# CONDUCTIVITY STUDIES OF CHLORINATED NATURAL RUBBER

## Abstract

Chlorinated natural rubber (CNR) was prepared by alkaline hydrolysis of chloroform using phase transfer catalyst. The chlorination in CNR was monitored by FTIR and UV spectroscopy and these studies indicated the formation of dichloro cyclopropyl ring to the double bond of natural rubber (NR). XRD and SEM analysis revealed the extent of chlorination in natural rubber. Electrical properties such as AC conductivity, dielectric constant and dielectric loss of CNR was higher than that of NR. Conductivity of NR increased with the increase in the concentration of chlorine percentage. LOI values indicated that the chemical modification imparts better flame resistant to NR.

**Keywords:** Natural rubber, Chlorination, Conductivity, Morphology, Electrical properties, Crystallinity.

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## I. INTRODUCTION

Elastomers are important class of materials for wide range of application, ranging from footwear to space vehicles, because of their unique mechanical properties such as elastic behavior at very large deformation and energy absorbing capability [1,2]. By properly controlling the properties in rubber, its ultimate mechanical properties can be made to match the requirements among elastomers; natural rubber (NR) has many attractive properties including their low cost, low hysteresis, excellent mechanical properties, high resilience as well as superior dynamic properties as compared to several synthetic elastomers [3,4]. The chemical modification of elastomers play an important role in enhancing the physical properties of rubbers [5,6]. However, number of double bond present in NR leads to the deterioration of the fabricated products. Also it has poor solvent, fuel, oil and flame resistance. It was shown that the reaction of double bond with various reagents could result in the improvement of flame retardancy, oil and solvent resistance [7]. Among the different type of chemical modification in rubbers, halogenations reactions are most common and effective one which imparts excellent flame and oil resistance [8,10]. In practice, rubber products in contact with oil or fuel will lead to swelling. So the rubber products under swelling are prone to undergo continuous or dynamic changes and these changes are large enough to cause failure in service.

Nowadays conductive elastomeric materials have much attention due to their excellent elasticity and electrical properties. The conductive elastomers are mainly used in electromagnetic shielding, pressure sensitive conductive materials, anti-static and other electronic industries [11,12]. Generally conductive rubber is prepared by adding conductive filler or blending with conducting polymers. Unfortunately, the properties of elastomeric matrix will be inevitably affected by the loading of conductive fillers or the incompatibility between the two matrixes by blending[13]. Another method for obtaining the electrical properties are the electroless deposition of materials from solvation with various substances, but the quantum yield of products limit its applications. For the better mechanical properties and economic point of view as well as the simplicity in experimentation it is desirable to develop a facile procedure for the preparation of chlorinated natural rubber. Therefore the aim of this study is to evaluate the effect at different content of chlorine on the electrical properties of natural rubber. In this paper functionalisation of natural rubber has been carried out by the alkaline hydrolysis of chloroform in presence of phase transfer catalyst at different time of intervals. The chemical composition and structure of the modified natural rubber has been investigated by UV-Visible spectra and Fourier transform infrared spectroscopy, X-ray diffraction analysis. The morphology of the halogenated natural rubber was investigated by scanning electron microscopy. The flame retardancy of NR and CNR were studied by limiting oxygen index (LOI) analysis. Finally the electrical properties such as AC conductivity, dielectric behavior of the modified and unmodified polymer was also evaluated.

## II. EXPERIMENTAL

1. **Materials and Methods:** Natural rubber was obtained from Rubber Research Institute of India. Analytical grade toluene, chloroform ($CHCl_3$), sodium hydroxide (NaOH), cetyl trimethylamonium bromide (CTAB), isopropyl alcohol is the reagents used for the chlorination reactions.

2. **Synthesis of Dichloro Cyclopropyl Natural Rubber (CNR):** The chemical modification of natural rubber was carried out by the reaction of chloroform with alkali in presence of cetyl trimethylamonium bromide as phase transfer catalyst. Natural rubber was first dissolved in toluene; the phase transfer catalyst was added and stirred the mixture well. To this solution chloroform was added followed by sodium hydroxide solution and stirred the solution for different time and the reciepe used for this synthesis is given in Table I. The product was separated from the solution and washed thoroughly with deionised water until the sodium chloride was completely removed. The product was then further purified by coagulation with alcohol and dried at 90$^o$C for 12 hours.

**Table 1: Amount of reagent used for the chemical modification**

| Materials | Amount |
|---|---|
| Natural rubber (NR) g | 10 |
| Toluene (ml) | 200 |
| Chloroform (ml) | 35 |
| NaOH - 50% (ml) | 40 |
| CTAB (g) | 0.85 |
| Time (hours) | 4,8,12,24 |

## III. CHARACTERIZATION

The FTIR spectra of the synthesized polymer was recorded on a JASCO (model-4100) Fourier transform infrared spectrophotometer in the region of 4000cm$^{-1}$ - 500cm$^{-1}$ using thin film of the modified polymer. The thin film was prepared by dissolving the chlorinated natural rubber in toluene and then the concentrated solution was directly cast onto the KBR plate. The UV-Visible absorption spectra of the polymer in toluene were recorded on a Hitachi 91-300 spectrophotometer. X-ray diffraction pattern of NR and modified polymer was recorded on Rigaku miniflux X-ray diffractometer using CuKα radiation ($\lambda$ =1.5406 A$^o$). The diffractogram as recorded in terms of 2θ in the range 10-80$^o$. Morphology of chemically modified natural rubber were, analysed using field emission scanning electron microscopy (FESEM) in a variable pressure, Hitachi SU-6600 FESEM. The fractured end of polymer surface were sputter coated with a thin layer of gold to a void electrostatic charging during the SEM analysis The flame resistance of NR and CNR were carried out by the LOI test as per the ASTM- D procedure No. 2863-77. The sample was burned in a Stanton Redcroft FTA flammability chamber under nitrogen-oxygen environment. The minimum concentration of the oxygen in the oxygen-nitrogen mixed gas environment just sufficient to sustain the flame for 30 second was taken as the LOI

$$\mathbf{LOI} = \frac{\text{volume of oxygen x 100}}{\text{volume of nitrogen x volume of oxygen}} \qquad (1)$$

Alternating current (AC) resistivity of the modified NR was measured by Hewlett - Packard LCR meter at a frequency range of 10$^2$ to 10$^6$ Hz at room temperature. Thin films of the samples were used for these studies. The electrical properties such as the dielectirc constant ($\epsilon_r$) was calculated by using the relation

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \qquad (2)$$

and the conductivity  was calculated by the equation

$$\boldsymbol{\sigma ac = ..\omega.\tan\delta} \qquad (3)$$

Where d be the thickness of the sample, C the capacitance, A be the area of cross section of the sample and  be the permittivity of free space. The relative permittivity of the material which is a dimensionless quantity. From these measurements tan δ was also determined.

## IV. RESULTS AND DISCUSSION

### 1. FTIR Characterization

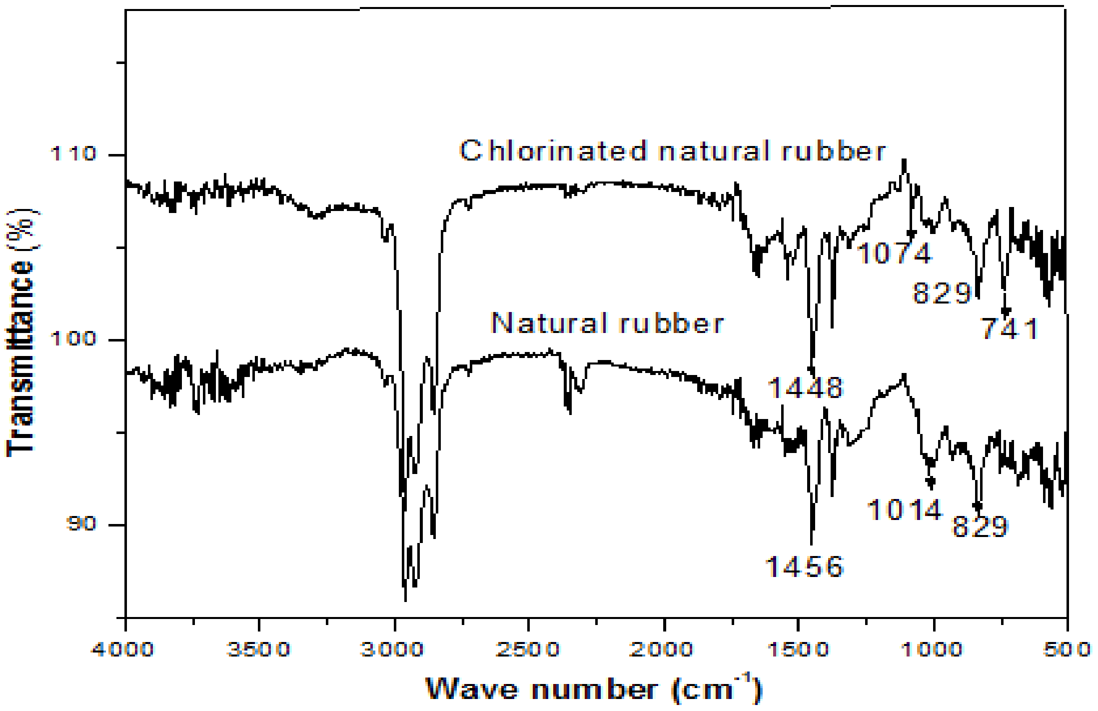

**Figure 1:** FTIR spectra of NR and chlorinated NR

The FTIR spectra of natural rubber and chlorinated natural rubber are shown in Figure 1 .The natural rubber shows an absorption band 2975cm$^{-1}$ and 2950cm$^{-1}$ are attributed to the C-H stretching of $CH_2$ group and the band at 1450cm$^{-1}$ is the -CH plane bending vibrations. The methyl group present in natural rubber showed the stretching vibrations band at 168cm$^{-1}$. The absorption at 972cm$^{-1}$ is due to the trans CH= where as cis appeared at 768cm$^{-1}$. In the case of chlorinated natural rubber the characteristic C-Cl absorption peak [14] appeared at 741cm$^{-1}$ and the attachment of cyclopropane ring [15] in the compound showed a band at 1074cm$^{-1}$. There is a shift of 690cm$^{-1}$ absorption to 710cm$^{-1}$ is due to the influence of chlorination in natural rubber and this may be attributed to the steric hindrances of the cyclopropane ring present in the chemically modified NR. It can be seen from Figure that, the addition of chlorine groups to the main chain of natural rubber reduces the intensity of double bond and few characteristic shift in peak along with the formation of new bonds can also be observed. Thus, it can be concluded that the dichloro cyclopropyl ring is successfully attached on the main chain of natural rubber.

2. **UV-Spectroscopy:** The chemical structure of natural rubber and dichloro cyclopropyl group attached natural rubber are further studied by UV-Visible spectroscopy. The UV spectrum for pristine natural rubber is shown in Figure 2. The absorption peak observed that 286 nm is attributed to the π - π* transition. The chloro functionalised natural rubber showed the characteristic peak of π - π* transition at 290nm compare the UV spectra of modified natural rubber with that of pristine NR, it can be observed that the attachment of dichloro cyclopropane system slightly shifted to a higher wave length (ie., from 286 nm to 290 nm) with an decrease in the intensity of peaks.

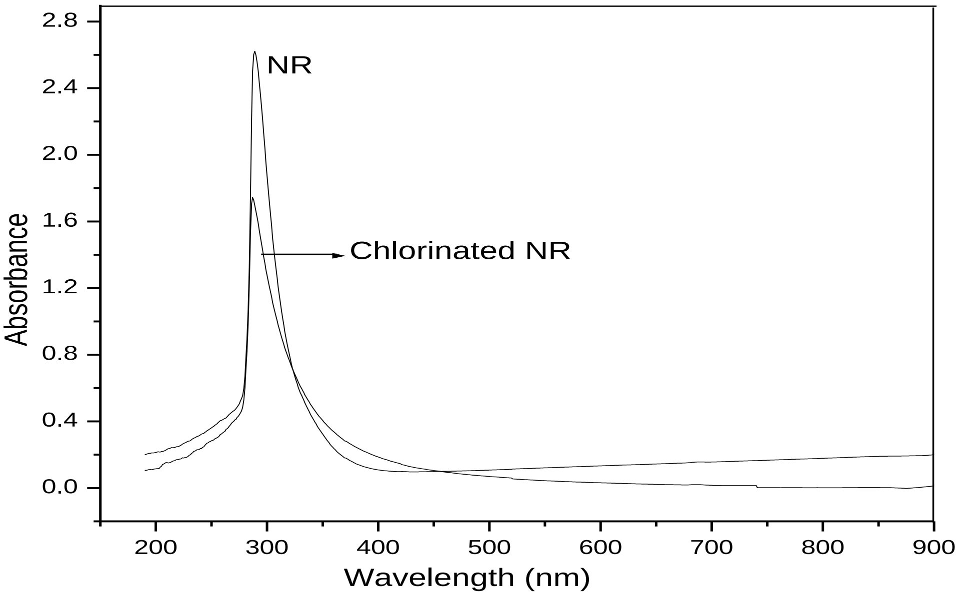

**Figure 2:** UV spectra of NR and CNR

The shift in peak is attributed to the decrease in conjugation of the double bond present in natural rubber. This observation is good agreement with the FTIR studies.

## 3. X-Ray Diffraction Analysis (XRD)

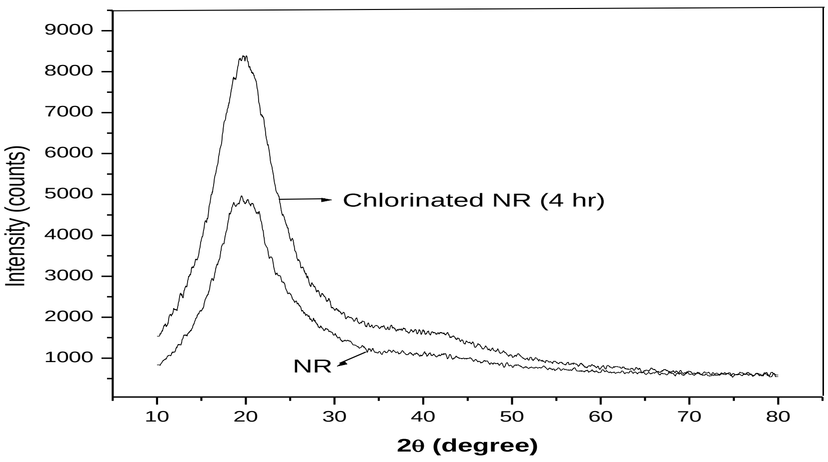

**Figure 3:** XRD pattern of NR and Chlorinated NR

X-Ray Diffraction Analysis (XRD) is a powerful technique to characterize the structural arrangement of a polymeric chains. The XRD pattern of NR and dichloro cyclopropyl ring with different time of reaction are presented in Figure 3 and 4 respectively. The natural rubber shows a broad diffraction peak at $20=20^{0}$, indicating the highly amorphous nature of the polymer, however the XRD of chemically modified NRwith 4 hour chlorination showed the characteristic amorphous peak of NR with a small diffraction peak at $20= 42^{0}$, while the sample with 8% chlorine exhibit a peak at $20 = 29^{0}$, revealing that the chemical modification on impart a slight crystalline nature to the highly amorphous compare the XRD curve of NR and CNR. It can be observed that the intensity of the amorphous peak slightly reduced and shifted to a higher value. This again proved that, higher degree of regularity in arrangement or well ordering of the macromolecular chain of natural rubber in degree of crystallinity is due to the stereoregular addition of dichlorocarbene regenerated from chloroform and alkali to the double bond of natural rubber. Further, the dichlorocyclopropyl system makes a dipolar interaction with the adjacent macromolecular chain in a stereoregular path. Hence, the orientation of macromolecular chain of chlorinated natural rubber is of much interest, due to the highly ordered polymer matrix could display conductive properties [16].

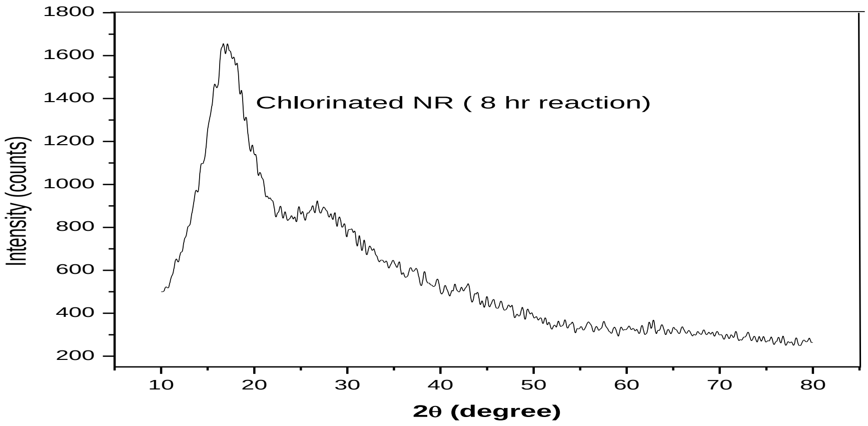

**Figure 4:** XRD Pattern of Higher Cl Content

### 4. Scanning Electron Microscopy (SEM)

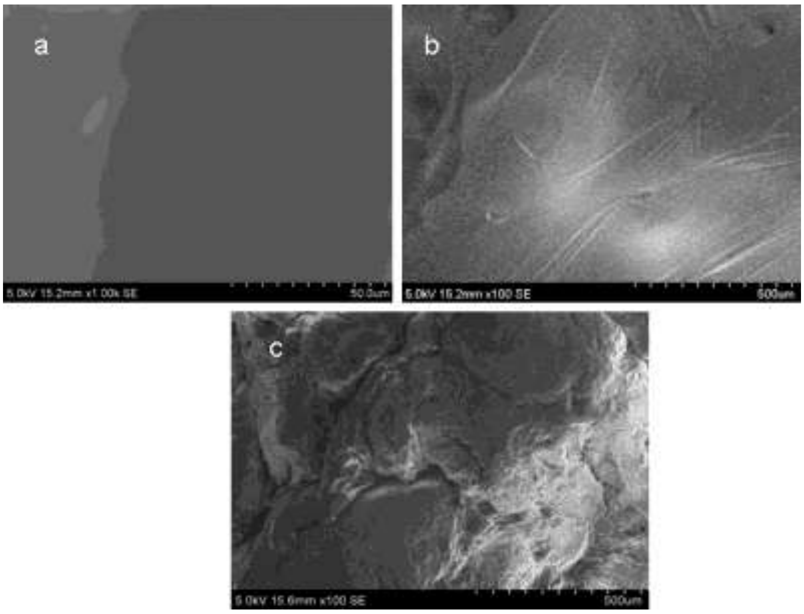

**Figure 5:** SEM images (a) NR (b) 4 and (c) 8 hr chlorinated NR

The change in surface topography of NR and dichloro cyclopropyl group introduced in natural rubber with different time of chlorination reaction are examined by scanning electron microscopy (SEM). The SEM images of pristine NR surface and the modified natural rubber surfaces are shown in Figure 5. It can be seen from Figure 5 (a) that the pristine natural rubber has smooth surface, compared with the natural rubber surface, chlorination on polymer matrix resulting in a distinctive layer on the modified natural rubber surface due to the attachment of chlorinated segments on the main chain of natural rubber. Moreover, as the level of chemical modification increases, the roughness of surface increases. This increase in surface roughness probably arises from the more number of polar groups attached on the surface of modified samples.

5. **Flame Retardancy:** Limiting oxygen index (LOI) is widely used for the determination of relative flammability studies of polymeric samples. It measures the minimum amount of oxygen in a nitrogen/oxygen mixture required to support the combustion of materials. The LOI value of NR and dichloro modified natural rubber with different level of chlorination at room temperature are given in table 2. It is interesting to point out that the fire retardancy of the chemically modified natural rubber is much improved compared to pristine NR. The halogen group present in the surface of the NR undergoes initially a swelling by the application of heat, this increases the volume of the chemically modified NR and that decreases the density of the polymer. The char formed after burning protect the polymer from further burning and thus restricted the heat transfer and this phenomenon is known as intumuscence effect. It is also clear from the table that the flame resistance of the samples increases with increases in the chlorination, which indicated that at higher level of chlorination, the thickness of the char developed at the surface of polymer is increased, so that the rate of intumuscence increases leading to superior flame retardancy. Materials with LOI value greater than 20.8 are generally classified as safe one while materials having LOI less than 20.8 are continue to burn in

oxygen deficient air, which are not safe for building materials [7]. Therefore the synthesised chlorinated natural rubber is considered as safe matrix for indoor applications.

**Table 2: The LOI values of NR wiwth different time intervals**

| LOI Value | Time |
|---|---|
| 18 | 0 |
| 22.6 | 4 |
| 24.8 | 8 |
| 27.0 | 12 |
| 29.8 | 24 |

## 6. AC Conductivity

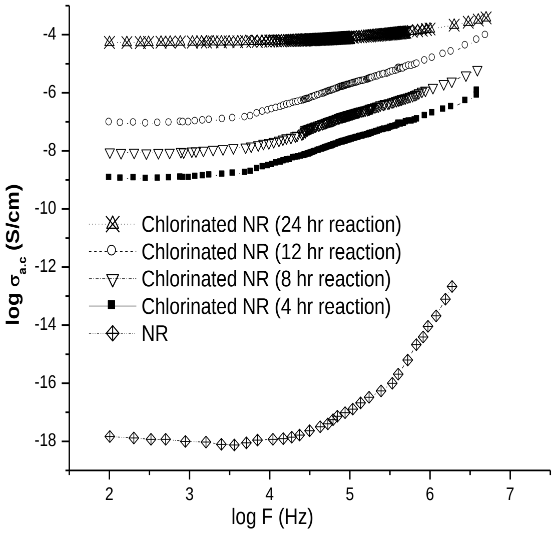

**Figure 6:** AC conductivity of NR and chlorinated NR

The effect of dichloro modification on the AC conductivity of NRs and different chlorine attached natural rubber at various frequencies ($10^2$-$10^{6}$ Hz) are shown in Figure 6. It is evident that all the chlorinated samples have higher conductivity than parent polymer. It is found that the conductivity of the modified natural rubber increases not only with frequency but also with the increase in chlorination time. The increase in conductivity with frequency of chemically modified natural rubber is attributed to the polarization arises from the restricted movement of bond charges such as dipoles. The chloro groups present in natural rubber acts as electron withdrawing group which pulls electrons from neighboring atoms and hence show more dipolar polarization. Natural rubber is non-polar polymer and the introduction of polarity in natural rubber after chemical modification becomes more heterogeneous than pure natural rubber that leads to an interfacial polarization. This interfacial polarization developed at the interface of electrically different materials with difference in permittivity or ionic conductivity. Generally the conductivity of a polymer matrix depends on microscopic or macroscopic conductivity [17]. The microscopic conductivity depends upon the interaction between the macromolecular chains, orientation of the polymer chain, length of the conjugation in polymers. In the present case, the microscopic conductivity is responsible for the increased conductivity of polymers. The conductivity behavior of all the modified samples show similar behavior up to 104 Hz, that is there is not much variation in conductivity with frequency at this range.

## 7. Dielectric Behavior

*Dielectric Constant*

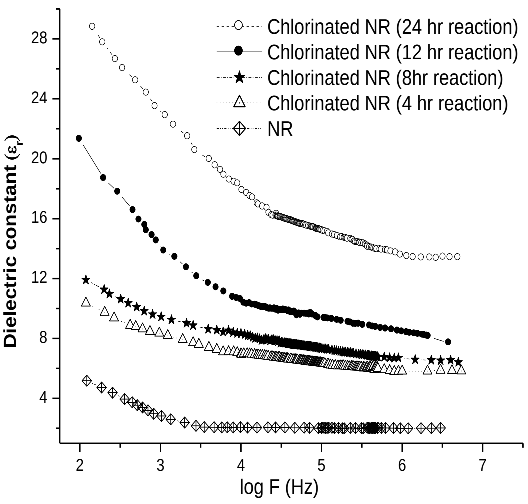

**Figure 7:** Dielectric Properties of NR and Chlorinated NR

Figure 7 shows that variation of dielectric constant (εr) with different frequency at room temperature for NR and modified natural rubber with various level of chlorination. It can be seen from figure that the dielectric constant continuously decreases with increase in increasing frequency and as the frequency increases the dielectric constant reached to a constant value. The dielectric enhancement is due to the interfacial polarization, which is also referred to as Maxwell-Wagner–Sillars (MWS) effect. Normally the polarization phenomenon appears in heterogeneous system consist of phases with different dielectric permitivities and conductivities that lead to accumulation of charges at the interfaces. In the present study modified NR become heterogeneous in nature due to the polarity of the polymer. Hence in presence of an applied field, more dipoles are created because of the imbalance in distribution of electrons and these dipoles align in the applied electric field. In all the samples the dielectric constant showed large dielectric value at lower frequencies.

When the applied field is increased, the dielectric constants remained almost constant value. The relatively large polar molecules are not able to arrange themselves in the direction of applied field and hence the dielectric constant remains almost same value with increasing the field. For electrical and electronic applications, a polymer should posses reasonably constant dielectric properties over a broad range of frequencies.

### 8. Loss Tangent

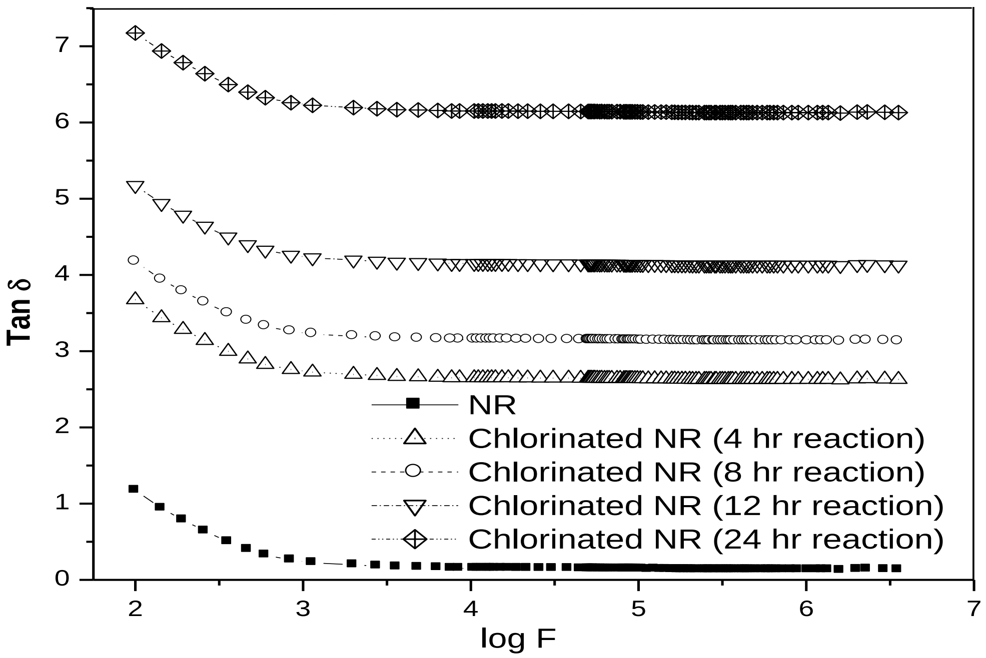

**Figure 8:** Tan δ values of NR and chlorinated NR

Loss tangent ( Tan δ) is the tangent of angle δ between the vector for the amplitude of total current and for the amplitude of charging current [18]. The variation of tan δ with different frequencies (102 -106 Hz) for NR and modified NR with different level of chlorination are presented in Fig. 8. It shows that the value of tangent loss increases on increasing the content of chlorination at lower frequencies whereas tangent loss has marginal change at higher frequencies. The dielectric loss is a direct function of the relaxation process and the origin of this relaxation is owing to the movement of polar group present in the system. Therefore at lower frequencies the high value of loss tangent is due to the free charge motion within the material [19]. The increase in tan δ value at higher level of chlorination of NR is due to the increase in polarity of the matrix. The lowest conductivity and dielectric behavior of NR is due to its high amorphous nature, however, after the chlorination on NR the macromolecular chain of polymer become closely packed and orderly arranged because of the semi-crystalline nature of chemically modified natural rubber (Evident from XRD). These semi-crystalline nature and a polarity of the polymer is responsible for the maximum space charge polarization leads to high dielectric behavior [20]. When the dielectric behavior compared with conductivity behavior of figure 8. It is pointed out that the behavior is opposite.

## V. CONCLUSION

Dichloro cyclopropane group introduced in natural rubber were prepared by the alkaline hydrolysis of chloroform using Cetyl trimethylamonium bromide as phase transfer catalyst. The dichloro reaction was monitored by spectroscopic technique such as UV-Visible and FTIR. The FTIR studies showed the characteristic C-Cl stretching at 807cm$^{-1}$ with a reduction in the double peak at 1663cm$^{-1}$. UV spectroscopy also gives an additional evidence for the formation of chloro group in natural rubber. XRD of natural rubber showed a broad amorphous peak at 200 and did not show any sharp or intense peaks , whereas the chemically modified natural rubber showed the characteristic amorphous peak of NR along with small peat at 30o, indicating the semi-crystalline nature of the synthesized polymer. The phase morphology of CNR studied by SEM showed an entirely different morphology than natural rubber. The increase in AC conductivity with increase in level of chlorination was due to the more number of dipoles developed by the increased polarity of the compounds. The dielectric properties such as dielectric constant and tan δ of NR was lower than that of dichloro functionalised NR and these properties increased with the increase in the level of chlorination. The enhancement in the dielectric properties suggests that this modified polymer can be used as multifunctional materials for various electronic industries. The Flame retardancy of the polymer was studied by LOI measurements and it showed that the flame resistance of dichloro group introduced NR is much higher than that of the pristine NR. Due to the intumuscence effect of chloro group present in NR the flame resistance of modified sample increased with increase in the level of chemical modification.

Since the conductivity of polymers depends upon different factors such as formation of polaron or bipolarons, the symmetric arrangement of the macromolecular chain, conjugation at the polymer and single or multiple helices [1**]. Hence the conductivity of chlorinated samples are due to the increase in crystallinity of the sample. During the chemical modification, the dichloro groups are added to the double bond leads to systematic alignment of polymer chain or by the formation of single or multimpe helices result in a semicrystalline nature of modified sample.

## REFERENCES

[1] Y. Coran and S. Lee,Rubber Chem. Technol .65, 231-244 (1992)
[2] N. Karak and S. Maiti, J. Appln. Polym. Sci., 98, 927-935 (1998)
[3] W. Arayaprance and G.L.A. Rempel, J. Appl. Polym. Sci., 109,932-941 (2008)
[4] Y. Manusamy, H. Ismail and M. Mariatti, J. Rein. Plast. Comp. 27,1925-1945 (2008)
[5] M. T. Ramesan and R. Alex, Kautsch.Gummi Kunstst., 53,596-600 (2000)
[6] M. T. Ramesan, A. Nihmath and J. Francis, AIP Con. Proc.1536, 255-256 (2013)
[7] S. T. M. Sang, J. Rubb. Res. Inst. Malaysia, 26, 48-59 (1978)
[8] J. M. M. Martinez, J. C. F. Garcia and A.C.O. Barcelo, Int. J. Adhesion Adhesives, 11, 192-198 (1991).
[9] M. M. P. Biass, M. S. S. Adsuar and J. M. M. Martinoz, J. Adhesion Sci. Technol. 8,1093-109-(1994)
[10] M.T. Ramesan and T. A. Kumar, J. Chil. Chem. Soc. 54, 23-27 (2009)
[11] W. E. Mahmoud, A. M. Y. El-Lawindy, M. H. E. Eraki and H. H. Hassan, Sens. Actuators A, 136, 229-233 (2007)
[12] J. G. Malleite, A. Marqnez, O. Mamero, R. C. Rodiguez, Polym. Eng. Sci. 40, 2272-2295 (2000)
[13] K. P. San, T. K. Chaki and D. Khastgir, Polymer, 39, 6461-64 (1998)
[14] M. T. Ramesan and R.Alex, J.Appl.Polym.Sci,68,153-160 (1998)
[15] M. T. Ramesan, Polym. Eng. Sci, 54, 438-445(2014)
[16] M. T. Ramesan, Polym. Plast. Tech. Eng., 51,1223-1229 (2012)
[17] C. C Ku, R. Lepins, Electric al properties of polymers: Chemical principles, Hanser Publishers, Munich, 92 (1987)
[18] A.Kyritsis, P. Pissis and V. Grammat:Kakis, J.Polym.Sci.B.Polym.Phys. 33,1737-1750 (1995).
[19] 1** J.Fink and G.Leising,Phy.Rev.B , 34,5320-5322 (1986).