

CHARACTERIZATION OF SPECTRAL AND THERMAL ANALYSIS OF NITRILE, BUTYL AND VITON RUBBER OF INDUSTRIAL RUBBER MATERIALS

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ABSTRACT: Longevity of a material is of prime importance apart from quality as for as consumers are concerned. It is essential that there is an authentic record elucidating and qualifying a variety of industrial rubber materials such as Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton). We have employed FTIR spectroscopy, which is a ever green and ever reliable technique to comment on the mechanical strength of the selected industrial rubbers. Infrared spectroscopic analysis provides much valuable information about the chemical and physical structure. It is found that the dielectric constant and the dielectric loss are both inversely proportional to frequency. Thermal analysis was carried out in a high-resolution thermo balance Instrument. The heating rate was 20 °C/min and the resolution used is "4". The surface morphology of selected rubber materials have been analyzed through optical microscopy. EPR Spectral analysis the spectrum and result obtained from EPR spectra. From Differential Scanning Calorimetry analysis and Thermo gravimetric analysis the results obtained from TGA technique show that all the chosen blends starts to thermal degradation or weight loss temperature was 360 °C.

Keywords: Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton), Impedance spectroscopy, dielectric constant, FTIR spectroscopy, mechanical strength, optical micrographs, EPR spectra and TGA study.

1. Introduction

A polymer is a large molecule built up by the repetition of small , simple chemical units. In some cases the repetition is linear, much as a chain is built up form as links. In other cases the chains are branched or interconnected to form three dimensional networks. The repeat unit of the polymers is usually equivalent to the monomer, or starting material from which the polymer is formed. The Rubber is a one of the polymer, but is also waterproof and is a good electrical insulator. Natural rubber is resilient and is resistant to tearing. In a raw state, natural and synthetic rubber becomes sticky when hot and brittle when cold. The vulcanization process modifies rubber so that these changes will not occur. In the typical vulcanization process, sulfur and certain other substances are added to raw rubber and the mixture is then heated. The process tends to increase rubber's elasticity and its resistance to heat, cold, abrasion, and oxidation. It also makes rubber relatively airtight and resistant to deterioration by sunlight. The molecules that make up rubber are long, coiled, and twisted. They are elongated by a stretching force and tend to resume their original shape when the force is removed, giving rubber the property of elasticity. Vulcanization sets up chemical linkages between the molecules, improving rubber's ability to return to its original shape after it is stretched.

2. EXPERIMENTAL METHODOLOGY

Sampling:

A variety of industrially important rubber materials based on structure, composition and properties were collected from the reputed industries. The samples chosen for the purpose of investigation were Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton) polymers.

2.1. FTIR SPECTROSCOPY

The sample of rubber derivatives were cut into small pieces. These were taken in boiling tubes and heated till fumes are evolved out of the tube. The fumes were allowed to get condensed on the walls of the tube which leave the sample in liquid state. A drop of the liquid is smeared in between a pair of NaCl discs forming a thin film of the sample in between the discs. The pair of discs along with the sample was placed in the FT-IR cell and the spectra were recorded.

2.2 DIFFERENTIAL SCANNING CALORIMETRY:

Differential scanning calorimetric measurements were carried out in a Perkin-Elmer instrument (DSC 7) in the temperature range of 373-573 K under nitrogen atmosphere with a flow rate of 2 ml/h and different heating rates of 10 and 100 °C/min. The following sample namely Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton) polymers was analyzed by DSC. This sample was cut into small pieces and the pieces were directly placed in the DSC sample holder and subject to heating.

2.3 THERMOGRAVIMETIC ANALYSIS:

TGA-DTA using high-resolution TGA approach obtained, from the samples Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton) polymers are displaced in the figure. The following sample namely Nitrile rubber, Butyl rubber, Flouro carbon rubber (viton) polymers were analyzed by TGA. This sample was cut into small pieces and the pieces were directly placed in the TGA sample holder and subject to heating.

2.4 DIELECTRIC CONSTANT

The dielectric behavior of the chosen rubber materials were studied at room temperature using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. The samples were prepared in the form of discs of 35 to 40 mm in diameter and 3.0 to 3.5 mm in thickness and placed between silver electrodes and their frequency responses were studied.

2.5 OPTICAL MICROGRAPH

Optical micrographs were recorded in Laborlux 12 ME (Leitz), equipped with an image analyzing system (Medi image). The images of Butyl rubber, Nitrile rubber, and viton rubber are seen through Optical microscope. The micrographs were recorded at different magnifications viz., 100×, 200×, 300×, 500× and 800× respectively. The solubility of these sample materials were tested in acetonitrile, carbon tetrachloride and methanol. It was found that they are insoluble in any of these solvents. As a result, alternately, these samples were taken in boiling tubes and heated till fumes are evolved. The evolved fumes were allowed to get condensed on micro glass slides and optical graphs were recorded.

2.6 EPR SPECTRAL ANALYSIS

Four industrially significant rubber materials viz., butyl rubber, nitrile rubber and nitrile rubber and viton rubber have been subjected to EPR analysis For EPR spectral recording of the above said samples; methanol and chloroform are employed as solvents. The analysis is performed in solution mode at liquid Nitrogen Temperature (LNT). There are several reports on conducting polymer, transition metal doped polymer, and carbon black doped polymers which can be anticipated to be EPR active.

RESULTS AND DISCUSSION

Longevity of a material is of prime importance apart from quality as for as consumers are concerned. It is essential that there is an authentic record elucidating and qualifying a variety of industrial rubber materials based on which they can be chosen for specific application. Spectroscopies find widespread application analysis of organic compounds. Since even slight chemical modification could be detected by IR spectroscopy even when combined with derivatisation reactions, except the loss of peaks associated with the catalyst and its solvent. Infra-red spectrum is known to contain information at the molecular level of the material i.e. microstructure.

3.1 FTIR SPECTRAL MEASUREMENT

The mechanical strength of these rubber materials have been analyzed by Calculating the internal ratio parameters (IRP) among the methyl and methylene group vibration frequencies obtained from FTIR spectroscopy. For recording IR spectra, the rubber materials were cut into small pieces. They were taken in a boiling tube and heated so as to bring them to semi liquid State. From the FTIR spectrum of nitrile rubber, the band arises at 1222 cm^{-1} attributes to C-N stretching of nitrile content. The band observed at 1081 cm^{-1} is assigned to Si-O-Si vibration however the weak band at 2905 cm^{-1} assigned to symmetric C-H vibrations of methyl group of silicon rubber. FTIR spectra of NR, it is found that there is medium absorption band at 1068 cm^{-1} . The analysis of mechanical strength of the selected rubber blends by calculating the internal ratio parameters (IRP) among the methyl and methylene group vibration frequencies obtained from FTIR spectroscopy show that internal ratio parameter (IRP) is fairly constant and is between 0.9 and 0.99 and the range is given the below table.

Table: Infrared spectra and vibrational frequencies (cm^{-1}) of title industrial rubber materials.

Rubber Materials	Asymmetrical Stretching Vibration		Symmetrical Stretching Vibration		Asymmetrical Deformation Vibration		Symmetrical Deformation Vibration		C=C Stretching (CH ₃)
	(CH ₃)	(CH ₂)	(CH ₃)	(CH ₂)	(CH ₃)	(CH ₂)	(CH ₃)	(CH ₂)	
Viton	3072	2963	2923	2834	1554	1458	1366	796	1644
Butyl Rubber	3022	3000	2955	2916	1469	1566	1365	760	1666
Nitrile	3020	2984	2930	2858	1446	1500	1355	755	1639

Table: Infrared ratio parameters (IRP) among the methyl and methylene group vibration of the industrial rubber.

Rubber Material	R1=A2964/A2950	R2=A2853/A2864	R3=A2950/A2964	R4=A2853/A2950	R5= A2864/A2964
Viton	0.9385	0.9697	0.9645	0.9565	0.9575
Butyl Rubber	0.9381	0.9868	0.9927	0.9720	0.9778
Nitrile	0.9640	0.9754	0.9881	0.9578	0.9702

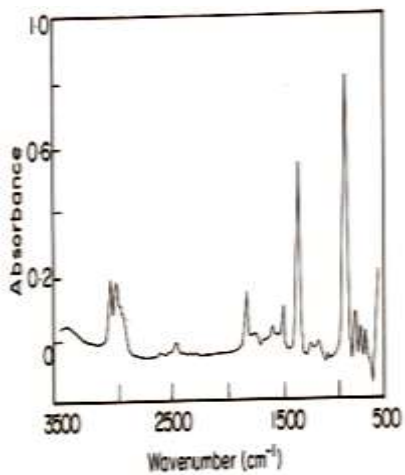


Fig1 Butyl Rubber

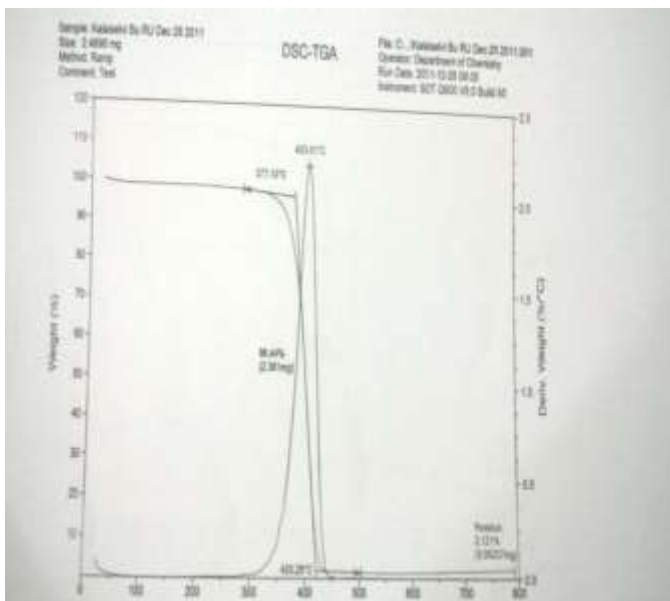


Fig2 Nitrile Rubber

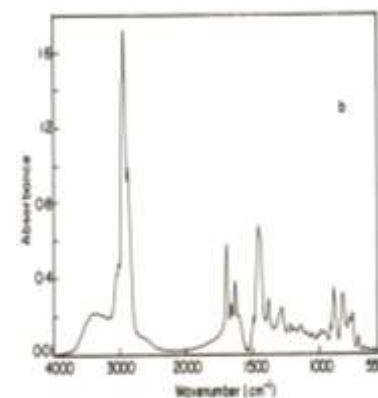


Fig3 Viton Rubber

3.2 Differential scanning calorimetry

The originate of a DSC curve represents the rate of energy absorption by the test sample, relative to that of the reference material; this rate naturally depends on the heat capacity of the sample. The idea of DSC was first put forward by Watson et al. I 1964 and has been subsequently exploited by the Perkin-Elmer corporation, who marketed commercial DSC apparatus. DSC monitors the heat effects associated with phase transitions and chemical reactions as a function of temperature. It is developed from DTA. In a power compensated DSC the heat to be measured is compensated with electric energy, by increasing or decreasing adjustable heat energy.

The measuring system consists of two micro furnaces of the same type made of Pt-Ir alloy, each of which contains a Pt resistance thermometer as a temperature sensor, and a heating resistor made of Pt wire. Both micro furnaces-separated from each other, are positioned in an aluminum block of constant temperature. The maximum heating power of a micro furnace is about 10W, the maximum heating rate is 200 K/min. The measuring range extends from 50 to 550°C. During the programmed heating, same heating power is supplied to both micro furnaces through a control circuit in order to change their mean temperature in accordance with the preset heating rate[12-14].

Fig 4 DSC and TGA of Butyl Rubber

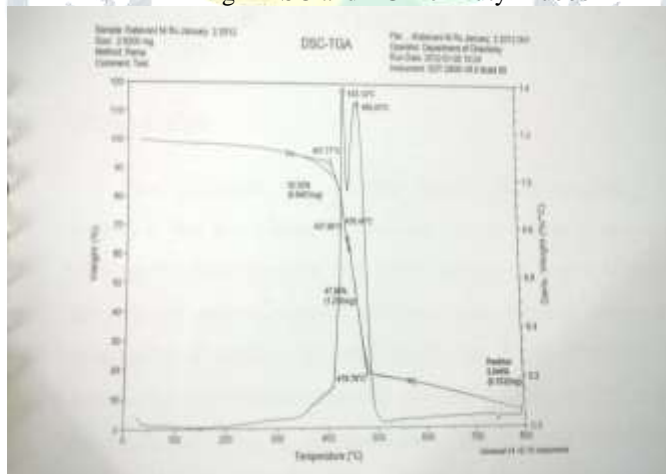


Fig 5 DSC and TGA graph of Nitrile Rubber

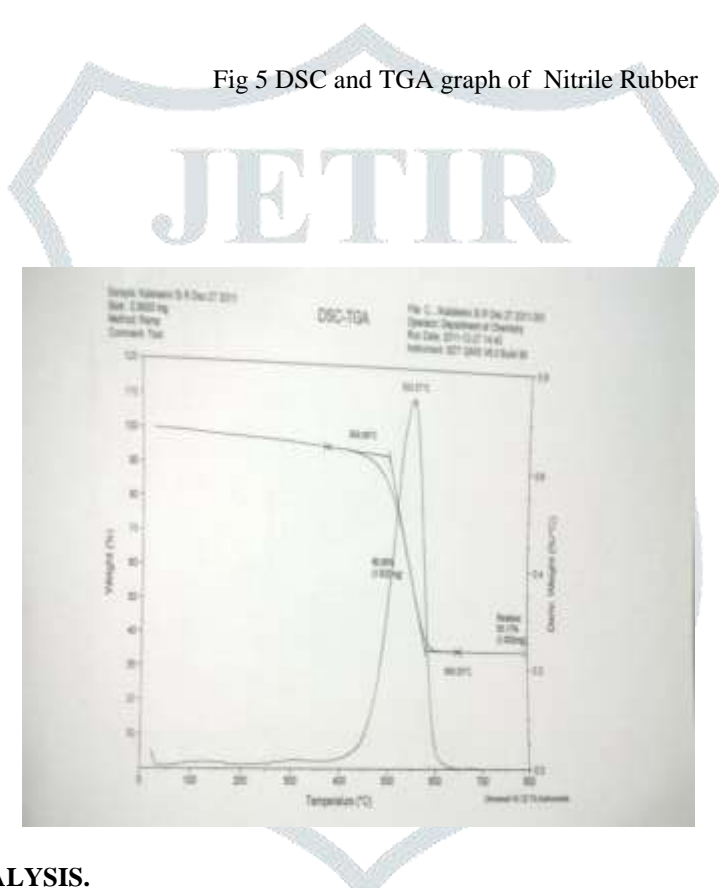


Fig 6 DSC and TGA graph of

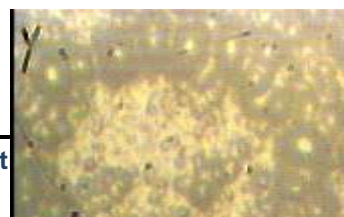
Viton Rubber

3.3 THERMOGRAVIMETRIC ANALYSIS.

Thermal analysis was carried out in a high-resolution thermo balance (Seiko Instrument Inc.) The heating rate was 20°C/min and the resolution used is “4”. This means that the apparatus operates similarly to the traditional constant heating rate ramp segment when no weight change is occurring. 20°C/min in this study, while the heating rate is varied dynamically when a weight change occurs[15-16]. When a loss of weight is detected in Hi-Res TGA technique, the heating rate slows in response to mass and the system tries to keep it at the lowest value (0.01 C/min) until the end of the weight loss.

3.4 OPTICAL MICROGRAPHS

The optical microscopy is an authentic and indispensable tool to look at the surface features of any material and it is more so in the case of rubber materials. Surface heterogeneities, phase separations, dissolution, dispersion and swelling of polymers, particle morphology, size, grain boundaries, grain sizes, and many more interesting features can be visualized by subjecting a particular sample for optical microscopic analysis. In the frequent course of investigations five commercially important rubber materials namely butyl rubber, viton rubber and nitrile rubber have been characterized and critically analyzed by optical microscopic technique.



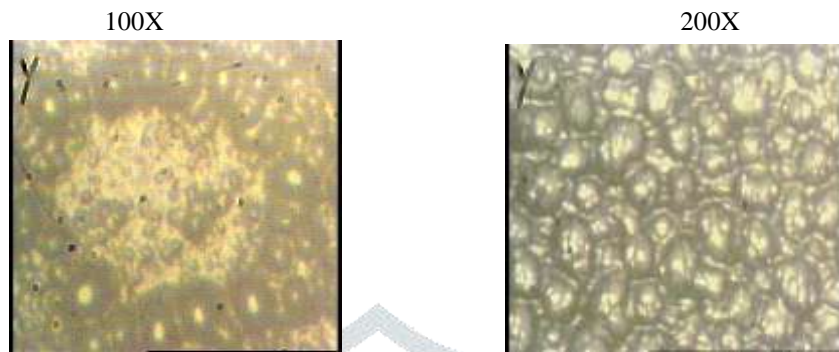


Fig 3.4 (a) Optical Micrograph of nitrile rubber in different magnifications.

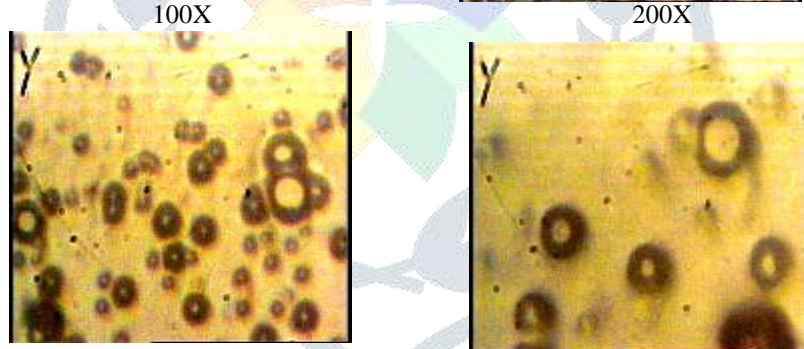
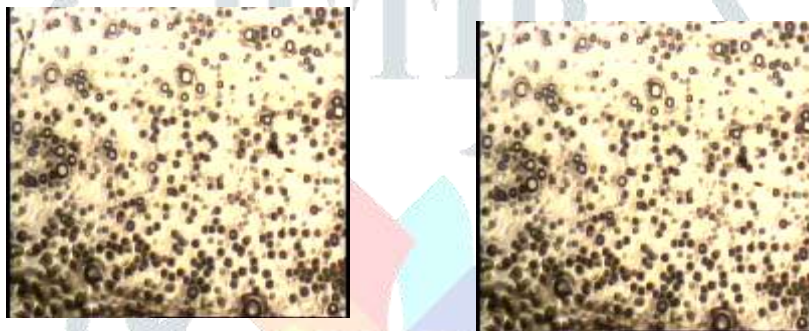
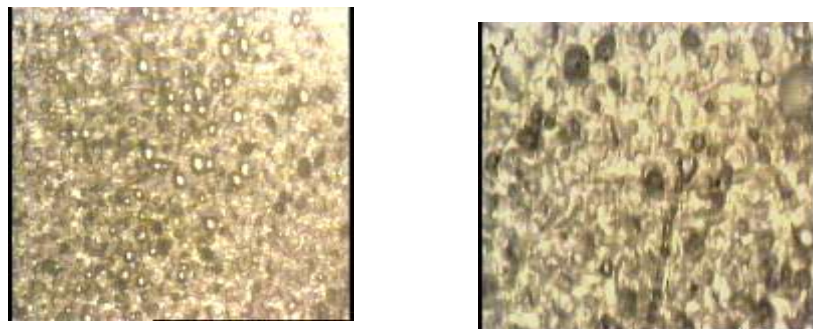


Fig 3.4 (b) Optical Micrograph of butyl rubber in different magnifications.



400X 800X

Fig 3.4 (c) Optical Micrographs of Viton rubber in different magnifications.

The pictures shown in Figs 3.4(a–c) revealed interesting surface topological features in magnification of 100×, 200×, 400× and 800×. The swelling of the butyl rubber when dispersed in chloroform solvent. The domains are of different sizes but only of spherical shape. They are of uniformly dispersed in the whole of the solvent. Droplets like features are evident in the case of viton rubber well dissolved in chloroform. The spherical shaped particles are well dispersed. Tailing of droplets can be seen. The optical micrograph gives the surface morphology of nitrile rubber. Nitrile rubber dissolved in chloroform exhibited homogeneous phase throughout. The surface is similar to that of foam. Better resolutions showed that the domains are well separated. The use of optical microscopy has provided valuable insight into the behavior of polymers in contact with solvents, but it is limited to a micrometer scale. Additionally, there is limited chemical specificity with an optical microscopic system.

3.5 EPR SPECTRAL ANALYSIS

Three industrially significant rubber materials viz., butyl rubber, viton rubber and nitrile rubber have been subjected to EPR analysis. For EPR spectral recording of the above said samples, methanol and chloroform are employed as solvents. The analysis is performed in solution mode at liquid Nitrogen Temperature (LNT). There are several reports on conducting polymer, transition metal doped polymer, and carbon black doped polymers which can be anticipated to be EPR active. The EPR spectra of chosen rubber materials undertaken in the present study are presented in Fig. 3.5(a-c) and it is observed that they are EPR active.

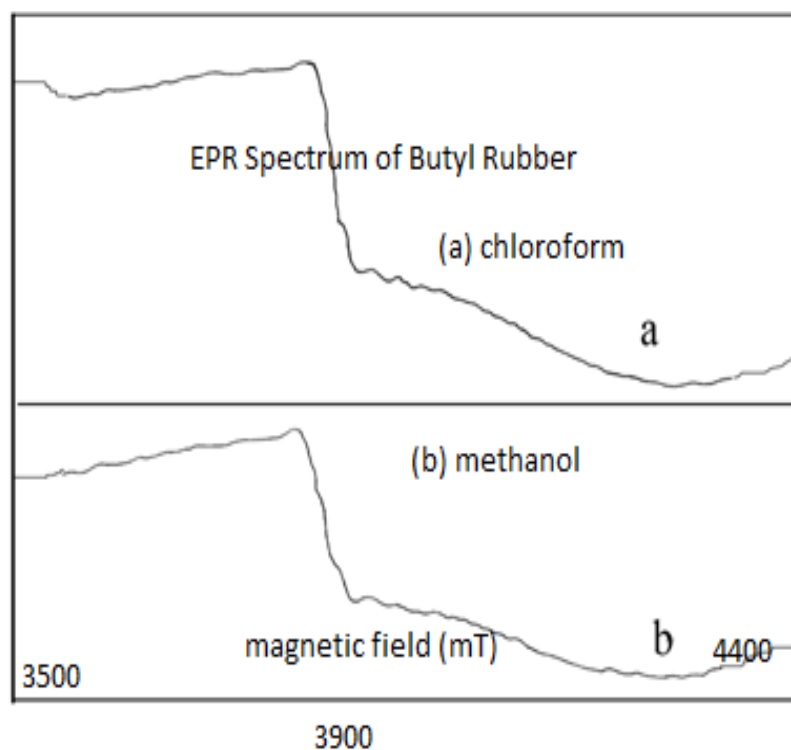


Fig 3.5 (a) Butyl Rubber

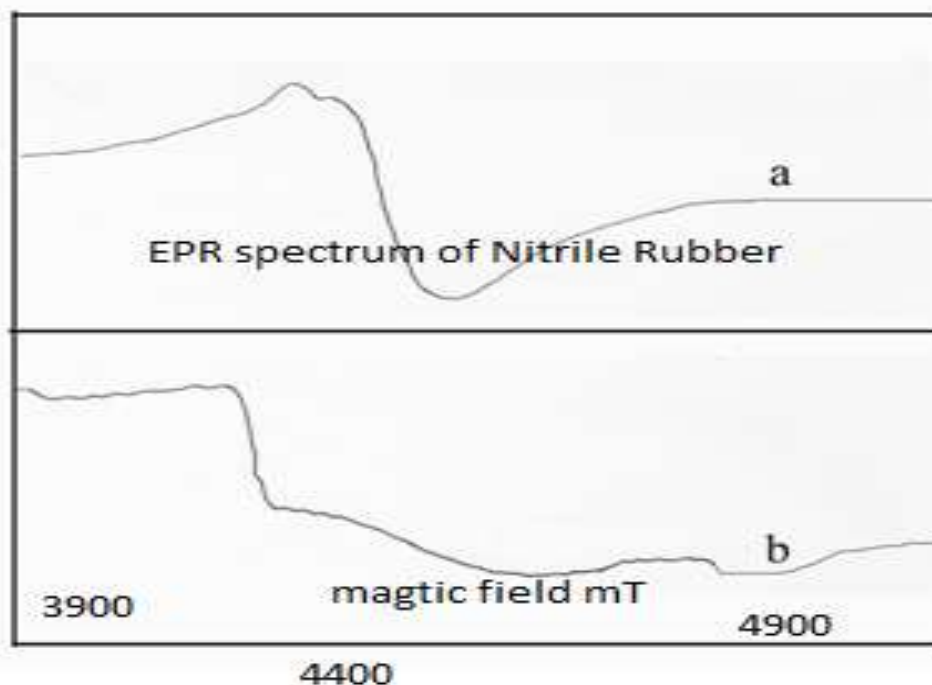


Fig 3.5 (b) Nitrile Rubber

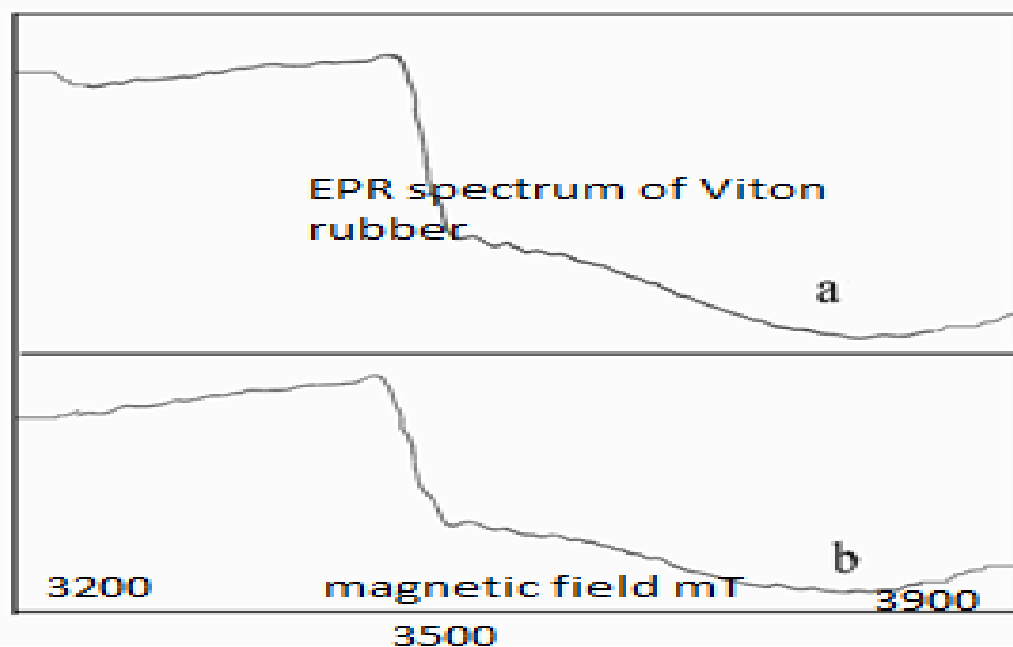


Fig3.5 (c) Viton Rubber

It is a very sensitive probe of electronic structure which provides information on the g-factor is a dimensionless constant and is equal to 2.002319 for free electron as stated above. Table 4.3 gives the g factors for Radicals which are accurately known.

Table 4.3 Radicals for which the g factors are accurately known.

Radical	Solvent	g factor
Napthalene ⁻	DME/Na -58 °C	2.002743 ± 0.000006
Perylene ⁻	DME/Na	2.002650 ± 0.000003
Perylene ⁺	Conc.H ₂ SO ₄	2.002569 ± 0.000006
Tetracene ⁺	Conc.H ₂ SO ₄	2.002590 ± 0.000007
p-Benzo semiquinone	Butanol/KOH at 23 °C	2.004665 ± 0.000006
Wurster's blue cation	Absolute Ethanol	2.003051 ± 0.000012
DPPH	Benzene	2.003540 ± 0.00003
DPPH	None (powder)	2.003700 ± 0.0002

From the EPR spectra recorded at constant microwave frequency attaining the magnetic field strength in two different solvents namely chloroform and methanol, the g factor values have been calculated by using the formulae:

$$h\nu = g\beta H$$

Where h - Plank's Constant = 6.626×10^{-27} erg sec, β_e = Bohr Magneto of electron = 9.274×10^{-27} erg Gauss, H = Magnetic field strength, ν = Micro wave frequency. and all the values have been tabulated in Tables 4. 4. Both in methanol and chloroform solvents the value of g Factor is close to 2.002319 which is well established constants for unbounded electron The spectroscopic splitting factor or g factor is one of the most important concepts in electron spin resonance studies. For an atom where L = 0 and S = 1/2, the $g_L = g_S = 2$; in practice the value now adopted for a free electron is 2.0023. In the crystalline salts of Mn^{2+} and Fe^{3+} the g-value is almost 2. In general, g approaches the value of 2 when the coupling of the orbital and spin momentum of electrons with in solids is broken down almost completely by the strong electric field existing with in the solid. However, in some paramagnetic solids the value of g may differ considerably from 2.

Table 4.4. The 'g' factor values of rubber materials in two different solvents

Sample	Solvent	g factor	Solvent	g factor
Butyl rubber	Chloroform	2.0951	Methanol	2.0772
Viton rubber	Chloroform	2.0588	Methanol	2.0568
Nitrile rubber	Chloroform	2.0427	Methanol	2.0523

In the majority of crystalline samples which have an internal electric field, $L \cdot h/2\pi$ and $S \cdot h/2\pi$ are neither totally uncoupled nor totally coupled, and the energy levels consists of a complex admixture of spin and orbital momentum. This really measures the residual contribution of the orbital angular momentum and is called the spectroscopic splitting factor. For many organic free radicals in the solid state g is approximately equal to 2 (19) An example of such a case is the value of g for poly crystalline 1-1-diphenyl, 1-2- picric hydroxyl which was found to be 2.0036. Thus, on comparison of this value with that of 2.0023 for the free electron, it might be deduced that the unpaired electron is nearly free and that there is almost complete quenching of the orbital momentum. This electron cannot be assumed to be confined to any single atom or ion for there is no such possibility .But the system as a whole contains free electron which is contributing to the resonance absorption of the microwave frequency corresponding to a g value close to 2.002319. (20)

4.CONCLUSION

From the present study of rubber elastomer silicon, viton, butyl, nitrile material in raw, gum rubbers are concluded that the mechanical strength from FTIR spectral measurements of these rubber materials are found to be normal by analyzing the ratio of methane, methylene group vibration frequencies and investigation of dielectric properties reveals that at high frequencies range. spectroscopy is an extremely powerful analytical technique for both qualitative and quantitative analysis of materials. Infrared spectroscopy is finding increasing application as a means for identifications of above rubber materials. The similar behavior is obtained for other rubber materials also. From Thermo gravimetric analysis the results obtained from TGA technique show that all the chosen blends starts to thermal degradation or weight loss around 360°C.

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