Oxygen-Sensitive Electron Beam Dosimeters
for Measuring Web Surface Inerting Efficiency

By Stephen C. Lapin, Ph.D.

Low-energy (less than 300 kV) electron beam (EB) technology has been used for industrial applications for more than 30 years. Well-known applications include:

- Crosslinking of polyethylene-based films for packaging applications

- Surface sterilization of food and medical packaging

- Crosslinking and curing of adhesives

- Curing of surface-applied inks and coatings

Curing of inks and coatings is now one of the largest industrial uses for low-energy EB technology. The use of EB inks and coatings is often driven by environmental, speed and performance advantages over conventional solvent-based inks and coatings. Packaging applications for EB inks and coatings are well-known and include folding cartons, pouches, multi-wall bags, labels and flexible packaging.

EB inks and coatings are based on the free-radical polymerization of acrylate-functional monomers and oligomers. The process of EB-induced polymerization is shown in Figure 1. EB irradiation easily ionizes monomer or oligomer components without the need for added photoinitiator components. This ionization leads the formation of free-radicals (Figure 1, eq. 1). The subsequent polymerization chain reaction (Figure 1, eq. 2) rapidly increases molecular weight resulting in solidification (curing) of the ink or coating. A crosslinked networked is formed due to multifunctional monomers and oligomers that are used. Oxygen from the air reacts very quickly with the carbon-centered radical to give slow-reacting peroxy radicals; thus, effectively inhibiting the curing reaction (Figure 1, eq. 3). Because of the oxygen-inhibition effect, most EB curing uses an inert gas to displace oxygen from the reaction chamber of the EB unit where the curing occurs. This is usually accomplished by purging the reaction chamber with high-purity nitrogen.

Assuming the ink or coating is

FIGURE 1

EB-induced polymerization

1. Initiation $M + EB \rightarrow M\cdot$

2. Propagation $M\cdot + nM \rightarrow M(M)_n\cdot$

3. Oxygen inhibition $M(M)_n\cdot + O_2 \rightarrow M(M)_nO\text{-}O\cdot$

4. Termination $M\cdot + M\cdot \rightarrow M\text{-}M$

properly formulated for the end-use application, two main factors are needed to ensure good curing—adequate applied dose and effective inerting at the surface in order to displace oxygen from the air.

Dosimetry systems for low-energy electron beams are well known. The most widely used systems consist of radiochromic compounds contained in polymer films. Upon EB irradiation, the radiochromic compounds undergo a color change. The change occurs in proportion to the absorbed EB dose and is measured by changes in the optical density of the film at a specific wavelength.[1] The response of these films are calibrated by reference to a standard radiation source or other reference measument methods such as the electron paramagnetic resonance (EPR) response of irradiated alanine[2]. For the most part, film dosimeters meet the needs of the industry[3]; however, they also have some recognized deficiencies that include:

- Dosimeter films are relatively thick which results in a gradient in absorbed dose across the film at the low energy (about 80 to 125 kV) end of the industrial EB energy spectrum

- Variation in dosimeter film thickness affects the optical density and must be controlled or measured to allow a correction factor to be applied

- Dosimeter films may be affected by environmental conditions, including heat, humidity and ambient lighting[1]

Alternative dosimetry systems have been reported, including the measurement of spectroscopic changes in polyethylene film that occurs upon EB irradiation.[4]

Fortunately, the energy output of EB equipment is very stable and the required dose for curing is well maintained and usually needs only

periodic confirmation by dosimetry measurements.[5]

Confirmation and measurement of inerting is also important to maintain proper curing. The current method that is most often used to measure inerting is to sample the gas through one or more small tubes located in the reaction chamber of the EB equipment. The gas stream from the sample tubes is then analyzed by an electrochemical oxygen sensor. An advantage of this type of system is that it provides continuous monitoring during production. The main problem with this type of method is that, while it provides a measure of the oxygen level inside of the reaction chamber, it does not measure oxygen at the surface of the ink or coating where the curing occurs. Web speeds in excess of 300 m./min. are often used in printing and packaging applications. The webs carry a thin boundary layer of air, on the surface. Schemes such as nitrogen knives are often used in attempt to strip the boundary layer of air, but there is no way to tell if this is effective by simply sampling the gas at points above the web in the chamber.[6]

The purpose of this work is to investigate a system that can measure inerting efficiency at the surface of the ink or coating where the curing occurs. The approach was to develop thin-film sensors that may be attached directly to the surface of the substrate.

The chemical reaction that is the basis for the sensor system in this investigation is the oxidation of triphenylphosphene (Ph$_3$P) to triphenylphosphene oxide (Ph$_3$PO):

$$2Ph_3P + O_2 \rightarrow 2Ph_3PO.$$

This reaction offers excellent possibilities for measurement due to the strong absorption of the P=O group in the infrared (IR) spectrum at 542 cm^{-1}. The reaction of hydroperoxides with Ph$_3$P is known to yield Ph$_3$PO and has been used to provide a measure of

hydoperoxide concentrations.[7, 8, 9] This is interesting because hydroperoxides are also expected to form as a result of oxygen inhibition of EB curing (Figure 1, eq. 3). The photocatalyzed oxidation of Ph$_3$P to Ph$_3$PO with molecular oxygen is also known and was shown to occur via radical cation intermediates in the presence of a photosensitizer.[10] These type of intermediates could also potentially be formed directly by EB-induced ionization and offers additional potential for measurements related to the concentration of O$_2$ during EB curing. The studies reported in the literature involve the solution phase oxidation of Ph$_3$P. Our investigation focused on the solid-state reaction in a polymer matrix due to the inherent advantages of handling a dry, tack-free sensor film.

Experimental

The sensors were prepared by dissolving measured amounts of Ph$_3$P and polymer matrix resins in methyl ethyl ketone (MEK) solvent. A small amount of blue pigment dispersion was also used to add a visible color to the sensors. Typical Ph$_3$P concentrations were 5 to 15% relative to the matrix resin. Initial polymer matrix resins investigated included polyvinyl butyral (Butvar B-76 from Solutia) and polyurethane (Versamide PUR 1010 from Cognis).

The solutions were applied on a 75-micron thick polyethylene (LDPE) film carrier using a wire-wound rod. The solvent was allowed to evaporate at ambient conditions to give a dry coating. The coating weight was controlled by the diameter of the wire on the application rod and also by the solids levels of the solution in MEK. The coating weight was confirmed by weighing a measured area of film, removing the coating with solvent and reweighing the film. Typical application conditions used a 10% solution applied

with a #22 wire-wound rod that produced a dry weight of about 3.0 g/m² (about 3 microns). Sensor coatings as thin as 1.0 microns were also prepared.

Squares (about 2 x 2 cm) of the sensor films were cut and mounted on paper cards. Conventional dosimeters (B3 film-based dosimeters from GEX Corporation) were mounted side-by-side with the sensor films for reference. Cards were attached to a moving carrier web and passed through the reaction chamber of a BroadBeam EP series EB accelerator. The atmosphere in the chamber was adjusted by purging at various rates with high-purity nitrogen.

The irradiated sensor films were mounted in Bruker model Alpha FTIR spectrometer equipped with a diamond crystal single bounce attenuated total reflectance (ATR) accessory. Twenty-four scans were collected in less than one minute, yielding a clear spectrum with little noise. The P=O peak centered at 542 cm⁻¹ was normalized and integrated. The measurement was repeated on two other spots on the sensor film. The average peak area from the three spots was correlated with the EB dose determined by the GEX films.

Results and Discussion

The initial testing involved characterizing the EB dose response of the sensor films. Figure 2 shows the P=O peak in the ATR spectrum after irradiation of three micron sensors based on 10% Ph_3P in a polyurethane matrix supported on 75-micron LDPE film. Various dose levels up to 22.4 kGy in a constant air atmosphere were used. The peak areas in Figure 2 were integrated and plotted in Figure 3. The results show a very sensitive response to EB dose levels below 10 kGy. The response was relatively constant from about 10 to 100 kGy. Typical cure dose levels for acrylate-based inks and
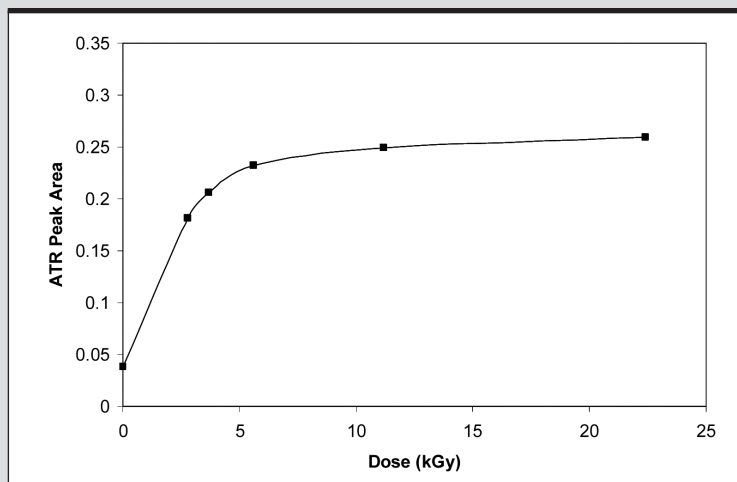
FIGURE 2

ATR spectra of the sensor after EB irradiation at various dose levels in air
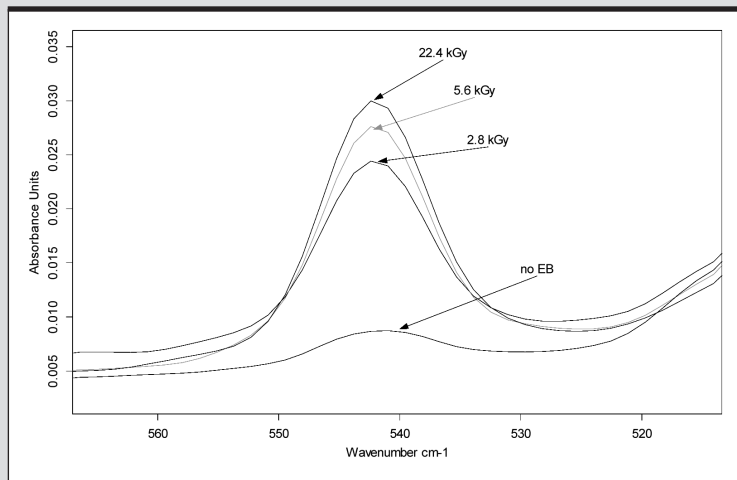
FIGURE 3

Integrated area of 542 cm⁻¹ sensor peak compared to GEX measured dose

coatings are on the order of 20 to 40 kGy. The fact that dose response is relatively constant at these levels could be useful for separating the response due to inerting and dose.

These results suggest that this system may be useful for radiation dosimetery in applications where inerting is not critical and are conducted in a constant atmosphere. It could be particularly useful in applications such as food sterilization where low doses are used.

An interesting aspect of this technology is that the coatings that form the active component of the sensors are very thin (in this case about 3 microns). At this thickness no

significant gradient in EB energy will occur from the front-to-back surface even with the lowest energy (ca. 80 kV) electron beams used in industrial-curing applications. This eliminates the need for correction factors that are used with thicker film systems to determine dose at low energies.[11]

Another interesting aspect of this technology is the use of ATR reflection measurement methods. The IR beam penetrates a constant distance into the sensor that is determined by the optics of the instrument as well as the optical properties of the sensor and the wave number (in this case 542 cm^{-1}) being measured. Penetration of about 1 to 2 microns was confirmed for this system by lowering the coating weight until peaks from the underlying LDPE carrier film were observed. Eliminating film thickness effects provides an advantage compared to current dosimeter film systems. Note, if desired, thickness-dependent IR transmission measurements could be used. This works particularly well for this system where the 542 cm^{-1} band is in a region that is free of interference

FIGURE 4

Comparison of ATR spectra of sensor after EB irradiation in air and nitrogen atmospheres
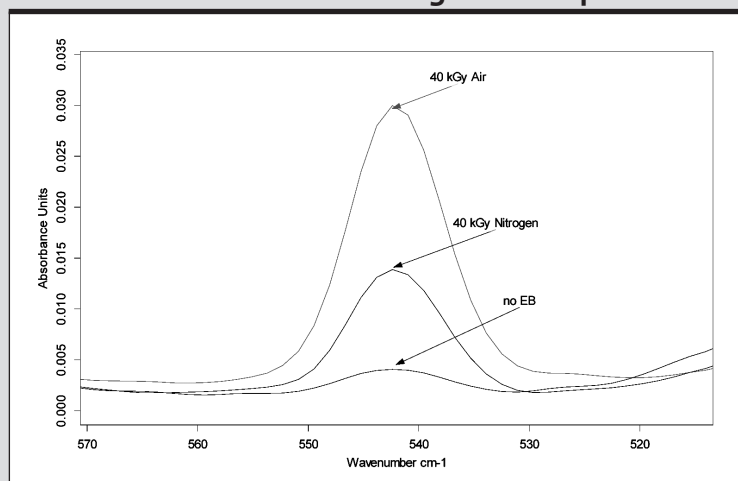
from many carrier materials, including LDPE.

Figure 4 compares the P=O ATR peak of the sensor film after EB irradiation in air and a thoroughly nitrogen-purged EB reaction chamber. The results show a clear atmosphere-dependent response with curing-in-air giving a larger peak area compared to

nitrogen.

In order to confirm the variable response of the sensors to the curing atmosphere, samples were run every 30 seconds using a slow nitrogen purge of 10 standard cubic feet per minute (SCFM) while maintaining a constant dose of 40 kGy. The resulting ATR spectra are shown in Figure 5. The P=O peak area decreased as the purge time increased. This indicated that the sensor was responsive to varying oxygen levels. The results were quantified by subtracting the peak area in air from the peak areas for the purged samples. The results are plotted in Figure 6. The plot plateaus after about 150 seconds of purge time, indicating that oxygen from the air has been displaced to a constant level.

In order for an inerting measurement system to be useful, it should be sensitive in a range of oxygen levels that can affect the curing of EB inks and coatings. A free-radical, acrylate-based coating was prepared consisting of a 50/50 mixture of trimethylolpropane triacrylate and epoxy acrylate oligomer (Cytec,

FIGURE 5

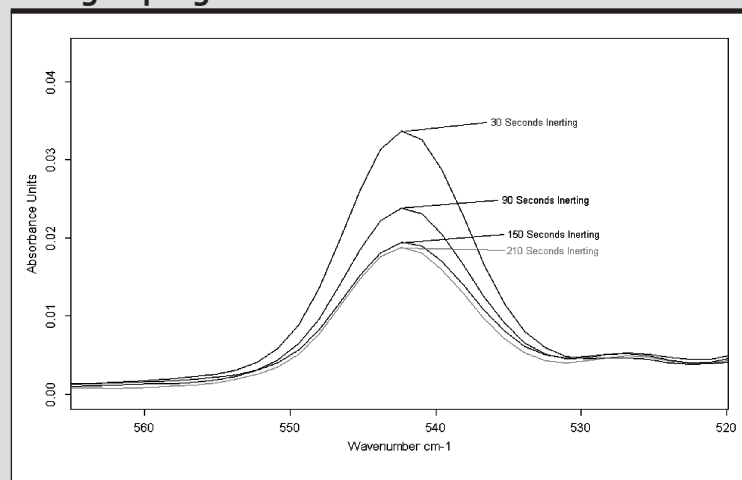**ATR spectra for sensor after EB irradiation at various nitrogen purge intervals**

FIGURE 6

Change in integrated area of sensor 542 cm⁻¹ ATR peak with increasing nitrogen purge time
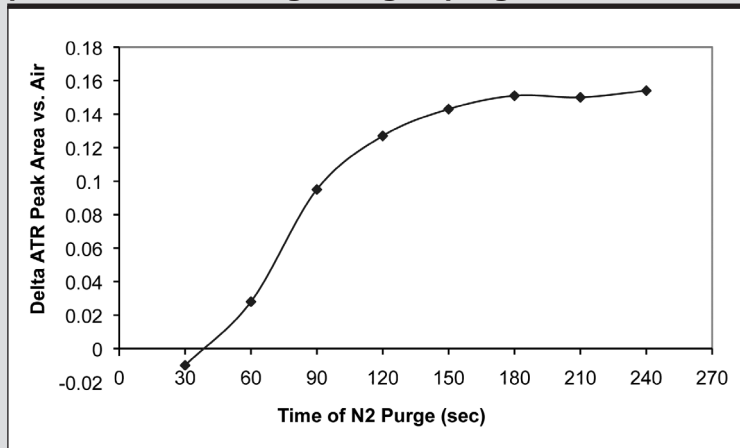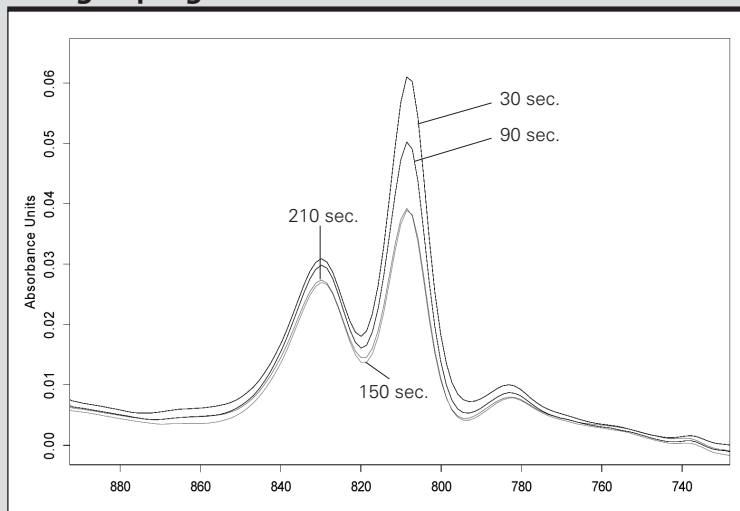

FIGURE 7

Decrease in acrylate ATR band with increasing nitrogen purge times

Ebecryl 3700-20T). The liquid coating was applied to a test card with a #3 wire-wound rod. Again, samples were EB-cured at 30-second intervals with a slow nitrogen purge of 10 SCFM using a constant dose of 40 kGy. After 30 seconds of purging, the coating was wet due to oxygen inhibition of the cure. After 90 seconds, the coating was partially dry but could still be smudged on the surface. After 150 seconds of purging, the coating had a dry, tack-free surface. The results show that inerting adequate for good curing occurs at about the same point as the plateau in the sensor response shown in Figure 6. This correlation shows that the oxygen sensitivity of the sensor

film is in a useful range relative to the inerting required to cure the coating.

A more sensitive measure of the coating cure was obtained by measuring the disappearance of the acrylate band in the ATR spectrum at 810 cm⁻¹. The spectra obtained as a function of the nitrogen purge time are shown in Figure 7. Results were quantified by subtracting the integrated area of the 810 cm⁻¹ peak at various purge times from the peak area before curing. These results are plotted in Figure 8. A comparison of Figure 6 for the sensor to Figure 8 for an actual coating shows similar shape curves with plateaus after about 150 second of inerting. This further demonstrates that the sensor film provides a useful measure of the inerting needed to achieve good cure.

Conclusions

A new thin-film dosimeter system was developed based on triphenyl phosphene in a polymer film matrix. The film was very sensitive to EB irradiation levels below about 10 kGy. The film was also sensitive to surface oxygen concentration and provided a measure of inerting in a range that affects the curing of EB inks in coatings. This type of system can potentially be used as a measurement tool for surface inerting to help ensure good curing of EB inks and coatings. ◗

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FIGURE 8

Change in acrylate ATR peak area with increased nitrogen purge time
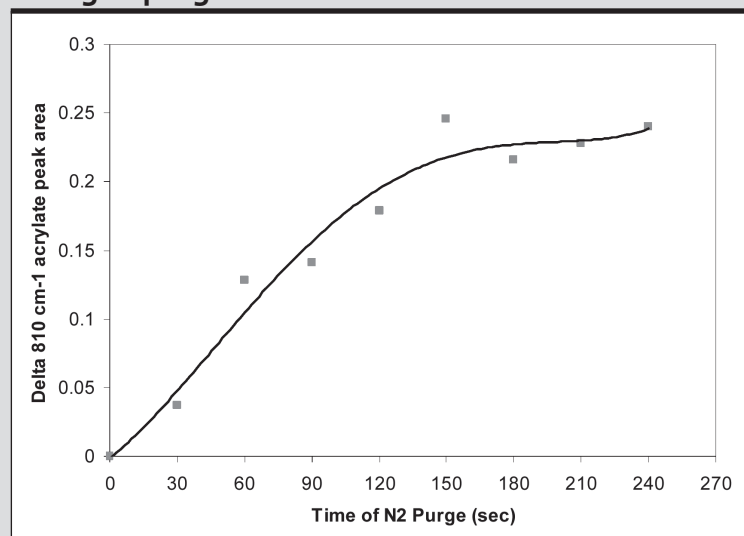
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