



## Development of Sensor using Surface Electronic Conduction of Natural Rubber†

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Development of gas sensors using non toxic natural materials has become a new trend of present day sensor research. In present paper application potential of natural rubber in gas sensing has been studied by exploiting the property of surface electronic conduction, worth of natural rubber as  $\text{NH}_3$  gas sensor and also its sensitivity to humidity and  $\text{CO}_2$ . Thus the typical gas sensing phenomenon in rubber surface claims importance in both theoretical and experimental research.

**Key Words:** Gas sensing, Natural polymer, Electronic conduction, Physisorption.

### INTRODUCTION

Natural rubber is used frequently in modern technological applications due to its various qualities like high degree of stereoregular structure, high gum tensile strength, strong building tack, green stock strength, high strength in non-black formulations, hot tear resistance, retention of strength at elevated temperatures, high resilience, low hysteresis (heat build-up), excellent dynamic properties and general fatigue resistance<sup>1</sup>. More than 200 species of rubber, *Hevea brasiliensis* only is of commercial importance. Apart from this a new profile of natural rubber as gas sensor can be projected exploring its typical response in surface mode towards environment threatening gas like ammonia. Potentiometric measurement shows an appreciable change in D.C. voltage for a shorter duration, on application of very small amount of  $\text{NH}_3$  to the rubber surface. Thus development of typical signal voltage on application of the said gas, can unfold the mode of surface electronic conduction as well as the chemical complexity of rubber surface. In this present work surface electronic conduction of natural rubber surface is measured from D.C. experiment and compared with result of A.C. experiment. The surface conductivity of natural rubber is very sensitive to some selective gases. The gas sensing aspect of the material is measured from potentiometric experiment and the same is verified by Fourier transform infrared spectroscopy (FTIR) study. In the following an account of the work undertaken in this present research is furnished.

### EXPERIMENTAL

Natural rubber is a natural polymer with high degree of stereo regularity in structure with repetitive arrangement of *cis*-1,4-polyisoprene<sup>2</sup>, in which presence of the reactive double bonds (unsaturation) added some surface conducting property to it. Protein molecules are also present in low percentages in it. Natural rubber latex in the form of strip is collected from Kottayam, India, is allowed to form experimental specimen using two narrow highly polished copper strips on its external surface at a distance about 3 mm. The total system is connected to a D.C. voltage source (6 Volt) and a resistor  $R_c$  (10 M $\Omega$ ) to form a simple proto sensor circuit shown below (Fig. 1). Variation of surface conductivity of the specimen with gas exposure will cause a change in current through  $R_c$  thereby potential difference (p.d) across it.

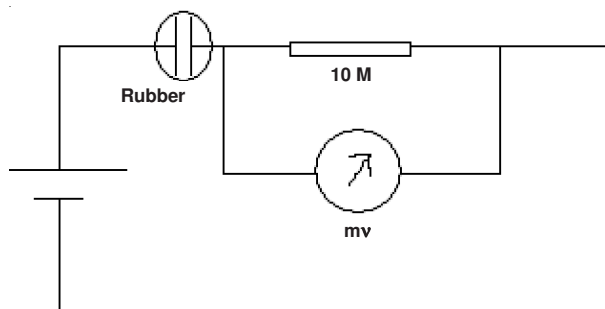


Fig. 1. Circuit for potentiometric measurement of gas sensing

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**General procedure:** The surface electrical conduction of natural rubber surface was measured by A.C. experiment. The said experiment was performed with Impedance spectroscopy [HIOKI model 3522-50 (Japan) LCR meter]. The gas sensing ( $\text{NH}_3$  gas) property of natural rubber surface exploits its surface electrical conductivity. The nature of surface conduction was found to be entirely electronic and hence it is possible to fabricate a gas sensor using complete D.C. set up. The simple circuit shows an abrupt change in uncompensated voltage across the resistor on projection of  $\text{NH}_3$  gas to the rubber surface. The initial reading of voltmeter is dependent on local parameters *i.e.* humidity, temperature, *etc.*

On exposure of humid air pulse to the rubber surface the potential across the resistor varies. The variation of surface current over the experimental specimen with applied potential difference was recorded. The observed variation in surface current shows its surface sensitivity towards humidity. All the experiments were performed at room temperature at a relative humidity level between 45-55 %.

**Detection method:** On exposure to  $\text{NH}_3$  gas, the surface conductivity of rubber specimen shows 100 % enhancement. In this present work the said enhancement was measured by direct electrical measurement using high sensitive digital millivoltmeter, which recorded a 100 % increment (from 3 millivolt it rises to 6 millivolt) for a very short duration of time and soon recovery to its initial reading. Even a small concentration variation of  $\text{NH}_3$  causes an appreciable voltage fluctuation. Moisture also causes increment of voltage, but with longer reaction and recovery time with a substantial voltage enhancement compared to that in case of  $\text{NH}_3$  gas.

Attenuated Total Reflectance spectrum in the IR region of rubber surface was studied using FTIR set up (Shimadzu IR Affinity 1 (Japan) in Zn Se window) between wave number 4000-700  $\text{cm}^{-1}$ . A marked change was observed near the wave number 3329  $\text{cm}^{-1}$  confirmed its sensing worth toward  $\text{NH}_3$  gas. The exposure of humid air pulse to the rubber surface shows about 15 % variation of surface current and indicates its surface sensitivity towards humidity. However dry carbon dioxide shows no such potentiometric change.

## RESULTS AND DISCUSSION

Table-1 shows a comparison between the qualities of sensing of the rubber towards different external gaseous stimuli. It is clear from the result that rubber surface shows sharp change in its surface electronic conductivity on application of humidity or ammonia to it. The response time for  $\text{NH}_3$  gas was recorded to be order of millisecond however a relatively larger response time (20-30 sec) was for humidity; the later reduces the worth of rubber surface to be a good sensor of humidity.

TABLE-1  
STUDY OF SENSING AND RESPONSE QUALITY OF RUBBER SURFACE TO DIFFERENT GASEOUS STIMULI

Name of parameters to be sensed	% Change in voltage on application of the sensing component	Response time (sec)	Remarks
Humidity	200-300 % increment	20-30	Moderately sensed
$\text{CO}_2$	No change	—	—
$\text{NH}_3$	100 % increment	$\sim 10^{-3}$	Highly sensed

The attenuated total reflectance spectra of rubber surface with and without ammonia has been shown in Fig. 2. Due to exposure of ammonia there is a sharp peak near 3329  $\text{cm}^{-1}$  confirms the gas addition to the surface. After 5 min from withdrawal of the gas exposure, the attenuated transmission reflection spectrum of the rubber surface returns back exactly to its initial pattern of fresh surface without any gas exposure. The mentioned nature thus confirms the phenomenon of physical adsorption of the gas.

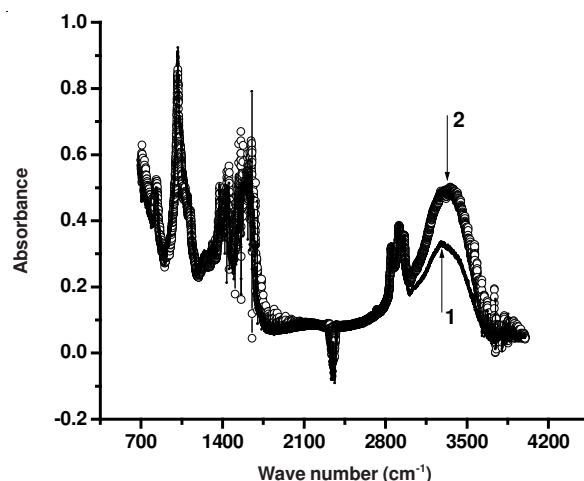


Fig. 2. Attenuated transmission reflection of rubber surface (1) without ammonia, (2) with ammonia

Fig. 3 shows on addition of humid blow to the surface, rubber shows 15 % variation of current in its V vs. I plot, which proves its surface sensitivity towards humidity. In the graph below plot 2 shows a raise in current compared to plot 1.

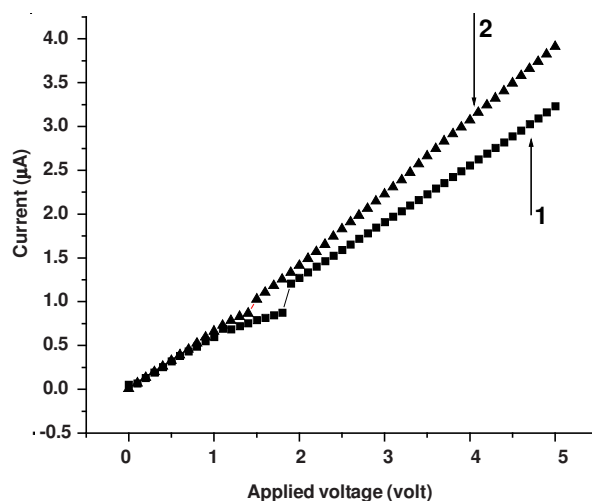


Fig. 3. Variation of current vs. I plot (1) without humidity; (2) with humidity

Fig. 4 shows variation of A.C. conductivity of the rubber surface with frequency. From the graph the electronic nature of conductivity of the natural rubber surface has been estimated. The results of impedance spectroscopy shows that the surface conduction of natural rubber is entirely electronic *i.e.* there exists no ionic part. The value of D.C. conductivity of the rubber surface has been calculated to be *ca.*  $10^{-14}$  S/m from the graph at zero frequency.

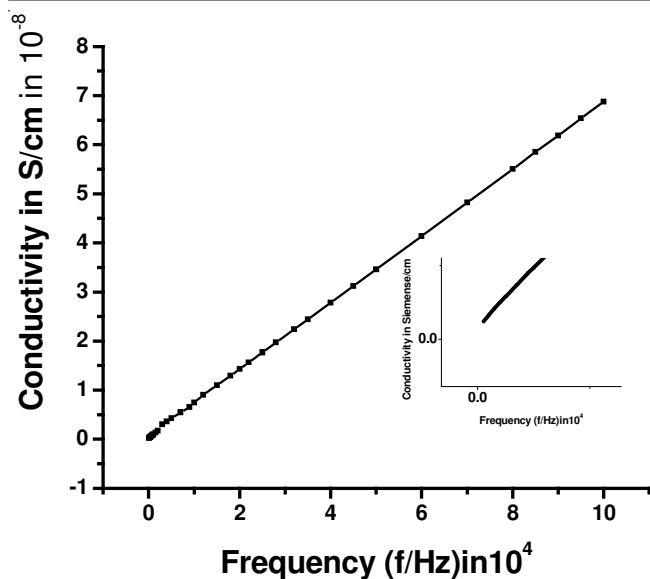


Fig. 4. A.C. surface conductivity plot (conductivity vs. frequency) (inset graph is a magnified layer near the origin of the main plot)

Surface phenomenon is quite different from bulk regarding structure, magnetic properties, *etc.* Here the interaction between gas and rubber surface leads to the phenomenon of an apparent physical adsorption *i.e.* physisorption<sup>3,4</sup>, in which weak van der Waal force comes into act in the form of self induced dipole interaction by adsorbate gas molecules. Eventually during the process  $\text{NH}_3$  gas turned into  $\text{NH}_4^+$  ion leaving electron in specimen surface for duration of response time and hence the

enhancement of surface conductivity took place. As the residence time of  $\text{NH}_3$  gas on the rubber surface is instantaneous and leaving the rubber surface almost chemically unaltered, therefore this interaction can be claimed to be a van der Waal interaction leaving the surface electrons under instantaneous weak perturbation.

### Conclusion

Thus natural rubber surface exhibits surface electronic conduction. The said conductivity is highly sensitive to the exposure of ammonia gas and humidity. The developed simple sensor of ammonia gas is found to be important for further development.

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