sub>2</sub> symmetric stretching
1641	vs	C = C stretching
1456	s	CH <sub>2</sub> asymmetric deformation
1420	s	CH <sub>2</sub> scissoring
1360	s	SO <sub>2</sub> asymmetric stretching
1315	s	CH <sub>2</sub> wagging
1266	s	CCH asymmetric bending
1119	ms	CCH symmetric bending/CH <sub>2</sub> twisting/SO <sub>2</sub> symmetric stretching
1058	ms	C-C stretching
730	mw	CH <sub>2</sub> rocking
710	mw	C-Cl stretching/C-S-O symmetric deformation
663	mw	C-S stretching/SO <sub>2</sub> in-plane deformation
560	vw	C-C deformation/SO <sub>2</sub> rocking

### 3.2 Dielectric measurements at microwave region

When assessing a potential insulating material, information on dielectric constant over a wide range of temperature and frequency will be required. Polymers with low dielectric constant, high resistivity and negligible power factor are considered to be good insulators. Thus dielectric constants of rubber materials have been evaluated with a view to get evocative results to substantiate their insulating nature. The measurements have been carried out in the microwave region with X and K band microwave test benches equipped with Klystron and Gunn oscillators respectively and guided with rectangular waveguides. Roberts and Von Hippel's method of determining the dielectric constant has been adopted for study and the results are summarized in Table 6. On placing the samples in the waveguide, standing wave pattern is produced during the microwave propagation. For different positions of the probe, the output voltages have been measured. In K-band microwave bench, the probe senses the field strength of the standing wave pattern which can be viewed in a CRO. From the values of the shift in minima of the standing wave, with and without sample, the dielectric constant is calculated using the relation,  $\epsilon_r = [(\lambda_o/\lambda_g)^2 + (\lambda_o/\lambda_c)^2]$ , where,  $\lambda_o$  is the wavelength of microwaves in free space,  $\lambda_c$  is the cut of wavelength,  $\lambda_g$  is the wavelength of dielectric filled space.

It is evident that dielectric constants at K-band frequency are lower than at X-band. Hence, dielectric constant decreases with increasing frequency and this is an expected result. HNBR and CSM in the cured state have greater dielectric constants than in the crude state [12-14]. Thus dielectric constant is an important factor in deciding the insulation property of the material, i.e. the rubber materials with low dielectric constant and high dielectric strength are excellent insulators [15].

**Table 6 Dielectric constants of rubber materials**

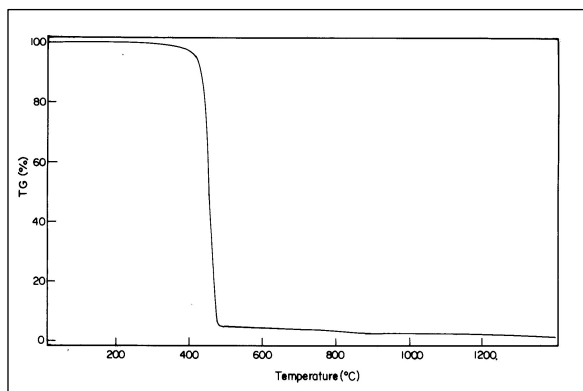
Rubber material	Dielectric constant ( $\epsilon_r$ )	
	X-band (9.65 GHz)	K-band (24.76 GHz)
HNBR	3.2462	1.8143
Cured HNBR	4.0621	2.9652
CSM	2.6050	1.3811
Cured CSM	4.9380	3.3690

**3.3 Thermogravimetric Analysis (TGA)**

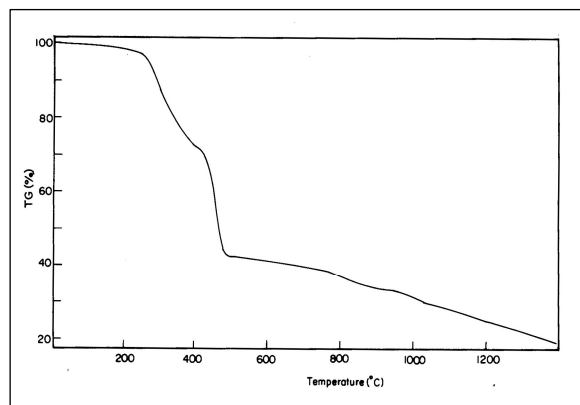
Knowledge of thermal behavior is not only essential for proper processing and fabrication, but also for complete characterization of materials especially thermal stability for selection of appropriate end users. The sample weight and its rate of weight loss were continuously measured as a function of temperature. The continuous weight loss curves for the thermal degradation of rubber materials are presented in Figs. 3 - 6. The thermal stability of the cured and uncured rubber materials at different temperatures are given in Table 7. The TGA curves reveal that the selected rubber materials are thermally stable upto 290°C. Comparison of HNBR and CSM in the uncured and cured states reveal that the cured rubber materials are more thermally stable than the uncured ones. Thus the rubber materials used for the present study after being reinforced with carbon black filler and vulcanized with sulphur system exhibit higher thermal stability than compared with uncured rubber materials. This result is supported by [16] according to which vulcanization increased the thermal stability of NR/SBR blends and the activation energies for the degradation of the blends are higher than that of the homopolymers. From the reported values in [17], it is found that vulcanization of the blend isotactic polypropylene/nitrite rubber improved the thermal stability.

**Table 7 Thermal Stability of Rubber Materials**

Sample	Temperature (°C) corresponding to weight loss								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
HNBR	425	436	443	450	454	458	462	468	473
Cured HNBR	291	365	410	436	455	475	730	-	-
CSM	295	342	427	450	466	653	1034	-	-
Cured CSM	380	506	905	1032	-	-	-	-	-



**Fig. 3 TGA Thermogram of uncured HNBR**



**Fig. 4 TGA Thermogram of uncured CSM**

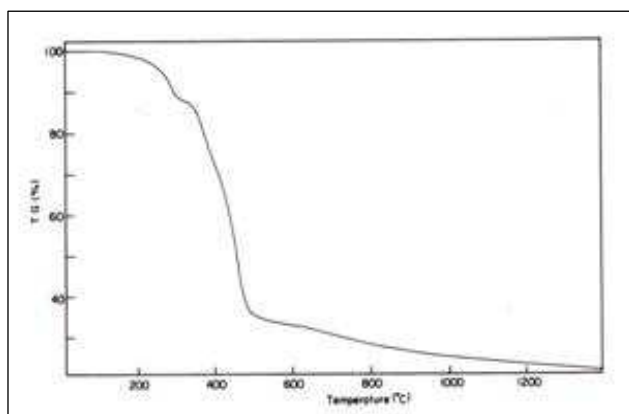


Fig. 5 TGA Thermogram of cured HNBR

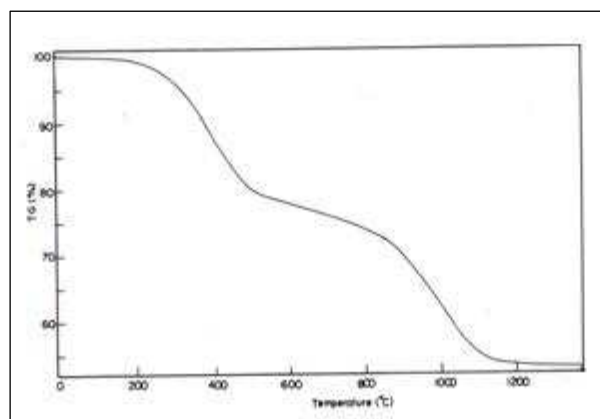


Fig. 6 TGA Thermogram of cured CSM

In uncured CSM, the first degradation step starts at 249°C and at 295°C, about 10% of the rubber was degraded. The second stage of degradation starts at 400°C and third stage of degradation starts at around 770°C. In the second stage 30% of the rubber gets degraded and in the third stage 5% of the rubber material gets degraded. About 70% of the rubber was degraded at around 1034°C. In cured CSM, the degradation takes place in three stages. The three stages show a weight loss of 19%, 8.5% and 17.5% respectively. The 40% degradation of cured CSM requires 1032°C which is a very high temperature. This signifies that cured CSM is highly thermally stable than compared with uncured CSM. Only 46% of the rubber material was degraded at 1400°C which further indicates the thermal stability of cured CSM. The TGA curve of uncured HNBR shows that the degradation takes place in single stage itself. HNBR shows 92% degradation between 403°C and 490°C. In cured HNBR, the first degradation step starts around 231°C and 10% of the material was degraded in the first stage. The second stage of degradation starts around 328°C to 393°C and nearly 15% of the sample gets degraded in this stage. The third stage of degradation is between 393°C to 510°C and 38% of the sample was degraded in this stage. 23% of the cured HNBR sample remains undegraded. P. Thavamani et al have reported that the thermal stability of EVA was improved on blending it with HNBR [18]. It can be concluded that thermal stability i.e., the ability to maintain required mechanical properties such as strength, toughness and elasticity at a high temperature is more for cured rubber materials.

### 3.4 Activation energies of degradation of rubber materials

Activation energy is the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. Basically, the activation energy is the height of the potential barrier separating two minima of potential energy of the reactants and of the products of reaction. For chemical reaction to have noticeable rate, there should be noticeable number of molecules with the energy equal or greater than the activation energy. Activation energy calculations for the degradation of rubber materials were made from TGA curves using Murray-White method and Coats-Redfern method [19, 20]. The calculation of activation energy for the degradation of cured HNBR is given in Table 8. Activation energy calculations were done for cured CSM and uncured HNBR and CSM rubber materials in a similar way.

A linear correlation was obtained by plotting the logarithm of heating rate against the reciprocal of the absolute temperature. In Murray and White plot, a linear correlation was obtained by plotting  $T^{-1} \times 10^{-3} (\text{K}^{-1})$  against  $[\ln(\ln(1-C)) - 2\ln T]$ . In Coats and Redfern plot, a linear correlation was obtained by plotting  $T^{-1} \times 10^{-3} (\text{K}^{-1})$  against  $\log [\ln(1-C)]/T^2$ . The calculated activation energy values are given in Table 9. Cured rubber materials have high activation energies than uncured ones. Hence, the rubber materials with high activation energy are more thermally stable and the extent of polymerization, the chain length and hence the molecular weight will be more for the elastomers that are less stable.

**Table 8 Calculation of Activation Energy for the degradation of cured HNBR**

% Degradation	$T^{-1} \times 10^{-3}$ ( $K^{-1}$ )	1-C	2lnT	ln(1-C)	og[ln(1-C)]	ln[ln(1-C)]- 2lnT	log[ln(1-C)]/T <sup>2</sup> X 10 <sup>-6</sup>
10	1.7730	90	12.670	4.49980	0.6531	-11.1660	2.053
20	1.5673	80	12.916	4.38202	0.6416	-11.4390	1.576
30	1.4641	70	13.052	4.24849	0.6282	-11.6063	1.346
40	1.4104	60	13.127	4.09434	0.6121	-11.7180	1.217
50	1.3736	50	13.180	3.91202	0.5924	-11.8165	1.117
60	1.3368	40	13.234	3.68887	0.5668	-11.9294	1.013

**Table 9 Activation energy for the degradation of Rubber materials**

Sample	Activation energy $E_a$ in KJ/mol	
	Murray-White Method	Coats-Redfern Method
HNBR	0.0841	0.0925
Cured HNBR	0.214	0.285
CSM	0.2324	0.2977
Cured CSM	0.637	0.778

### 3.5 Hardness of Rubber Materials

The hardness is defined as the resistance of a material to indentation. The greater the hardness of the material, the greater resistance it has to deformation. The usual method to achieve a hardness value is to measure the depth or area of an indentation left by an indenter of a specific shape, with a specific force applied for a specific time. The rubber materials used for the hardness study were rectangular in dimension with 6mm-8mm thickness. The hardness of the rubber material is obtained by forcing the standard indenter of the Shore A durometer onto a flat surface of rubber material and measuring the degree of penetration. The deflection of the pointer in the durometer scale directly gives the hardness of rubber materials. The hardness values of all rubber materials are presented in Table 10. It is observed that reinforced and vulcanized HNBR and CSM have higher hardness values than compared to uncured ones. This shows the intense effect of sulphur and carbon black on the rubber materials. The hardness of the rubber material is enhanced after being reinforced with carbon black and vulcanized with sulphur [21].

**Table 10 Shore A Hardness**

Rubber material	Hardness
HNBR	43
CSM	48
Cured HNBR	66
Cured CSM	78

## 4 Conclusion

The cured and uncured rubber materials are studied in the present work by utilizing important experimental techniques. Qualitative analysis on the vibrational bands of specific modes of rubber materials was carried out from the FTIR spectra. Roberts and Von Hippel's method was used to determine the dielectric constant of rubber materials in the X-band and K-band microwave frequency region. Dielectric constant is found to decrease with increasing frequency. The results show that cured rubber materials have greater dielectric constants than the uncured ones. The TGA thermograms show that the cured rubber materials exhibit better thermal stability than the unvulcanized raw rubber materials. Activation energy was calculated for the degradation of rubber materials using Murray-White method and Coats-Redfern method. Finally, the hardness



of all rubber samples was determined using shore A durometer. The reinforced and vulcanized rubber materials have greater hardness than the uncured ones. Thus the characterization study was successfully carried out for the chosen rubber materials.

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