Routine Low-energy Dosimetry with Thin Gauge Polyethylene Films

Mark Driscoll, SUNY-ESF, Syracuse, New York, USA
Daniel Montoney, Strathmore Products, Syracuse, New York, USA
Anthony J. Berejka, Ionicorp[+], Huntington, New York, USA

Abstract

Dosimetry in the low-energy electron beam (EB) area presents challenges given the limited electron penetration into materials. There is a dose-deposition profile in dosimeters used in high-energy EB when exposed to low-energies. Using Fourier Transformation Infrared spectroscopy (FTIR), the development of a transvinylene peak in thin gauged (25 micron) polyethylene (PE) films is shown to be indicative of EB exposure and can be correlated with reference dosimeters and calibrations based on modeling which rely upon Monte Carlo codes. PE films are made in very constant gauges and not subject to environmental factors such as humidity or ambient light.

Polyethylene as a Dosimeter

The use of polyethylene as a dosimeter was suggested by Arthur Charlesby, one of the pioneers of radiation chemistry, in the late 1950's.[1,2] This was elaborated upon by John Lyons and Bill Johnson from the Raychem Corporation, now Tyco Electronics, in the 1990's and within the past few years.[3,4,5,6] Raychem/Tyco Electronics operates many EB accelerators in different parts of the world and has been acknowledged to have more combined kilowatts of EB power than any company. In the total EB end-use market, PE, a commodity plastic, is far and away the most commonly used material, being formulated into irradiation crosslinked wire and cable jacketing and heat shrinkable tubing and being used for heat shrinkable food packaging films.[7] As Charlesby, Lyons and others observed (as Malcolm Dole, who first noticed that PE would crosslink when irradiated)[8], a transvinylene peak in the infrared region of the spectrum develops in PE that is proportional to the degree of irradiation exposure. This is the kind of response one would want from a dosimeter.

Two ASTM International Standard Methods of Test have been developed for using Fourier Transformation Infrared spectroscopy (FTIR) to determine the transvinylene concentration in PE. One was developed for use mainly with virgin, non-crosslinked PE, ASTM D-6248 "Standard Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry."[9] This method calls for molding plaques of PE with heat and temperature to obtain 0.5 mm pieces. Using a FTIR spectrophotometer, the PE is scanned between 1050 and 850 cm^{-1} to determine an integrated peak around 965 cm^{-1}, a characteristic peak for the transvinylene in PE. The other test method was developed for use with irradiated ultra-high molecular weight polyethylene (UHMWPE), which is used in medical devices such as implants. ASTM F-2381, "Standard Test Method for Evaluating Trans-Vinylene Yield in Irradiated Ultra-High-Molecular-Weight Polyethylene Fabricated Forms Intended for Surgical Implants by Infrared Spectroscopy" calls for microtoming slices of PE that are ~200 μm thick and then using FTIR to determine a transvinylene index (TVI) which is the ratio of the absorption peak area between 950 and 980 cm^{-1} (i.e. around the 965 cm^{-1}peak) and the absorption peak area between 1330 and 1396 cm^{-1}.[10] The TVI or ratio approach is used to correct for variations in specimen thickness.

In their work, Lyons and Johnson used extruded tapes of PE and compared the peaks at 965 cm^{-1} with the peak at 2019 cm^{-1} also to correct for variations in thickness. A 750 keV electron beam in the Raychem product development laboratory was used for various experiments. Lyons also studied the influence of other factors when combined with irradiation of PE, such as additives and irradiation temperature. Many types of PE were evaluated and exposures taken up into to the thousands of kilograys (1000+ kGy). There was a preference for using low-density PE (LDPE).[3]

Low-energy EB Considerations

At RadTech 2006, Art Heiss and Tony Berejka pointed out several concerns when attempting to do dosimetry with low-energy electron beams. Using Monte Carlo (ITS Tiger code) calculations, they showed how energy deposition from low-energy beams is dependent upon beam window thickness and upon the air gap between the beam window and the material to be irradiated.[11] Calculations were done using beam energies from 80 keV to 300 keV, covering the scope of commercially available low-energy EB units. Window thickness and beam energies for low-energy EB equipment made by Advanced Electron Beams and Energy Sciences, Incorporated, were used. Figure 1 below illustrates the loss of beam energy in air at gaps of 1 cm, 3 cm and 5 cm for an 80 keV beam, assuming a 6 micron titanium foil window. The inflection in each curve is the transition between the air gap and the energy deposition into a uniform alanine coating of 144 µm (adjusted to include both the alanine itself and its binder) on a 150 µm polyester film. As with all dosimeters, at these very low beam energies there is a depth-dose profile within the coating or dosimeter itself and not the equal-entrance, equal-exit conditions encountered with higher energy EB units. At a 5 cm air gap, very little of the beam energy is left to penetrate into the dosimeter, around only 20% or less. These results show the sensitivity of low energy electron beams, 80 keV to 300 keV, to loss of beam in air indicating that, for optimum performance, tight control over the air gap between the beam window and target substrate should be maintained.

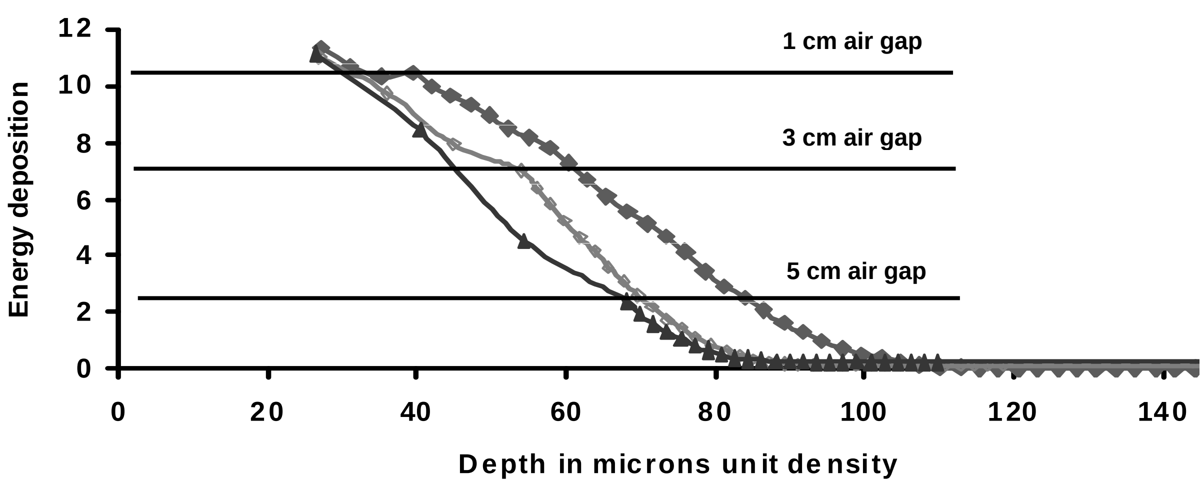

Figure 1. Loss of 80 keV Electron Beam Energy in Air with Change in Gap Distance

Dosimeters based on photochromatic effects are known to pose several problems in an industrial environment. Photochromatic responses induced by ionizing radiation are also induced by exposure to ambient light, especially the ultraviolet emissions from common fluorescent lighting. Gauge thickness variations have been observed that influence the determination on such properties as optical density.[12] Binders that are sensitive to moisture and pose concerns over ambient humidity have been used. PE itself has none of these deficiencies. PE is not sensitive to ambient light, is well known for its moisture resistance and can be extruded into films and sheets of very tight tolerances. Using a high-energy 3 MeV electron beam, 890 µm (35 mil) extruded high density (0.96) sheet was irradiated using different beam currents and found to give strong FTIR responses in the transvinylene, 965 cm^{-1}, region. At 3 MV, there was no concern over energy deposition into the PE sheet since sufficient EB voltage was used. To overcome concerns over the depth-dose gradient found in dosimeters when used with low-energy EB equipment, a thin gauged 25 µm (1 mil) commercially available high density polyethylene (HDPE) blown film was chosen for evaluation with low-energy EB. Monte Carlo simulations showed that with a 6 µm titanium window and 2 cm air gap, at 120 keV there would be an equal-entrance, equal-exit energy deposition in the film, as shown in Figure 2. At 80 keV, there would still be a depth-dose gradient, as shown in Figure 3, even if the air gap was reduced to 1 cm. The inflections indicate the transitions from the air gap to the HDPE film to a thick film backing. HDPE films are routinely made in even lower gauge thicknesses, down to 12 µm (0.5 mils). At 80 keV, the loss in air is significant so that even with a 12 µm film, there is a still a depth-dose gradient, as in Figure 4.

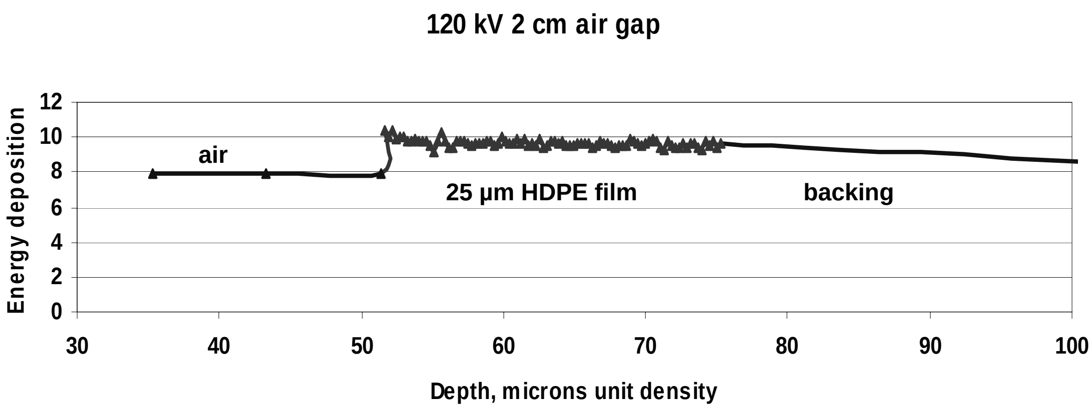

Figure 2. Energy deposition in 25 micron HDPE film

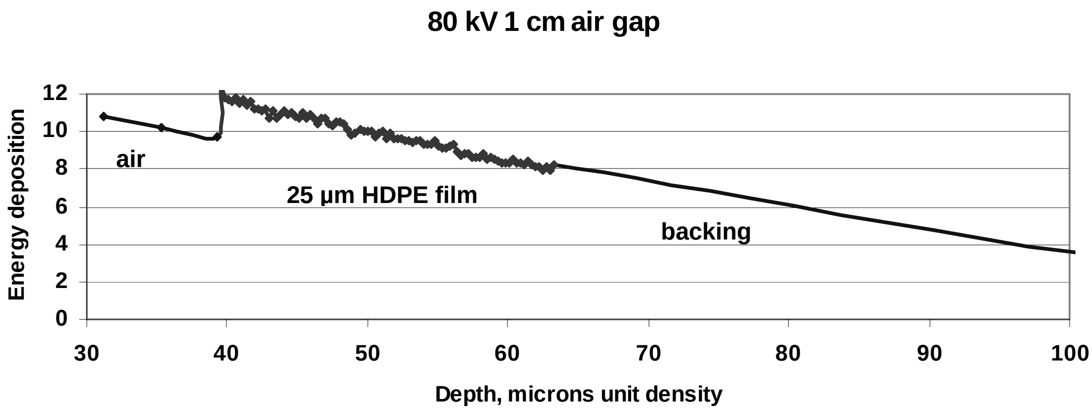

Figure 3. Energy deposition in 25 micron HDPE film

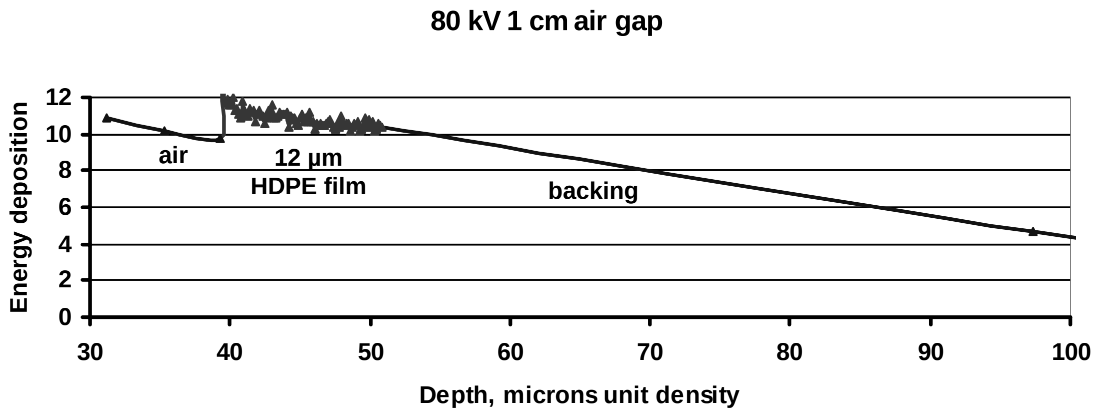

Figure 4. Energy deposition in 12 micron HDPE film

Since one can control the beam energy for very low-energy systems by adjusting the voltage between 80 and 120 kV, it would be preferred to do any dosimeter tests at the higher, 120 kV, beam voltage. Likewise, maintaining a very tight 1 cm air gap can also pose problems. A more controllable 2 cm air gap can be used. This would avoid any possibility of film contact with the beam window. Monte Carlo calculations can be used to convert measured responses to a thin surface layer.[13]

Polyethylenes

The transvinylene double bond, as illustrated in Figure 5, in polyethylenes is present in the amorphous phase, not within crystalline domains. Its formation is not molecular weight dependent.[14] The formation of this double bond is linear over a very broad dose range. The formation of transvinylene unsaturation is a primary process within polyethylene resulting from the abstraction of a hydrogen atom from the polymer backbone when exposed to ionizing radiation.[15]

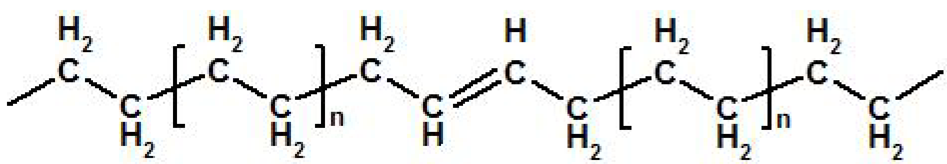

Figure 5. Transvinylene double bond structure in polyethylene

As illustrated in ASTM F-2381, the FTIR peak in the 965 cm^{-1} region can be very subtle at relatively low levels of exposure of the polyethylene to ionizing radiation, as show in Figure 6.[10] As with other spectrophotometer measurements, care must be take to define this area of interest. Given the uniformity of the thickness of PE films, corrections for variations in film thickness do not have to be made and ratios, such as the TVI (transvinylene index), may not be needed.

Thin gauged high density (HDPE) film was chosen for experimental work because of its inherent stiffness, being less prone to distortion when handling. The 1% secant modulus (ASTM D-882, “Standard Test Method for Tensile Properties of Thin Plastic Sheeting”) is an indication of the stiffness of the polymer.[16] The higher melt transition (T_m) of HDPE also would mean less distortion due to any thermal effects that could be incurred should high levels of EB exposure be used. Table I compares some typical properties of four types of PE: HDPE, low density PE (LDPE), linear low density PE (LLDPE) and ultra-high molecular weight PE (UHMWPE).[17] HDPE, LDPE and LLDPE are used in thin gauged blown films. UHMWPE is used in the medical device area as a molded part of an implant and is not commonly produced in low gauge thicknesses.

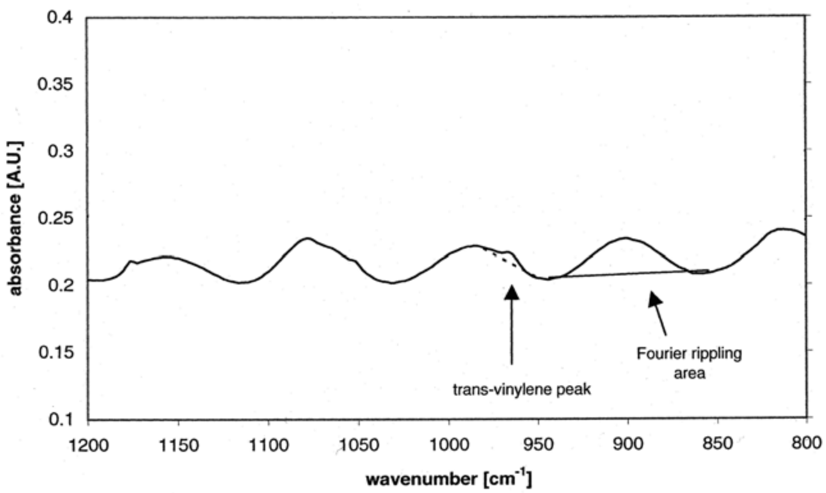

Figure 6. Transvinylene FTIR peak in polyethylene

Table I. Typical Properties of Polyethylenes

Type	Density	T_m, °C	1% Secant Modulus
HDPE	0.952-0.965	130-137	1150 MPa
LDPE	0.917-0.932	98-115	250 MPa
LLDPE	0.918-0.940	122-128	150 MPa
UHMWPE	0.940	125-135	945 MPa

Experimental Studies

An Application Development Unit **(**laboratory unit) manufactured by Advanced Electron Beams was used to determine the low-energy EB response of a thin, 25 µm (1 mil), commercial HDPE film.[18] The voltage on the touch-screen panel was set to 125 kV and the under-beam transport speed to 15.2 m/minute (the slowest speed attainable) and pieces of 25 µm film were adhered to a wooden block to assure that the distance between the beam window and the film was maintained at 2 cm. For "dose" settings of 25 kGy (4.2 ma) and 50 kGy (9.5 ma), the exposure was delivered in a single pass. At the 9.5 ma (50 kGy) setting, multiple passes were used to deliver nominal "doses" of 100, 200, 300, 400 and 500 kGy. Two such experiments were conducted using the same film, the same laboratory unit with results being analyzed using the same Perkin Elmer Paragon 500 FTIR spectrometer. The FTIR was set for 1 cm^{-1} resolution and 64 scans were conducted for each run. Films were taped to an IR card and slid into the sample holder in the spectrometer. For the "25 kGy" samples two films were adhered to the card to increase the response. Samples were analyzed the day after irradiation. Seven points on the film were examined for changes in the absorbance in the 965 cm^{-1} region. Figure 7 shows the linearity of the absorbance with respect to "dose" setting over the range investigated. Changes due to the development of the transvinylene peak within the HDPE could be found even at the 25 kGy level, the "dose" commonly prescribed for sterility assurance and used in the medical device area. The data plot from the second experiment would super-impose upon this with there being practically no difference in average absorbance in the 965 cm^{-1} region.

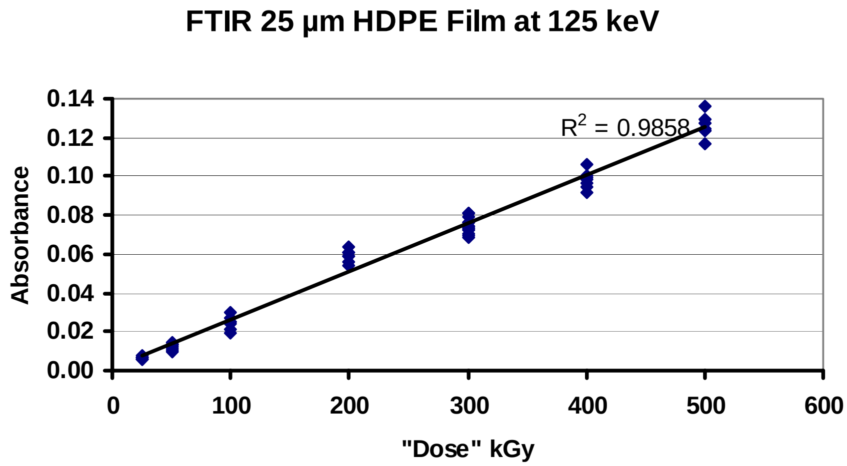

Figure 7. FTIR transvinylene absorbance with change in EB exposure

Repeatability

Thin gauge (25 to 12 µm) blown films of HDPE are common articles of commerce. Such films are not subject to the environmental effects of ambient light and humidity as are films now used as dosimeters. Since HDPE is produced in bulk and the manufacture of blown films is a well established practice, should such films be used as dosimeters, concerns over lot-to-lot variability of dosimeters will be eliminated. Repeatability studies have been conducted using what is generally recognized as the most precise dosimeter, alanine.[19] Multiple strips of uniformly alanine coated films with no measureable variation in thickness were simultaneously passed under high-energy, scanned electron beams (one set using a Dynamitron™ at 1.0 MeV and another with a Dynamitron at 4.9 MeV, with variations in beam currents. At these energies, there is no concern over attaining equal-entrance, equal-exit EB penetration within the alanine coating (135 µm for one lot; 150 µm for another). Depending upon the test run, as many as sixteen strips were run adjacent to each other, or as few as seven. All alanine/marker readings were performed by Bruker Biospin, the manufacturer of spin resonance equipment. The coefficients of variation or variance for the alanine/marker ratios for seven such test runs ranged from 0.69% to 1.49%. Since the same equipment was used in these tests, these meet the ASTM International criteria for repeatability.[20] Reproducibility tests using multiple laboratories were not conducted.

Conclusions

It has been shown that:

1 – The development of transvinylene in thin films of common high-density polyethylene (HDPE) can be used as a dosimeter with low-energy electron beams. This is in keeping with the insights of Arthur Charlesby and as elaborated upon by John Lyons, who was the senior scientific advisor at one of the foremost industrial firms using radiation processing.

2 – Polyethylene films will not be subject to problems that have plagued the EB processing industry in using photochromic dosimeters, such as variations in gauge thickness, sensitivity to environmental factors as light and humidity. PE films will also be considerably lower in cost. The extrusion and blowing of PE films down to very think gauges is a very routine industrial practice.

3 – Further investigation is warranted to delineate analytical techniques that should be followed when using FTIR, such as sample positioning, concentration or diffusion of the light source, and possible use of attenuated total reflectance (ATR) infra-red spectroscopy. Such investigations should include an evaluation of new, compact low cost infra-red spectrophotometers.

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