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# Qualitative Analysis of High Density Polyethylene Using FTIR Spectroscopy

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FTIR spectroscopic technique is projected in the present work to make complete qualitative analysis on high density polyethylene (HDPE) and commercial HDPE polymers. Infrared spectra have been used for the molecular structure study of the repeating unit of polyethylene. The qualitative analysis of the commercial HDPE samples has been made by evaluating the internal standards with the standard source sample as the reference. The internal standards are ratios indicative of the quality of the sample. The internal standards are computed for certain specific modes of vibration and are compared to identify the quality and purity of the samples. Thus, FTIR spectral measurements have been made to differentiate the commercial HDPE samples with the source HDPE. The growth of polyethylene products has acquired enormous heights owing to its application as insulating material. The dielectric constants have been determined for all polymer samples in the GHz range using the microwave benches. The magnitude of dielectric constants for all samples observed in X band is of the same trend as that in K band, *i.e.* a decrease in dielectric constant with increase in microwave frequency has been observed. Materials with lower dielectric constant would be preferred for insulation application due to their high dielectric strength.

**Key Words: High density polyethylene, Frequency assignment, Qualitative analysis, Internal standards, Dielectric constant.**

## INTRODUCTION

Today, the polymer industry has grown to be larger than the aluminum, copper and steel industries combined. Polymers already have a range of applications that far exceeds that of any other class of material available to man[1,2]. Current applications extend from adhesives, coatings, foams and packaging materials to textile and industrial fibers, composites, electronic devices, biomedical devices, optical devices and precursors for many newly developed high-tech ceramics. Development of microprocessor and silicon chips has meant that the components are becoming smaller and lighter paving way for usage of plastics. Today there are primarily 6 commodity polymers in use, namely polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene and polycarbonate. These make up nearly 98 % of all polymers and plastics encountered in daily life[3].

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The ability of polyethylene to act as an excellent insulator at high frequencies was of great significance in the early development of radar. Polyethylene is a thermoplastic commodity mostly used in consumer products. Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene. The basic structure of the homopolymer polyethylene is the chain $-(CH_2-CH_2)_n-$. In commercial polyethylene, 'n' may vary from 400 to more than 50,000. It is the variation of 'n' and the addition of copolymer substitutes that allow for the variation of melt index, density and numerous physical properties[4]. Polyethylene is classified into several different categories based mostly on its density and branching. High density polyethylene (HPDE) has a low degree of branching and thus stronger intermolecular forces and tensile strength. Presently, HDPE and commercial HDPE have been analyzed using FTIR and dielectric measurements.

Extensive research work has been carried out in the recent past on these widely used polyethylenes for a quantitative and qualitative analysis using different experimental techniques. The quantitative analysis of binary polyethylene blends by FTIR spectroscopy has been achieved based on the ratio of two absorbance peaks in an FT-IR spectrum by Cran *et al.*[5]. Miller[6] reported the blend ratio of HDPE and LDPE in extruded films using NIR spectroscopy. Fatahi *et al.*[7] studied the structural parameters and property correlation of polyethylene blown films. Zeid *et al.*[8] studied the structure-property behaviour of LDPE and HDPE films exposed to different types of radiation and the structural changes of unirradiated and irradiated polyethylene films were characterized by FTIR, FT-Raman and UV spectrometric techniques. The present work deals with the quality analysis of the selected high density polyethylenes by FTIR.

Plastics are generally considered insulators, but they can transmit some electrical energy at higher frequencies. The effectiveness of a material as an insulator is usually measured by quantities like dielectric constant and dissipation factor. Relatively little data currently exists for plastics' dielectric behaviour at frequencies above 1 GHz. With speed at a premium, computers and other electronic devices are moving to higher frequencies. Many systems now operate in the 1 to 10 GHz range, while new applications will run at frequencies as high as 20 GHz. Hence, it becomes necessary for the designers to understand the performance of materials of construction in such devices at these frequencies[9]. Many variables affect a plastic's dielectric constant, including the frequency used, the filler and additives it contains, part thickness and environmental conditions such as moisture. Dielectric constant is a parameter that indicates how well an insulator stores electrical energy so as to isolate electrical elements from each other and the ground. This quantity is important in designing connectors, electronic circuits, microwave devices, RF transmission lines, antennae and waveguides. For the present study the dielectric constants were evaluated for source and commercial HDPE polymers at high frequencies such as 9 and 26 GHz by utilizing the microwave test bench systems.

## EXPERIMENTAL

Spectroscopically pure sample of high density polyethylene (HDPE) has been procured from Central Institute of Plastic Engineering and Technology (CIPET), Chennai, India. Two commercial samples, HDPE(A) and HDPE(B), have been collected from a reliable industry for analyzing their quality and insulation characteristics with the source HDPE. The Fourier transform infrared spectra have been recorded in the range 4000-400 cm$^{-1}$ using Bruker IFS 66V spectrophotometer at Indian Institute of Technology, SAIF, Chennai, India. The FTIR spectra of source HDPE and two commercial HDPE are presented in Figs. 2-4. As different plastics have distinguishable light absorption spectra, the most direct means of identification of polymers is accomplished by FTIR spectroscopic technique[10,11].

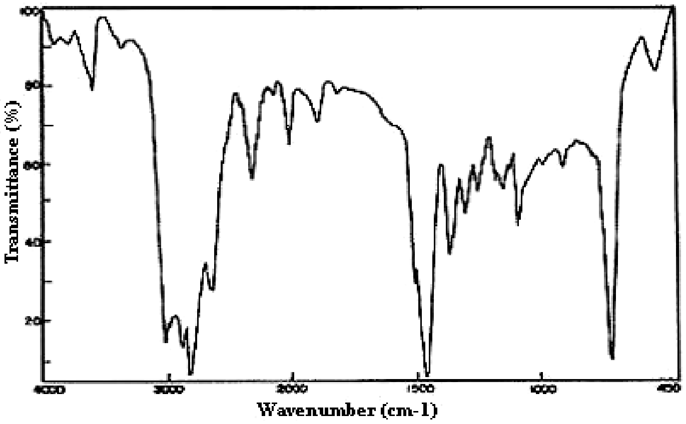

Fig. 2. FTIR spectrum of HDPE

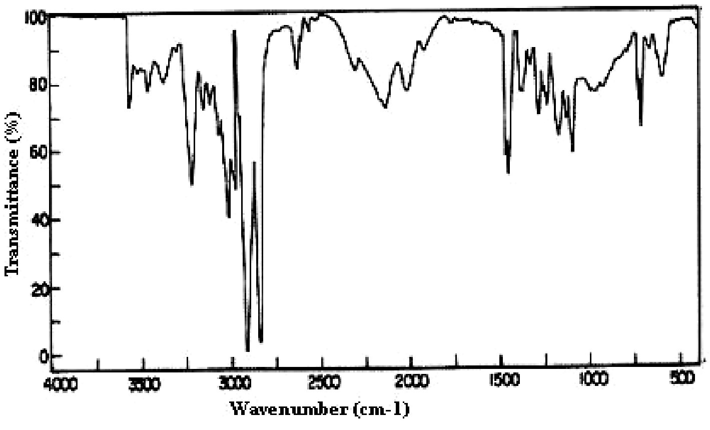

Fig. 3. FTIR spectrum of HDPE (A)

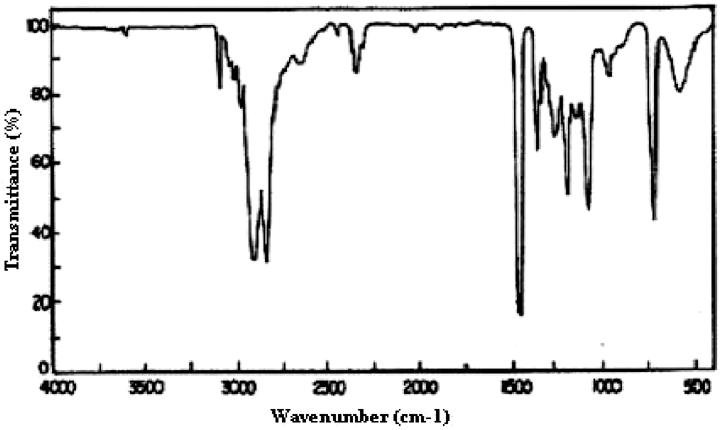

Fig. 3. FTIR spectrum of HDPE (B)

The resonant cavity and waveguide method have been employed here to determine dielectric constant (or dielectric permittivity) of the polymeric materials using the X-band and K-band microwave test benches. A direct and accurate method of Robert and Von-Hippel has been considered here[12]. A microwave test bench system with an X-band in the frequency range 8.4-12.2 GHz and a K-band in the frequency range 18.0-26.5 GHz were employed for the measurements. The samples are shaped to suit the dimensions of the rectangular waveguide *i.e.* 2.2 × 1 cm for X-band and 1.1 × 0.4 cm for K-band. In order to minimize the error due to the presence of air gap between the dielectric sample and the inner walls of the rectangular waveguide, for a given frequency, the measurements are repeated for all the four faces of the sample. The samples of identical thickness have been chosen for proper comparison of the results. The standing wave measurements are made on both the microwave test benches with and without sample materials. The position of the first minima from load end is noted. On placing a sample of thickness 't' in the waveguide, standing wave pattern is produced during the microwave propagation. For different positions of the probe, the output voltages have been measured using a multimeter in X-band microwave test bench. In K-band microwave bench, the probe senses the field strength of the standing wave pattern can be viewed in a CRO. From the values of the shift in minima of the standing wave, with and without sample, the dielectric constant is calculated using the relation, $\varepsilon_r = [(\lambda_o/\lambda_{g'})^2 + (\lambda_o/\lambda_c)^2]$ where, $\lambda_o$ is the wavelength of microwaves in free space, $\lambda_c$ is the cut of wavelength, $\lambda_{g'}$ is the wavelength of dielectric filled space.

## RESULTS AND DISCUSSION

FTIR spectrum is based on the absorption of infrared radiation at frequencies that match those of the normal modes of vibration within the macromolecule. These absorption features are characteristic of the molecular configuration, sequencing and conformation and state of order. The intensity of an absorption band is related to the dipole moment change associated with the molecular vibration. Infrared spectroscopy is highly specific and the frequencies of all the sharp bands are accurate to ± 1 $cm^{-1}$.

Using FTIR, the molecular structure of the repeating unit $-(CH_2-CH_2)_n-$ of HDPE has been studied. The frequency assignments have been made on all the fundamental modes of vibration. The complete vibrational band assignment made available for source and commercial HDPE confirms their chemical structure. The observed frequencies of the polymers and probable assignments are presented in Table-1.

TABLE-1
VIBRATIONAL SPECTRAL ASSIGNMENT OF SOURCE AND COMMERCIAL HDPE

| Frequency ($cm^{-1}$) | | | Vibrational band assignment |
|---|---|---|---|
| Source HDPE | Commercial HDPE (A) | Commercial HDPE (B) | |
| 3022 | 3019 | 3024 | Asymmetric C-H stretching |
| 2980 | 2975 | 2975 | Symmetric C-H stretching |
| 2891 | 2918 | 2912 | Asymmetric $CH_2$ stretching |
| 2825 | 2849 | 2847 | Symmetric $CH_2$ stretching |
| 1511 | 1471 | 1472 | Asymmetric $CH_2$ bending |
| 1462 | 1462 | 1463 | $CH_2$ scissoring |
| 1367 | 1376 | 1367 | $CH_2$ wagging |
| 1257 | 1234 | 1268 | Asymmetric CCH bending |
| 1158 | 1177 | 1175 | Symmetric CCH bending |
| 1132 | 1131 | 1149 | $CH_2$ twisting |
| 1095 | 1093 | 1085 | C-C stretching |
| 719 | 729 | 719 | $CH_2$ rocking |
| 550 | 590 | 584 | C-C bending |

The strong asymmetrical ($\nu_{as}$ $CH_2$) and symmetrical ($\nu_s$ $CH_2$) stretching vibrations of methylene group present in all polymeric samples are observed *ca.* 2915 and 2840 $cm^{-1}$, respectively[13]. The spectra of all polymeric materials show two strong bands occurring at around 3020 and 2975 $cm^{-1}$, respectively due to asymmetrical ($\nu_{as}$ C-H) and symmetrical ($\nu_s$ C-H) stretching vibrations of the methylene group[13]. Medium to weak intensity bands occurring at around 1090 and 580 $cm^{-1}$ in the FTIR spectra of polyethylenes are attributed to C-C stretching vibrations and C-C bending vibrations, respectively[14]. The band observed *ca.* 1470 $cm^{-1}$ is due to the asymmetric deformation vibrations of the methylene group.

The sharp band occurring at around 720 $cm^{-1}$ is due to $CH_2$ rocking vibrations. Due to the crystallinity of polyethylene, the 720 $cm^{-1}$ peak is split and additional peak is seen at around 730 $cm^{-1}$ in all polymers[15]. The band occurring around 1462 $cm^{-1}$ is due to $CH_2$ scissoring vibrations of all polyethylenes[13]. This band is very strong in the FTIR spectrum of HDPE and the same band is found to have strong and medium intensities in the FTIR spectra of commercial HDPE (A) and HDPE (B), respectively.

It is observed that the band at around 1250 cm$^{-1}$ is due to the asymmetric CCH bending vibration and the band at around 1160 cm$^{-1}$ is a consequence of symmetric deformation of the CCH group[13]. The bands occurring around 1367 and 1135 cm$^{-1}$ are due to $CH_2$ wagging and $CH_2$ twisting vibrations, respectively[15].

The internal standards for certain specific modes of vibration of source and commercial HDPE plastics are given in Table-2. The sets of internal standards of commercial HDPE plastics are compared with source HDPE in order to differentiate the quality of commercial samples. Since HDPE is used for packaging and storage purposes, it becomes absolutely necessary for the manufacturers to check its purity at the industries. The internal standard is one such technique to find the purity or quality of the commercial polyethylenes. The commercial HDPE (A and B) samples

TABLE-2
INTERNAL STANDARD AT DIFFERENT FREQUENCY (cm$^{-1}$) FOR HDPE PLASTICS

3022

| Sample | 2980 | 2891 | 2825 | 1511 | 1462 | 1367 | 1257 | 1158 | 1095 |
|---|---|---|---|---|---|---|---|---|---|
| | 3022 | 3022 | 3022 | 3022 | 3022 | 3022 | 3022 | 3022 | 3022 |
| HDPE | 0.8566 | 1.0333 | 1.4551 | 0.6276 | 1.5301 | 0.5056 | 0.3264 | 0.3168 | 0.4104 |
| HDPE(A) | 0.8147 | 5.7988 | 3.8356 | 0.6113 | 0.7197 | 0.2860 | 0.3369 | 0.4679 | 0.5811 |
| HDPE(B) | 1.4993 | 6.5363 | 6.5363 | 8.0924 | 8.4306 | 2.7054 | 2.2285 | 1.9075 | 4.4914 |

2825

| Sample | 3022 | 2980 | 2891 | 1511 | 1462 | 1367 | 1257 | 1158 | 1095 |
|---|---|---|---|---|---|---|---|---|---|
| | 2825 | 2825 | 2825 | 2825 | 2825 | 2825 | 2825 | 2825 | 2825 |
| HDPE | 0.6872 | 0.5886 | 0.7101 | 0.4313 | 1.0515 | 0.3475 | 0.2243 | 0.2177 | 0.2820 |
| HDPE(A) | 0.2607 | 0.2124 | 1.5118 | 0.1593 | 0.1876 | 0.0745 | 0.0878 | 0.1220 | 0.1515 |
| HDPE(B) | 0.1529 | 0.2293 | 1.0000 | 1.2380 | 1.2898 | 0.4139 | 0.3409 | 0.2918 | 0.6871 |

1462

| Sample | 3022 | 2980 | 2891 | 2825 | 1511 | 1367 | 1257 | 1158 | 1095 |
|---|---|---|---|---|---|---|---|---|---|
| | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 |
| HDPE | 0.6535 | 0.5598 | 0.6753 | 0.9509 | 0.4101 | 0.3304 | 0.2133 | 0.2070 | 0.2682 |
| HDPE(A) | 1.3893 | 1.1320 | 8.0567 | 5.3291 | 0.8494 | 0.3974 | 0.4681 | 0.6502 | 0.8074 |
| HDPE(B) | 0.1186 | 0.1778 | 0.7753 | 0.7753 | 0.9598 | 0.3209 | 0.2643 | 0.2262 | 0.5327 |

1257

| Sample | 3022 | 2980 | 2891 | 2825 | 1511 | 1462 | 1367 | 1158 | 1095 |
|---|---|---|---|---|---|---|---|---|---|
| | 1257 | 1257 | 1257 | 1257 | 1257 | 1257 | 1257 | 1257 | 1257 |
| HDPE | 3.0634 | 2.6242 | 3.1657 | 4.4577 | 1.9227 | 4.6877 | 1.5491 | 0.9706 | 1.2575 |
| HDPE(A) | 2.9678 | 2.4181 | 17.210 | 11.383 | 1.8145 | 2.1361 | 0.8489 | 1.3889 | 1.7247 |
| HDPE(B) | 0.4487 | 0.6727 | 2.9330 | 2.9330 | 3.6312 | 3.7830 | 1.2139 | 0.8559 | 2.0154 |

1095

| Sample | 3022 | 2980 | 2891 | 2825 | 1511 | 1462 | 1367 | 1257 | 1158 |
|---|---|---|---|---|---|---|---|---|---|
| | 1095 | 1095 | 1095 | 1095 | 1095 | 1095 | 1095 | 1095 | 1095 |
| HDPE | 2.4361 | 2.0868 | 2.5174 | 3.5448 | 1.5289 | 3.7277 | 1.2319 | 0.7952 | 0.7718 |
| HDPE(A) | 1.7207 | 1.4019 | 9.9783 | 6.6001 | 1.0520 | 1.2385 | 0.4921 | 0.5797 | 0.8052 |
| HDPE(B) | 0.2226 | 0.3338 | 1.4552 | 1.4552 | 1.8017 | 1.8770 | 0.6023 | 0.4961 | 0.4247 |

can be considered to be of good quality when a good number of their internal standard ratios coincide with the pure sample of source HDPE. Table-2 is self-explanatory and it is clearly evident that the quality of the two commercial HDPE polymers is not similar to that of the source polymer. The internal standards evaluated for HDPE (A) and HDPE (B) does not coincide with the source HDPE. Only few IRP ratios of commercial samples are found to match with the IRP ratios of source HDPE.

Dielectric constant ($\varepsilon_r$) in plastics is directly related to the polarizability of the polymer. Good dielectrics tend to have a low dissipation factor. That is, they do not let the charge they hold dissipate easily and they lose little energy as heat as the electric field reverses rapidly at high frequencies. Dissipation factor represents the inefficiency of dielectric materials. Dielectric constant is a central design variable in tuning an electronic structure to a desired impedance. The dielectric constants were evaluated for the polymeric materials *viz.*, HDPE and commercial HDPE using the X-band and K-band microwave test bench systems. The dielectric constants were determined in the microwave frequency region such as 9.6 and 26 GHz respectively and the values are given in Table-3.

TABLE-3
DIELECTRIC MEASUREMENTS FOR POLYMERIC MATERIALS IN X-BAND AND K-BAND

| Sample | Dielectric constant in X-band (9.6 GHz) | Dielectric constant in K-band (26 GHz) |
|---|---|---|
| HDPE | 5.035 | 2.406 |
| HDPE(A) | 5.422 | 2.538 |
| HDPE(B) | 6.136 | 2.795 |

It is observed from Table-3 that as the microwave frequency decreases, the dielectric constant increases as reported by Weldon[16]. Among the commercial HDPE polymers, HDPE(A) has lower dielectric constant than HDPE(B) in both X and K band frequencies. This implies that HDPE(A) has better insulation properties in comparison with HDPE(B) and it will find extensive application as dielectric materials.

In fact, there is not much difference in the magnitude of the measured values of dielectric constants of all polymers. This shows that polyethylene is most suited as insulating material in high frequency applications on account of its low dielectric constant and high dielectric strength[17]. The dielectric studies on polyethylenes directly relate the property of dielectric constant to the chemical structure of the polymer[18]. The increase in dielectric constant of HDPE(B) may be due to the increase in the dipole moment which causes an increase in the absorbance of infrared light in the FTIR spectra[19]. Das-Gupta[20] reported that the behaviour of dielectric relaxation and electrical properties with AC and DC fields needs to be correlated with the viscoelastic molecular motions of the polymer chains.

## Conclusion

Spectroscopic investigation on polyethylenes has been made through FTIR spectroscopy and the results have been discussed. A complete vibration band assignment has been made available for HDPE and commercial HDPE plastics which confirm their chemical structure. Internal standard calculations from the IR spectral measurements have been used to differentiate the commercial HDPE from the source. This analysis leads to the fact that internal standard calculations are able to assess the quality of the commercial samples on comparison with the standard source. The study clearly shows that the quality of the two commercial HDPE polymers is inferior to source HDPE polymer. The decline in quality may be due to the additives which are essential to increase the mechanical strength and electrical property of the polyethylenes. Since HDPE is extensively used for storage of water, foodstuff and pharmaceutical compounds and the contents have to be necessarily stored for long periods of time *i.e.* from time of manufacture to the time it reaches the consumer, its quality/purity is a very important factor that has to be checked before using it for storage purposes. The microwave measurements give the dielectric constant of all polymeric materials in the low and high frequency GHz ranges. The sample with low level of permittivity is most suited for insulation applications in high frequency ranges. The dielectric constants of commercial HDPE polymers are found to be slightly higher than source HDPE polymer.

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