Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1447–1454

Spectroscopic Studies of Quality of Commercial Polyethylene Terephthalate Storage Containers

S. GUNASEKARAN† and HEMAMALINI R.*
Department of Physics, Queen Mary's College, Chennai-600 004, India
E-mail: raj_hema03@rediffmail.com

FTIR spectral measurements have been made to differentiate the commercial polyethylene terephthalate (PET) containers with the source polyethylene terephthalate (PET). 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. The purity of the commercial PET containers has been confirmed by UV-Visible spectroscopy. Further, microwave measurements have been made on all the commercial and source samples to study their dielectric behaviour in K and X bands using microwave bench equipped with Gunn and Klystron oscillators respectively and guided with rectangular waveguide. A suitable correlation between dielectric constant and their infrared spectra has been achieved.

Key Words: Polyethyene terephthalate, FTIR,Dielectric constant, Internal standard, UV-Visible spectroscopy.

INTRODUCTION

Polyethylene terephthalate (PET), a versatile polymer, has got many interesting properties. PET has excellent thermal stability due to which it is used as a coating material for microwave and conventional ovens[1]. In the late 1970s the benefits of biaxial stretching PET were extended from film to bottle manufacture, producing carbonated beverage storage containers. PET bottles by blow moulding have gained prominence, because PET has low permeability to carbon dioxide[2, 3]. The demand for PET bottles for storage of mineral water and for other purposes such as storage of fruit juice concentrates and sauces has shot up in the market for plastics. The containers, being airtight, are used for storage of all kinds of powders, wide-necked jars for coffee and other materials. PET containers are lighter, unbreakable and are easily portable. PET as storage containers has created a revolution and has become indispensable for humanity[4]. Its large scale production has also created concerns for reuse of PET. The recycling of PET bottles is more important due to the high volume of scrap. This is done by recycling PET bottles in the production of injection mouldable, extrudable and thermoformable PET resins[5] that could be used for structural parts of vehicles,

†Department of Physics, Pachaiyappa's College, Chennai-600 030, India.

car textiles, food contact containers, bottles and raw materials for polyurethane. Depolymerisation of PET under pressure has also been investigated[6]. A new process for complete PET recycling has been developed to depolymerize dirty curbside PET for re-polymerizarion into high grade PET. Most of the recycled PET bottles go into low end products, such as fibrefill for pillows and outwear, polyester foams and strappings. Keeping in mind the enormous applications of PET as storage container, its quality being a major factor for storage, has prompted us to take a deep insight into the quality of commercial PET containers.

EXPERIMENTAL

Samples of PET containers have been procured from different commercial sources all over the globe. The structure of the repeat unit OCH_2CH_2O of this polymer is presented in Fig. 1. The Fourier transform infrared spectra have been measured in the range 4000–400 cm^{-1} using Perkin-Elmer spectrophotometer at Medopharm, Chennai, India. The FTIR spectra of the samples of commercial PET containers are presented in Figs. 2 and 3.

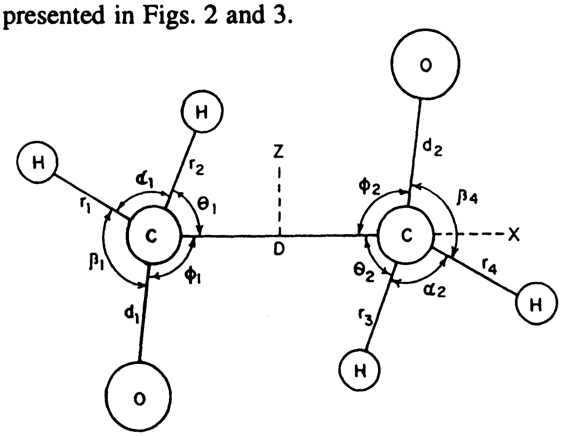

Fig. 1. Structure of repeat unit of polyethylene terephthalate

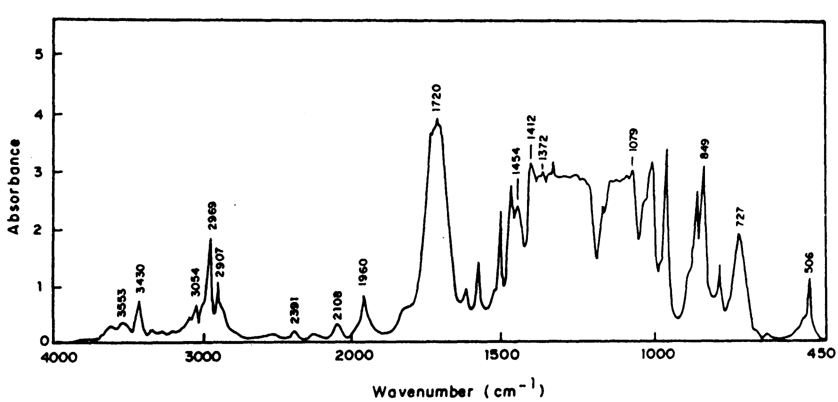

Fig. 2. FTIR spectrum of source PET sheet

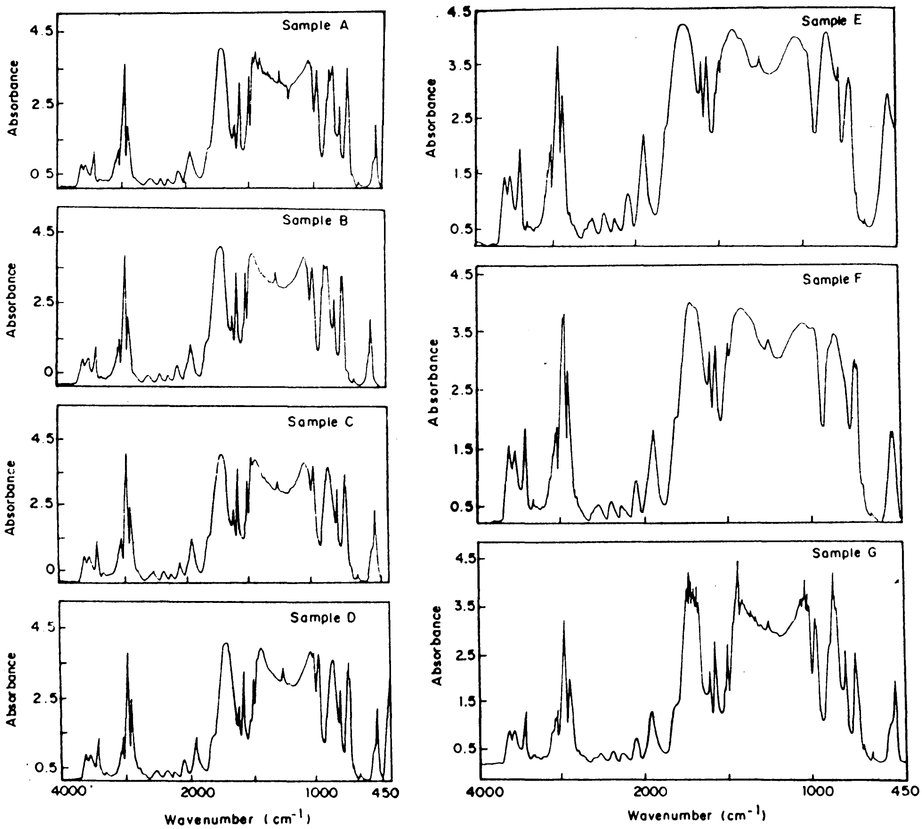

Fig. 3. FTIR spectra of commercial PET containers (Samples A–G)

Vibrational band assignment

The vibrational band assignments of PET storage containers have been made. The frequencies of the source PET and commercial container test samples with their relative intensities and probable assignments are summarized in Table-1.

Internal standards of storage containers

Internal standards are ratios used as standards for identity/quality of the samples used. Internal standards of specific modes of vibration are arrived at by finding the internal ratio of absorbance of various bands[7]. The sets of internal standards of commercial PET containers are compared with source PET to differentiate the quality of commercial sample. Table-2 shows internal standards for certain specific modes of vibration of PET containers. The scatter plot for the internal standard of commercial PET containers is given in Fig. 4. The figure is self-explanatory and it is clearly evident that sample F has quality similar to that of the source PET.

An important reason for the transmission of infectious diseases in developing countries is the lack of adequate and safe water. Purchase of mineral water for consumption is more a reality than an exception in urban areas of developing

TABLE-1
FTIR VIBRATIONAL BANDS (cm^{-1}) ASSIGNMENTS OF SOURCE AND COMMERCIAL PET CONTAINERS*

Sample	δ_s(OCH)	δ_{asy} (OCH)	ν(C—C)	δ_{asy} (CCH)	$\rho_w(CH_2)$	$\delta(CH_2)$	ν_{asy} (CH_2)	ν(C—H)
Source	730 (3.250)	834 (3.500)	1038 (3.556)	1119 (3.500)	1262 (3.167)	1434 (3.667)	2975 (3.889)	3053 (3.083)
A	732 (3.250)	848 (3.538)	1041 (3.692)	1112 (3.009)	1264 (3.231)	1444 (3.692)	2969 (3.500)	3054 (1.154)
B	737 (3.423)	853 (3.431)	1044 (3.731)	1111 (3.308)	1265 (3.322)	1462 (3.731)	2966 (3.712)	3054 (1.308)
C	730 (3.385)	863 (3.692)	1045 (3.769)	1110 (2.923)	1264 (3.308)	1442 (3.386)	2966 (4.115)	3054 (1.481)
D	737 (3.538)	864 (3.577)	1042 (3.923)	1120 (2.962)	1262 (3.385)	1444 (3.885)	2972 (3.808)	3054 (1.346)
E	732 (3.333)	866 (4.133)	1041 (4.033)	1115 (3.466)	1264 (3.733)	1426 (4.117)	2968 (3.900)	3054 (2.067)
F	732 (3.187)	869 (3.578)	1050 (3.75)	1100 (3.578)	1262 (3.469)	1423 (3.969)	2978 (3.797)	3054 (2.938)
G	736 (2.365)	872 (3.998)	1045 (4.015)	1113 (2.923)	1265 (3.154)	1444 (4.308)	2975 (3.231)	3054 (1.231)

*Values in parentheses correspond to absorbance

TABLE-2
INTERNAL STANDARD AT 730 cm^{-1} FOR PET CONTAINERS

Sample	$\frac{3053}{730}$	$\frac{2975}{730}$	$\frac{1434}{730}$	$\frac{1119}{730}$	$\frac{1038}{730}$	$\frac{834}{730}$
Source	**0.948**	**1.196**	**1.128**	**1.077**	**1.094**	**1.078**
A	0.512	1.552	1.641	1.337	1.608	1.572
B	0.382	1.084	1.090	0.966	1.090	1.002
C	0.437	1.215	1.003	0.863	1.113	1.090
D	0.380	1.076	1.098	0.837	1.108	1.011
E	0.620	1.170	1.285	1.039	1.210	1.240
F	**0.921**	**1.191**	**1.245**	**1.122**	**1.076**	**1.122**
G	0.520	1.366	1.821	1.235	1.697	1.690

countries. The mineral water produced by different sources like the solar water disinfection plants[8] and other water treatment plants have to be necessarily stored for long periods of time, from time of manufacture to the time it reaches the consumer. Hence for storage, the most sought after plastics being PET, its purity

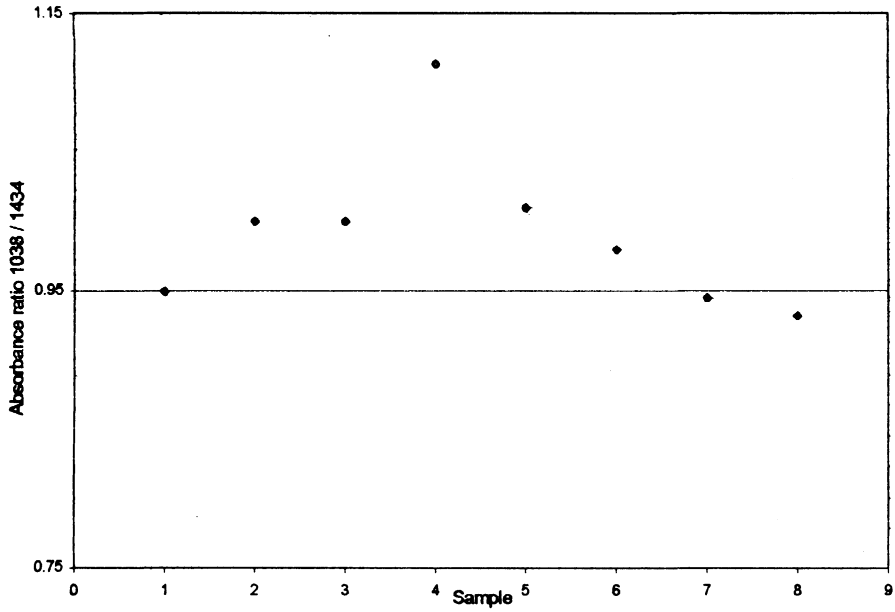

Fig. 4. Scatter plot of internal standard of source and commercial PET containers (1. Source, 2. A, 3. B, 4. C, 5. D, 6. E, 7. F, 8. G)

has to necessarily be checked at the industries. The internal standard is one such technique to find purity of the commercial containers. The internal standards evaluated show that the sample F is of good quality, as a good number of its internal standard ratios coincide with the pure sample of source PET. As far as purity/quality is concerned this sample is followed by other commercial PET container samples. Polymer degradation from prolonged UV exposure, particularly in the presence of heat, moisture, oxygen or atmospheric pollutants, can result in embrittlement, chalking, surface crazing, discoloration and loss of physical properties such as strength and impact. Stabilization can be achieved by adding UV screening agents. The decline in quality of some of the commercial samples may be due to the additives like UV screening agents as the interaction of this with the contents could cause harmful diseases as PET is largely used for storage of water and other soft drinks[8].

Quality confirmation by UV-Visible spectra

Most polymers are affected on exposure to light, particularly sunlight. However, the polyethylene especially PET and PVC are expected to have good light stability and high UV resistance, because the linkages present do not absorb light at the damaging wavelengths present on the earth's surface. It is of interest to note that most polymers of monosubstituted ethylene crosslink, whereas most polymers of disubstituted ethylene degrade[9, 10].

PET containers have been cut into small strips of about 0.6 cm × 3 cm and pasted on an optically plane glass plate and placed in the sample compartment and a similar optically plane glass plate has been used as the reference. The

UV-Visible absorbance spectra have been recorded in the range 290–350 nm in the Elico SL 159 UV-Vis spectrophotometer in the Spectrophysics Research Lab at Pachaiyappa's College, Chennai, India. The comparative UV-Visible spectra of all the samples are presented in Fig. 5. All the samples show absorbance peak[8, 11] around 315 nm. The absorbance values are presented in Table-3. Sample F has absorbance close to that of the source PET and sample G shows maximum absorbance. This result establishes that no UV screening agents or additives[10] are present in sample F and it is most suited for storage purposes than other commercial PET containers.

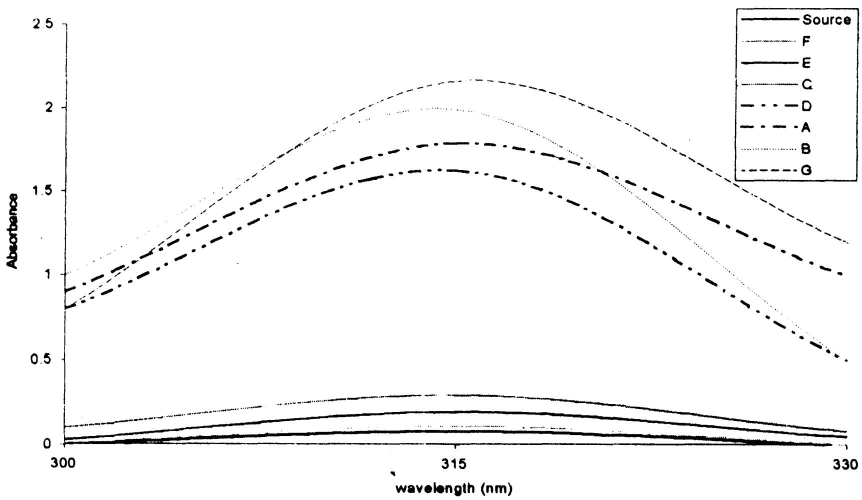

Fig. 5. Comparative UV-Visible spectra of source PET and commercial PET containers

TABLE-3
PURITY AND UV ABSORBANCE OF PET CONTAINERS

Sample	UV absorbance at 315nm
Source	**0.031**
F	**0.049**
E	0.195
C	0.292
D	1.627
A	1.790
B	1.992
G	2.164

Dielectric constant of storage containers

The resonant cavity and waveguide method has been employed here using microwave test benches (X band and K band) to measure the permittivity of the dielectric material, PET. The X band consists of a Klystron oscillator and a rectangular waveguide of dimensions 2.2 × 1 cm. The K band mainly comprises of a Gunn oscillator and a rectangular waveguide of dimension 1.1 × 0.4 cm in the dominant $TE_{1,0}$ mode. All the samples are shaped to the dimensions of the waveguide. A direct and accurate method of Roberts and Von Hippel[12] has been considered here. This method is based on the measurement of shift in the minimum of the standing wave produced by a short circuit when a sample is placed before the short circuit. The measurements are repeated for all the four faces of the shaped samples. The dielectric constant is calculated using the relation $\varepsilon_r = [(\lambda_0/\lambda_g')^2 + (\lambda_0/\lambda_c)^2]$ where λ_0 is the wavelength of microwaves in free space, λ_c is the cut of wavelength, λ_g' is the wavelength of dielectric filled space. The dielectric constant at X band lies between 3.5 and 7.7 and it is presented in Table-4. The dielectric constant at K band has been found to be around 2 for source and commercial samples[13] and this is as reported by Schonhals[14]. As the microwave frequency decreases the dielectric constant increases[15]. The dielectric constant of sample F is close to that of source followed by samples E, G, C, B, A and D in both the K and X bands.

TABLE-4
DIELECTRIC CONSTANT OF PET CONTAINERS

Sample	Dielectric constant	
	X Band (9.25 GHz)	K band (20 GHz)
Source	**3.47**	**1.91**
F	**3.65**	**1.96**
E	4.84	1.98
G	5.99	2.00
C	6.48	2.01
B	7.16	2.09
A	7.56	2.16
D	7.72	2.23

Conclusion

A complete vibrational band assignment has been made available for all the source and commercial PET containers. Internal standard calculations from the IR spectral measurements have been used to differentiate the commercial PET from the source. UV-Visible spectroscopy has been exploited to confirm the quality of the samples for their use as storage containers. Computations of the dipole moment which are complex have been done away with, by obtaining a suitable correlation of this with ε_r in polymers. Dielectric constants for PET containers in X and K bands have been determined from microwave measurements, as they allow useful qualitative predictions to be made. The IR spectra vouchsafe for the ε_r values obtained experimentally. The results obtained agree well with literature values and confirm that the high symmetric PET molecules have very low dielectric constant and high dielectric strength and can be used for electrical insulation.

ACKNOWLEDGEMENT

The authors wish to express their grateful thanks to the University Grants Commission, New Delhi, for sanctioning a minor research project under which this work has been carried out.

REFERENCES

1. C.Y. Liang and S. Krimm, *J. Mol. Spectrosc.*, **3**, 554 (1959).
2. G. Kumaravel and S.A. Jabarin, *Adv. Polym. Tech.*, **15**, 191 (1996).
3. J.P. McEvoy, C.G. Armstrong and R.J. Crawford, *Adv. Polym. Tech.*, **17**, 339 (1998).
4. S. Birch, J. Yamaguchi, A. Demmler and K. Jost, *Automot. Eng.*, **2**, 101 (1993).
5. Wellman International, *Mat. Reclam. Week*, **163**, 6 (1994).
6. Society for Plastics Industry, "A thirsty marked for recycled PET beverage bottles", *Polyurethane News*, **3**, 3 (1990).
7. A.L. Smith, Treatise on Analytical Chemistry, 2nd Edn., Wiley, NewYork (1991).
8. M. Wegelin, S. Canonica, A.C. Alder and D. Marazeula, *J. Water Supply Res. Tech., AQUA*, **50**, 125 (2001).
9. D.B.G. Jaquiss, W.F.H. Borman and R.W. Campbell, Encyclopedia of Chemical Technology, Vol. 18, John Wiley, New York (1982).
10. J.Y. Jadhav and S.W. Kantor, Encyclopedia of Polymer Science and Engineering, Vol. 12, John Wiley, New York (1988).
11. Perkampus, UV- Visible Atlas of Organic Compounds, Heinz-Helmut, Weinheim-New York (1992).
12. N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, New York (1967).
13. A.R. Von Hippel, Dielectric Materials and Applications, MIT Press, Cambridge (1954).
14. A. Schonhals, *J. Am. Chem. Soc.*, **3**, 81 (1997).
15. S. Roberts and Von Hippel, *J. Appl. Phys.*, **7**, 17 (1996)

(*Received*: 5 November 2003; *Accepted*: 7 April 2004) AJC-3384