

# Humidity Sensors from cis 1,4 polyisoprene

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## ABSTRACT

Humidity sensors convert ambient moisture variations into detectable electrical signal changes. They have wide application potential in electronic devices for detecting and controlling ambient humidity effects. In this work an attempt has been made to develop cost effective and simple humidity sensor materials from an easily processable and flexible elastomeric polymer, cis 1,4 polyisoprene (natural rubber). By a simple doping technique, highly conducting natural rubber nano particles are prepared by doping. This powder when kept in open atmosphere, is found exhibit drastic changes in electric conductivity. This property makes the materials to be used as a humidity sensor. Main focus of this work is to prepare water resistive humidity sensors from natural rubber powders thus prepared.

**Keywords:** conducting polymers, doping, polyisoprene, humidity sensor

## 1. INTRODUCTION

In recent years research on conducting polymers [1-2] are of great importance as they possess wide application potential in electronic and opto-electronic devices ranging from sensors to diode and transistors and polymeric light emitting diodes, photovoltaic and solar cells. These semi-conducting organic compounds are characterized by the presence of  $\pi$ -electron conjugated backbone, which makes them very rigid and insoluble. Common examples of these materials include polyacetylene, polyaniline, polypyrrole, polythiophene etc. However the full application potential of these conducting polymers is not yet tapped owing to difficulties in processing, and environmental and thermal instabilities. In contrast, high flexibility easy processability and good mechanical properties make the rubbers attractive polymeric materials to be made intrinsically conducting. Cis 1,4 polyisoprene (Natural Rubber, NR) is one of our largest natural products and abundantly available. Its low cost and easy processability makes it very attractive in various applications. Humidity sensors are important for a wide range of application such as meteorological services, air conditioning etc. Generally there are two types of humidity sensors, resistive and capacitive humidity sensors. Resistive humidity sensor usually consists of a moisture sensitive conducting material. In this device resistance varies exponentially with variation in relative humidity. The chemical properties of conducting polymers make them very useful for use in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents or via their instability to moisture and heat. In this work, synthesis of cis 1,4 polyisoprene nano particles and their application potential as humidity sensor are discussed.

## 2. EXPERIMENTAL

### 2.1 Materials

The polyisoprene used in this work is obtained from Rubber Research Institute of India, Kottayam, India. The dopant Iodine (Merck) is used after sublimation. Carbon tetrachloride (Merck) of analytical grade is used without any further purification.

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## 2.2 Synthesis of Conducting NR

$0.43 \times 10^{-3}$  kg of NR (6 mmol of NR unit) is dissolved in  $30 \times 10^{-6}$  m<sup>3</sup> carbon tetrachloride taken in a flask. A solution of  $3.81 \times 10^{-3}$  kg (15 mmol) of iodine in  $150 \times 10^{-6}$  m<sup>3</sup> carbon tetrachloride is added drop wise to the above solution, while stirring at room temperature. When the drop wise addition is complete the mixture is boiled under reflux for 5 hrs. After 48 hrs the solution is filtered off. The precipitate obtained is washed three times with CCl<sub>4</sub> and dried at 50<sup>0</sup>C. A dark-brown insoluble powder is obtained. The immediate filtering of the solution failed to produce any precipitate. The process is repeated by varying the refluxing period, time interval between refluxing and filtering, and also by varying amount of iodine which is used as dopant. Also reaction is allowed to proceed without refluxing and the resulting powder is collected separately. The corresponding yield and conductivity of powders are measured.

## 2.3 Sensor Fabrication and measurements.

The humidity sensor consists of glass substrates with two elongated Cu electrodes fixed 1 cm apart with silver paste. A thick layer (1cm) of NR conducting powder sandwiched between a glass substrate and the porous membrane which prevents from dust particles and allows the NR powder to absorb the moisture from atmosphere.

The conductivity of the sensor material is measured at different time intervals after exposing it to the atmosphere using Keithly 6514 electrometer. The observations are repeated a number times..

## 3. RESULTS AND DISCUSSION

The conducting powders prepared are characterized by measuring DC electrical conductivity, analyzing UV/Vis and FTIR spectra and using X-ray diffraction pattern and Scanning Electron Microscopic (SEM) technique. For conductivity measurements the powders are pressed into pellets. The measurements are done using Keithly 2000 DMM and 6154 Electrometer. Optical absorption spectra of the powders are obtained in the wavelength range of 200-900 nm. FTIR spectra are monitored in KBr medium using FTIR impact 410 spectrometer. UV/Vis and FTIR spectra of the pristine sample are also taken after casting their solution in CCl<sub>4</sub> on glass plates. Color of the conducting powders prepared, with and without refluxing, are identical and is dark brown.

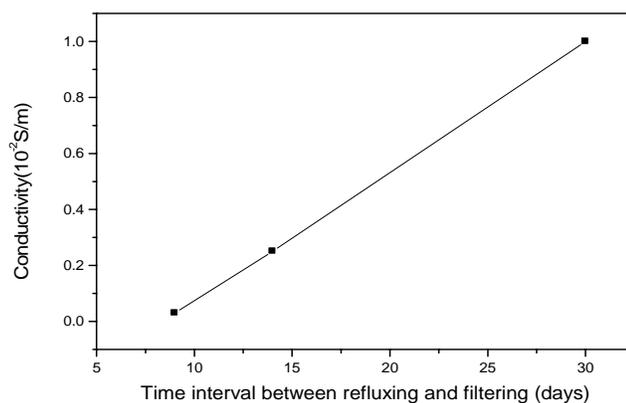


Figure 1: Conductivity of NR powder as a function of time interval between refluxing and filtering

Figure 1 shows the variation of yield of conducting powder, prepared by doping  $0.43 \times 10^{-3}$  kg of NR with  $3.81 \times 10^{-3}$  kg of iodine, as a function of time period of refluxing, filtered after two days of refluxing. It can be seen that yield of the powder decreases with increase in refluxing period. The values of conductivity shows only a slight variation and lies in the range of  $10^{-4}$  S/m.

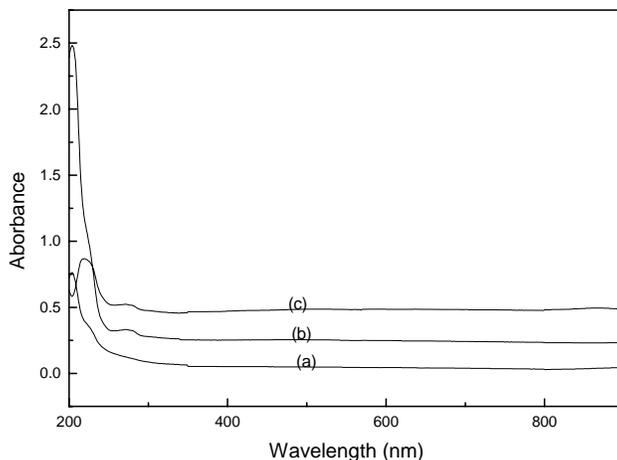


Figure 2: UV/Vis spectra of (a) pristine NR (b) Conducting powder prepared by doping  $0.43 \times 10^{-3}$  kg of NR using  $3.81 \times 10^{-3}$  kg of iodine (c) Conducting powder prepared by doping  $0.43 \times 10^{-3}$  kg of NR using  $1.9 \times 10^{-3}$  kg of iodine .

The optical absorption spectra of pristine NR and conducting powders prepared by doping same amount of NR using different amount of iodine are given figure 2. No absorption is observed for the pristine state. In this state the polymer is colorless because of the isolated double bond structure. Polydienes with isolated double bonds have absorption below 200 nm. Polymeric powder prepared absorb strongly in the UV/Vis region and absorption increases with increasing dopant amount. This result indicate the formation of conjugated sequences of  $(-\text{CH}=\text{CH}-)_n$  with various lengths in the back bone powder prepared. The peaks that are seen between 200 and 300 nm corresponds to the transition from the ground state to the excited state of the charge transfer complexes that are formed upon doping. These results indicate that iodine doping reaction produces conjugation in the backbone NR by the addition of iodine to  $\text{C}=\text{C}$  bonds, followed by the E-2 elimination of HI as shown in scheme 1. The iodine atoms interact with the conjugated  $-\text{C}=\text{C}-$  group in the NR chain and charge transfer takes place to generate outer and inner charge transfer complexes.

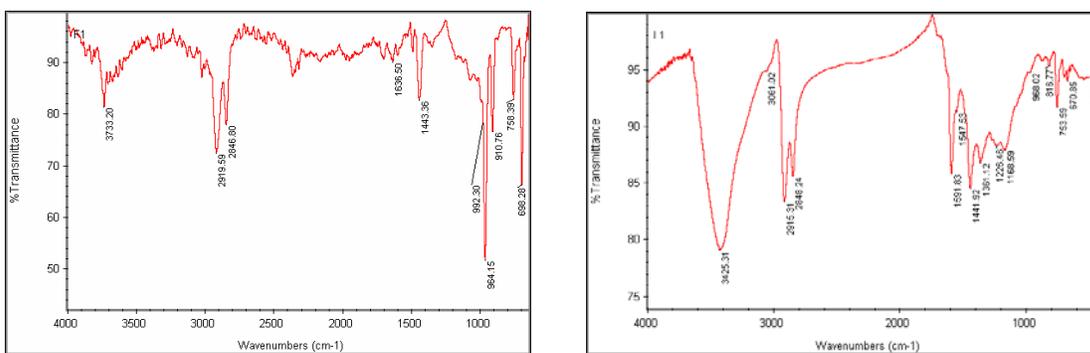


Figure 3: FTIR spectrum of pristine NR (left) and conducting powder prepared by iodine doping NR using reflux boiling (right)

The delocalized charges formed on the polymer chain upon doping are mobile and act as current carrying species for conduction. These charges hop from chain to chain, as well as move along the chain causing bulk conductivity to the material.

FTIR spectrum of pristine state is shown in Figure 4 and that of doped samples prepared without refluxing and with refluxing are shown in Figure 5 and 6 respectively. The isolated double bonds stretching vibration of  $-C=C-$  at  $1636.50\text{ cm}^{-1}$  is completely disappeared and new conjugated  $-C=C-$  stretching vibrations [10] are found to appear at  $1594.41\text{ cm}^{-1}$  and  $1591.83\text{ cm}^{-1}$  in figures 5 & 6 respectively. Intensity of bands seen at  $964.15\text{ cm}^{-1}$  and  $698.28\text{ cm}^{-1}$  due to [11] C-H out of plane bending vibrations of trans and cis components almost disappeared upon doping. But the band seen at  $758.39\text{ cm}^{-1}$  indicating [11] the presence of benzene ring remain unchanged upon doping. The band seen at  $2919.59\text{ cm}^{-1}$  and  $2846.80\text{ cm}^{-1}$  corresponding [11] to symmetric and asymmetric C-H stretching vibrations remains unshifted.

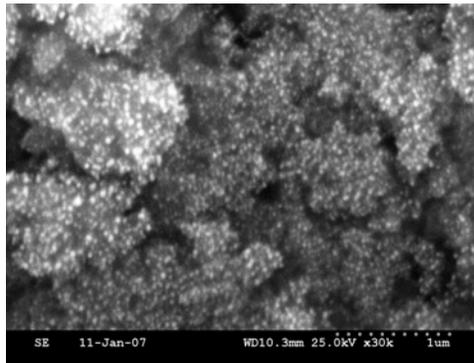


Figure 4: SEM image of the sensor materials prepared by iodine doping in NR. It consists of particles of irregular shape with an average size 250 nm distributed non uniformly

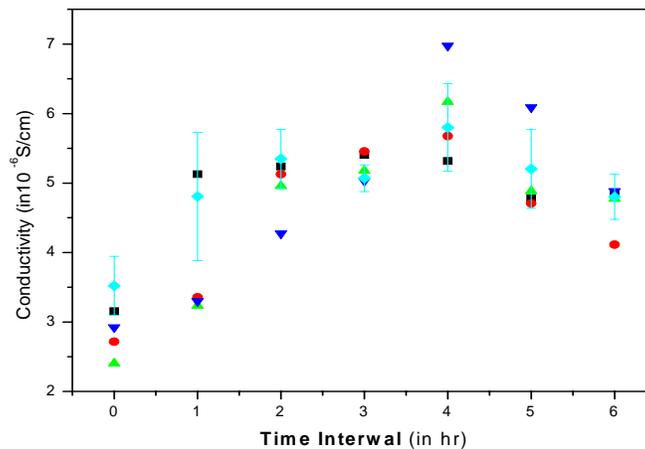


Figure5: Variation of conductivity with time.

A new bond formed at frequency  $465\text{ cm}^{-1}$  may be assigned [12] to C – I stretching vibration. One of the important points observed in spectra of powders prepared without refluxing and with refluxing is that all the bands observed are identical in nature. This indicates that the refluxing at elevated temperature for preferably short periods has not made any appreciable structural change or degradation in the rubber.

The observed variation in conductivity of the sensor set up at various intervals after exposing to the atmosphere is shown in the figure 5. It can be seen that conductivity increases with the moisture content, reaches a maximum and then falls. Due to rapid changes in the climatic conditions the error rating of the reproduced results are found to be litter bit higher. However the results follows a general pattern indicating the potential of the material to be used in humidity sensors. The advantage of the materials is that being an elastomer, it is easily processable and cost effective.

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