Spectroscopic Study of Iodine Doped Ethyl Cellulose

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Abstract

In the present study Infra-red and UV spectrum of pure and iodine doped (i.e. iodine percentage i.e.0.002, 0.02 and 0.04 are added in pure polymer solution of ethyl cellulose and benzene). The pure and different iodine doped samples were designated as P0, P1, P2 and P3 respectively). In IR spectrum, intensity of bands gradually decreases as iodine concentration increases in the polymer matrix. UV spectrum of ethyl cellulose: iodine matrix shows the formation of strong CTCs, also the formation of clath rates type of compounds and the opening closing of cage formed between EC:I2 matrices is reflected. Various band formation and shifting has been explained on the basis of present theories.

Keywords:

Ethyl Cellulose(EC);
Doping;
Infra-red (IR);
Ultra violet (UV);
Charge transfer complex (CTC).

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1. Introduction

The word spectroscopy is used as collective term for all the analytical techniques based on the interaction of light and matter. The spectroscopic methods are the most direct and most powerful means of obtaining information on the electronic structure of materials [1]. When energy in the form of electromagnet radiation (or photons) interacts with a material, the absorption and re-emission processes that occur depend largely on the electronic structure of the material [2]. The different types of spectroscopy depend chiefly on the energy range used and the nature of the interaction involved. Properties of a polymer are party dependent on their physical as well as chemical structure. Chemical structure of polymers may be modified by doping, copolymerization, substitution and blend formation etc. These processes affect the electrical behaviour to various extents.

The structure information and effect of structural modification in polymers can be investigated by using a number of techniques, i.e. X-ray diffraction electron microcopy (XRD), NMR, infrared

(IR) and Ultraviolet (UV) spectroscopy. In case of polymers these techniques are used to analyze the relation between microstructure and electrical properties.

Infrared (IR) studies of polymers are useful in studying structural modifications occurring during electret formations on doping with impurities. Tadokoro et. al., using polarized light, showed that the intensity of IR band increases with the increase in the orientation of dipoles [3]. IR studies have also been extended to estimate the crystallinity in polymers.

The infrared spectrum is plot of percentage or radiation transmitted by the sample (vertical axis) against liner wavelength or frequency (horizontal axis). The absorption band in the IR spectrum arises from the vibrations of pairs or small groups of atoms in the molecules. In many cases the vibration of these groups are independence of the nature of the rest of the molecule, hence absorption bands from these groups always occur at the same frequency. These are known as characteristic bands. In addition to the characteristic band there is usually a large number of weaker band in the molecule, it follows that the entire spectrum must be characteristic of the entire molecule.

Ultra violet (UV-vis) absorption spectra investigate the promotion of electrons from lower state to the higher energy state in UV and visible region. UV-vis absorption and transmission spectra are helpful to investigate the change in bandgap and reflective index of polymeric material.

Spectrophotometry is one of the branches of spectroscopy where we measure the absorption of light by molecules that are in a gas or vapour state or dissolved molecules/ions. Spectrophotometer investigates the absorption of the different substances between the wavelength limits 190 nm and 780 nm (visible spectroscopy is restricted to the wavelength range of electromagnetic radiation detectable by the human eye that is above 360 nm; ultraviolet spectroscopy is used for shorter wavelength). In this wavelength range the absorption of the electromagnetic radiation is caused by the excitation (i.e. transition to a higher energy level) of the bonding and non-bonding electrons of the ions or molecules. A graph of absorbance against wavelength gives the samples absorption spectrum. Modern spectrophotometers draw this automatically. The measured spectrum is continuous due to the fact that the different vibration and rotation states of the molecules make the absorption band wider [4].

A. Infra-red (IR)spectroscopy

In polymers the infrared absorption spectrum is often surprisingly simple, if one considers the large number of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and therefore appear in the spectrum as one of the vibration band and second from the strict selection rules that prevent many of the vibrations from causing absorptions.

Infrared (IR) absorption technique has been used extensively for qualitative as well as quantitative analysis particularly in the field of organic chemistry. The analytical aspect of IR absorption is of the great importance to determine the structural changes observed due to particular species.

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques by organic and inorganic chemists. It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample structural elucidation and compound identification.

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly 13,000 to 10 cm^{-4}. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies [5]. IR absorption positions are generally presented as either wavenumbers or wavelength. Wavenumber defines the number of waves per unit length. Thus wavenumbers are directly proportional to frequency as well as the energy of the IR unit length. The wavenumber are directly proportional to frequency as well as the energy of the IR absorption. The wavenumber unit (cm^{-1}, reciprocal centimetre) is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast wavelengths are inversely proportional to frequency and their associated energy.

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. It is of especial use in forensic analysis in both criminal and civil cases, enabling identification of polymer degradation for example. It is perhaps the most widely used method of applied spectroscopy.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Techniques have been developed to assess the quality of tea-leaves using infrared spectroscopy. This will mean that highly trained experts (also called noses) can be used more sparingly at a significant cost saving [6]. Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics [7] for example infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide gallium nitride, zinc selenide, amorphous silicon, silicon nitride etc.

B. Ultraviolet (UV)

The ultra violet (UV) technique provides information about the transmission characterization and other related parameters associated with the polymers materials. Further the type and concentration of impurity residual solvent, plasticizer, etc present in a polymer can often be determined if the spectrum of the host polymers is known and the foreign compound has absorption bands which are not masked by the spectrum of the host polymers.

Ultraviolet visible spectroscopy or ultraviolet visible spectrophotometer (UV-Vis or UV/Vis) involves the spectroscopy of photons in the UV- visible region. This means it uses light in the visible and adjacent (near ultraviolet (UV) and near infrared (NIR)) ranges. The absorption in the visible ranges directly affects the colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronics transitions. This technique is complementary to fluorescence spectroscopy in that fluorescence deals with transitions from the excited state to the ground state while absorption measures transitions from the ground state to the excited state [8].

The instrument used in ultraviolet visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through sample (I), and compares it to the intensity of light before it passed through the sample (Io). The ratio I/Io is called the transmittance and is usually expressed as percentage (%T). The absorbance A, is based on the transmittance:

$$A = -\log (\%T/100\%) \qquad\qquad ……(1)$$

An ultraviolet visible spectrum is essentially a graph of light absorbance versus wavelength in a range of ultraviolet or visible regions. Such a spectrum can often be produced directly by more sophisticated spectrophotometers or the data can be collected one wavelength at a time by simpler instruments. Wavelength is often represented by the symbol λ. Similarly for a given substance a standard graph of the extinction coefficient (e) v/s wavelength (λ) may be made or used if one is already available. Such a standard graph would be effectively concentration corrected" and thus independent of concentration.

The woodward Fieser rules are a set of empirical observations which can be used to predict λmax the wavelength of the most intense UV-Vis absorption for conjugated organic compounds such as dienes and ketones. The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecular. UV-Vis absorption is not however a specific test for any given compound. The natures of the solvent the pH of the solution temperature, high electrolyte concentrations and the presence of interfering substances can influence the absorption spectra of compounds as can variations in slit width (effective Bandwidth) in the spectrophotometer.

2. Research Method

Samples of pure and iodine doped ethyl cellulose (EC) has been prepared using solution cast technique in which Ethyl Cellulose was dissolved in chemically pure benzene. The different iodine percentage i.e.0.002, 0.02 and 0.04 are added in pure polymer solution for the preparation of doped samples. The pure and different iodine doped samples were designated as P0, P1, P2 and P3 respectively. The solution thus prepared was then poured onto an optically plane cleaned glass plate floating on mercury. The solvent was allowed to evaporate in an oven at 50 ºC for 24h to yield the desired samples. This was followed by room temperature out gassing at 10^{-5} torr for a further period of 12h to remove any residual solvent. The plate was then drawn slowly out of the solution, leaving a uniform film on the plate. Samples thus obtained were uniformly smooth and could be easily peeled from the glass surface. The preconditioned samples were sandwiched between aluminized electrodes over a central circular area of 36 mm diameter. The thickness of the sample was of the order of 40 μm. The samples were cut into desired size to fit into IR and UV apparatus.

The absorption spectra of different pure and iodine doped ethyl cellulose samples were recorded with the help of Perkin-Elmer UV-VIS spectrophotometer (Mobada-12) in the wavelength range from 200 to 600 nm. All the observations were carried out with the accuracy of ± 5% experimental error and results are reproducible.

The infra-red spectra of different samples of pure and iodine doped ethyl cellulose were recoded with the help of SIMADZU infra-red spectrometer. The scanning range is 4000 cm^{-1} to 400 cm^{-1}.

3. Results and Analysis

The IR spectrum, in transmittance mode, of pure ethyl cellulose (EC) and doped samples in the frequency range 4000-400 cm^{-1} are shown in Figures 1 – 4. The band centered at about at 3583 cm^{-1} owes to O–H stretching vibration and the band at around 2992 and 2719 cm^{-1} is assigned to C-H stretching vibration. The absorption bands for C=O can be seen at 1738 and 1632 cm^{-1}. The absorption at 1389 cm^{-1} corresponds to C–H bending. For –C–O–C– stretching vibration a band can be seen at 1165 cm^{-1}. Another band can be seen at 873 corresponding to C-O. The bands in the range 600-400 cm^{-1} are related to C-H bond.
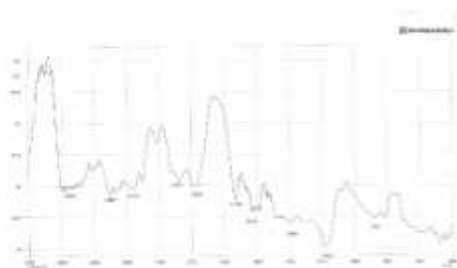
Figure 1 : IR Spectra for P_0 Sample

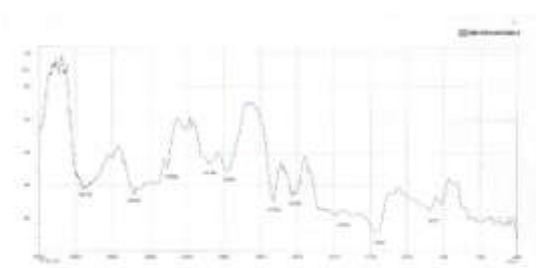**Figure 2 : IR Spectra for P_1 Sample**
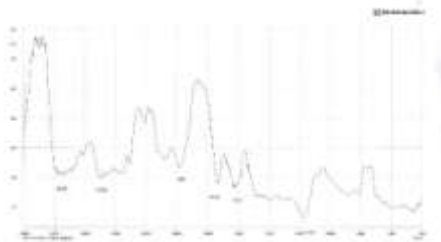

Figure 3 : IR Spectra for P_2 Sample
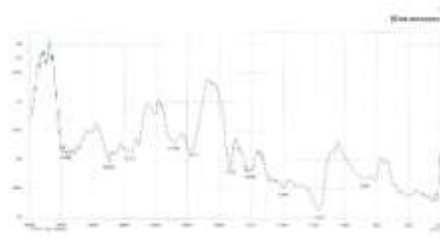

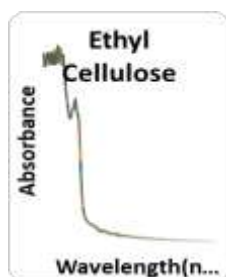**Figure 4 : IR Spectra for P_3 Sample**

Figure 5 : UV vis spectra for P_0 sample at room temperature.
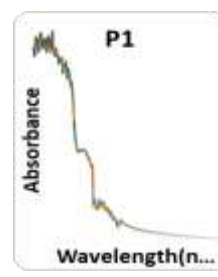

Figure 6 : UV vis spectra for P_1 samples at room temperature.
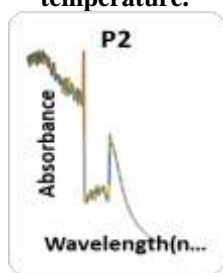

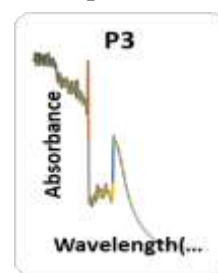**Figure 7 : UV vis spectra for P_2 samples at room temperature**

Figure 8 : UV vis spectra for P_3 samples at room temperature

The IR spectrum, of iodine doped ethyl cellulose (EC) samples (Figures 2-4) is characterized by the presence of important bands as observed for pure sample. Intensity of bands gradually decreases as iodine concentration increases in the polymer matrix. In addition to the important bands, spectrum also contains a large number of ill-defined/weak bands. The decrease of absorption intensity with increase in iodine concentration may be due to the conformational arrangement between iodine and ethyl cellulose matrix. The two lags in the chair-chair stature of ethyl cellulose having oxygen is mediating atom may be playing a vital role of forming clathrates 67 with iodine. At lower concentration the cage may be weak only at the surface absorption and

continuous showing weak interaction. The increasing dose of iodine concentration assists in realizing other carrier of traps or gives its own, thus contributing to the intensity of absorption. On further impregnation of iodine with EC the surface absorption may turn to bulk absorption phenomenon due to closing of the adjacent chair lags that gradually tightens the cage formed during CTCs formation. This may results in gradual decrease of intensity because of low release charges from traps.

The UV-visible absorption spectra of pure and doped ethyl cellulose are given in Figures 5 to 8. For pure ethyl cellulose a peak around 275 nm is observed and absorbance decreases continuously as wavelength increases. A close examination of UV spectra (Figure 6) of P1 sample exhibit decreases in peak intensity and appearance of peak around 400 nm is observed for P2 and P3 samples (Figures 7 and 8) with again increase in intensity. The UV spectrum of pure and doped ethyl cellulose shows the formation of strong CTCs also the formation of clathrates type of compounds and the opening closing of cage formed between EC:I_2 matrices is reflected . Distributed position of bands in the spectra indicates the formation of CTC. I_2 present in the EC:I_2 matrices as a neutral molecule may form clath rates and develop conformational changes which enhance the conductivity on supplying any type of treatment (electrical, thermal or both).

4. Conclusion

The electrical resistivity of molecular complexes have been found relatively lower compound with those of pure organic semiconductors this lowering   suggest that the charge transfer interaction between the donor and the accepter molecules is responsible in some way for the electrical conduction through the crystal of molecular complex. In all cases, the incorporation of the iodine into the polymer system induces spectroscopic changes with respect to the theoretical spectrum, obtained from the weighted addition of the component spectra, according to their concentration in the system.

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