

Measurement and control of barrier layers

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Absorption of specific wavelengths of near infrared radiation can be used to measure and control film thickness in multilayer packaging materials.

The 1980s saw many new developments in the packaging industry brought about by ecological concerns, as well as by conventional economic and marketing pressures. This activity was paralleled in the instrument industry as established companies improved their existing products and as new suppliers sprang up to exploit any attractive concept that promised a solution to some of the problems resulting from the new packages. In the ensuing excitement, some confusion has arisen regarding the methods actually being used to measure the new products, the merits of each method in a given application, and the validity of some of the claims. The following paper is presented in the hope of clarifying some of these topics.

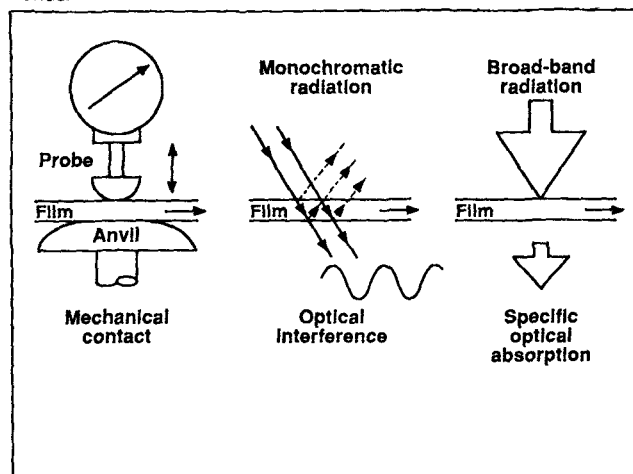
Measuring techniques

The thickness of a film can be measured in many different ways, but all of them can be classified into one of three categories: mechanical contact, physical by optical interference, or chemical by optical absorption related to the chemical bonds (Fig. 1).

The mechanical category includes the simple micrometer and a number of on-line versions in which measuring sensors contact both sides of the film. A way is found to measure the separation of the two sensors, usually using magnetic or inductive techniques. Sometimes the sensors are made noncontacting by floating them on an air film of constant thickness, or the sensors are replaced by light beams that measure the position of each surface by triangulation. In all cases, these devices measure total thickness of a simple or composite film. Although they may be usefully combined with other techniques to be described, they do not fall within the topic of measuring barrier layers.

The second category, interferometry, utilizes the mutual interference of radiation reflected from surface boundaries to give a measurement of the optical path length between the surfaces and therefore a direct indication of the film thickness. To obtain usable reflections, boundaries

1. Three principal ways to measure thickness are mechanical contact, optical interference, and optical absorption related to the chemical bonds.



must be well defined, both materials must have different refractive indices, and none of the components may cause scattering of the radiation. The technique is most useful for the measurement of extremely thin clear films. It cannot be used where coatings are applied to paper or board.

Near infrared absorption

The third category is the one of prime interest to the packaging industry and is the subject of most of the research. The property utilized in this technique is the partial absorption of specific wavelengths of near infrared (NIR) radiation by different materials. The measured value is not thickness but basis weight (M_p) in units of mass per unit area, which is directly proportional to the absorbance.

$$\text{Basis weight } (M_p) = A/a_p$$

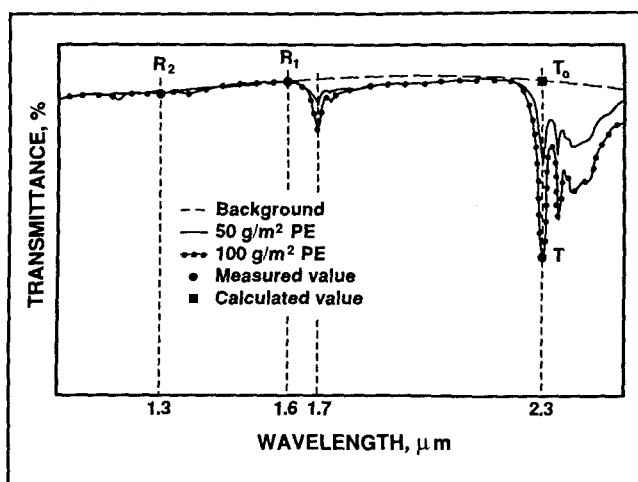
$$\text{Absorbance } (A) = \ln T_0(\lambda)/T(\lambda)$$

where

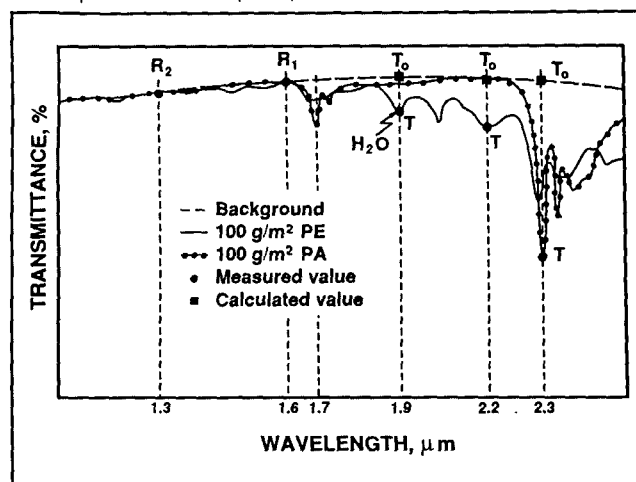
Absorptivity (a_p) = the coefficient of absorption for a given material at a given wavelength

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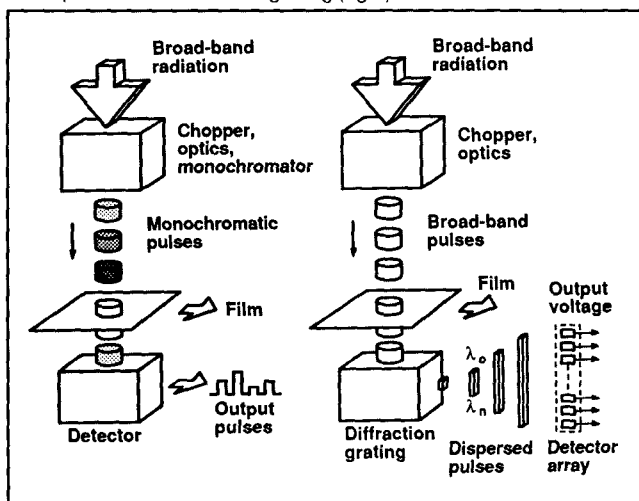
2. NIR spectra for two thicknesses of PE



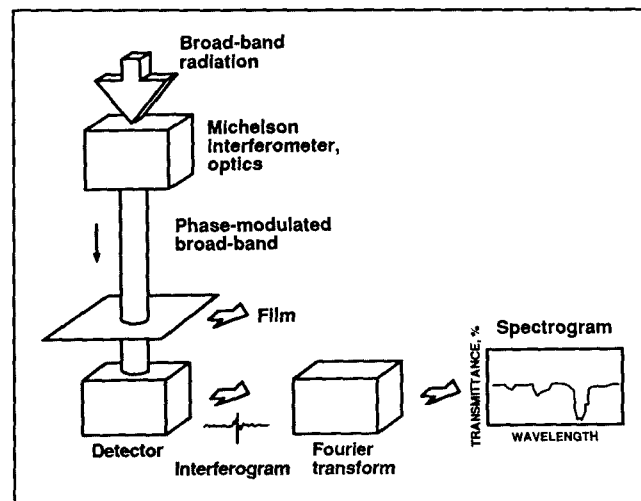
3. NIR spectrum of PA superimposed on PE



4. Film measurement using monochromatic pulses (left) and broad-band pulses with diffraction grating (right)



5. Film measurement using a Michelson interferometer and Fourier transform



T_0 = the intensity of the incident radiation
 T = the intensity of the transmitted radiation.

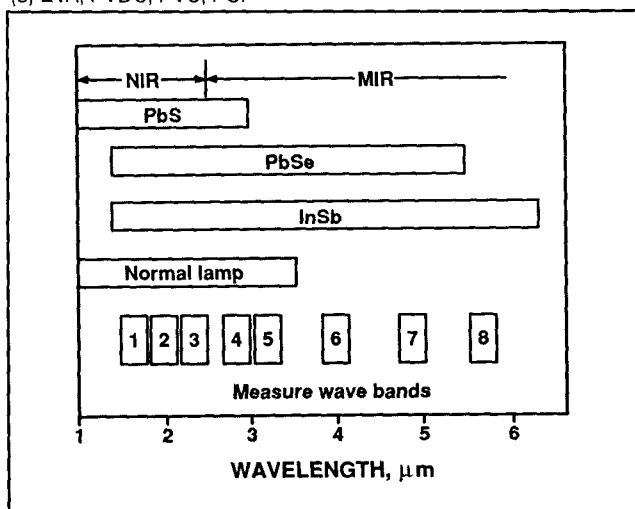
Any technique utilizing specific absorption to measure film thickness is unable to distinguish between different layers of the same material. It will always indicate the total weight of each polymer. When the second layer of a polymer is laid down by a separate extruder, however, its thickness can be determined by the difference measured by two gauges, one before and one after the extruder. Also the recently announced ability to distinguish between low- and high-density polyethylene (LDPE and HDPE) offers a solution to this problem in some applications.

The measurement is independent of density but is subject to errors if the optics permit unknown changes in the path length of the radiation passing through the film.

The technique has been described in detail many times (1), but one more repetition will highlight some of the areas of confusion.

Figure 2 shows NIR spectra of two clear polyethylene (PE) films of different thicknesses. Clearly, there are a

6. Commonly used lead salt detectors. Wave bands and specific absorptions are: (1) water, polyolefins; (2) cellulose, PA; (3) polyolefins, PS; (4) EVOH, PA, PET, PVC; (5) ionomers, acid copolymers, PPL, PET, PVDC; (6) EVOH, PET; (7) isocyanate adhesives, PET, ionomers; (8) EVA, PVDC, PVC, PC.



number of wavelengths where the grammage of the film could be measured, e.g., 1.7 μm or 2.3–2.5 μm . In addition, a reference is needed to eliminate errors caused by changes in hardware, such as the lamp intensity. This could be at 1.6 μm , where there is no absorption. For the highest accuracy, a third measurement could be provided at another wavelength where there is no absorption, say at 1.3 μm , to measure and correct for the effects of scatter caused by haziness. Monitoring these three wavelengths is all that is required to measure, to the highest practical accuracy, PE film of any color or degree of haziness over a very large range of thicknesses. None of three measurements can be omitted, but the addition of more measurements at different wavelengths brings no improvement.

Figure 3 shows a polyamide (PA) spectrum superimposed on one of PE. If one imagines both spectra added together, the result would be the same as a single spectrum of coextruded PE and PA. It can then be seen that a fourth measurement, at 2.2 μm for example, is all that is needed to measure both components in any ratio. If the elimination of the effect of water in the PA is required, a fifth measurement can be added at 1.9 μm . All this is possible because the individual components—PE, PA, and water—are available as pure substances for study, in which the analysis of the NIR spectrum of a single sample of known weight yields both the optimum wavelengths and the complete calibration constants. If for some reason the components to be measured cannot be isolated, but it is suspected that there might be specific absorption somewhere in the NIR region of the spectrum, then a correlation to the quantities of each component often can be found by scanning the whole spectrum and using sophisticated computer algorithms. These mathematical techniques are known under many different names, including principal component analysis (PCA) and factor analysis (FA) (2). Although they are widely accepted in some industries, the principal drawback is the need for extensive calibration on all products to be measured, using large numbers of samples with known characteristics.

Definitions

Definitions and brief information for other terms often encountered in texts describing on-line measuring systems may be helpful.

The near infrared (NIR) region of the spectrum covers 1–2.5 μm and the middle infrared (MIR) region covers 2.5–25 μm .

Specific absorption is the unique pattern of absorption of energy, within a given spectral range, after passing through a given material.

The Beer-Lambert model is a mathematical statement describing the relationship between the absorption, at a given wavelength, of energy passing through a known amount of a given material. Modified versions are used to compute film thickness independently of scatter phenomena and errors caused by carbon black or other broad-band pigments used in printing. Advantages include universal adaptability and simple calibration from pure polymers.

An interferogram is the coded output of a Michelson interferometer that contains all the information on the specific absorption.

Sampling systems include all measuring systems in which the signals required to compute one measurement derive from different parts of a moving film (see monochromatic pulse example in **Fig. 4**). Such systems are widely used on single color structures but have a low signal-to-noise ratio (S/N) on printed surfaces.

Same-spot measurements include all measuring systems in which the signals required for one measurement originate from the same spot on a moving film. They improve the S/N on printed surfaces, but the technique alone is not sufficient to correct errors caused by the use of carbon black in printing. They give a marginal increase in the total area of the film being measured.

A full spectrum measurement uses an instrument that makes available all wavelengths within given limits (as in **Figs. 2 and 3**) instead of selected discrete wavelengths. It permits use of correlation algorithms (such as PCA and FA), if required, and allows change of wavelengths using only software. A disadvantage is that inefficiency of diffraction grating and small detector array elements lead to low energy throughput and therefore low S/N. An example is shown in the broad-band section of **Fig. 4**.

The Fourier transform infrared (FTIR) is a device built around a Michelson interferometer to produce a full spectrum measurement (**Fig. 5**). In theory, it is a same-spot system, but low S/N necessitates long integrating times. It is mechanically complex, expensive, and vibration sensitive.

The filter wheel is a rotating wheel containing optical filters that chop broad-band radiation into narrow-band pulses. It has good energy throughput, is reliable, and has a high S/N except on printed film. Spectral range is unlimited.

A diffraction grating is an optical device that disperses broad-band radiation into a continuous spectrum. It is a compact, rugged optical element. Disadvantages are that the best efficiency is only approximately 1% and that it is difficult to apply over a wide spectral range.

An acousto-optic-tuneable filter consists of two bonded single crystals in which an acoustic wave is used to disperse incoming radiation. Features are similar to the diffraction grating with the advantage that it can be switched rapidly between wavelengths. Disadvantages are the need for complex power supplies and the fact that the output radiation is polarized.

A detector array packages a number of small discrete detectors of optical energy into a single unit. It is more stable than multiple discrete detectors. A disadvantage is the difficulty in directing diffuse radiation onto small elements, which leads to low energy throughput and low S/N.

The most commonly used lead salt detectors (**Fig. 6**) are PbS for the NIR region and PbSe, which operates in both the NIR and MIR regions where many materials can be measured but it has less than 10% of the sensitivity of PbS. Therefore, efficient optics with good throughput are necessary to measure barrier materials.

Study of the basic measuring problems has shown that the most important features of an on-line barrier measuring system are, in approximate order of importance:

1. Efficient optics for fast, stable measurement and high S/N

2. Spectral range up to $5.8\ \mu\text{m}$
3. High resolution in cross direction (CD)
4. Same-spot measurement with up to eight wavelength channels as standard, expandable to more should the need arise
5. Measurement independent of any movement of the sample.

These are the features required for instruments that will be usable to the end of the century.

On-line measurement

The packaging engineer has at his disposal a vast number of products, including an ever increasing number of coated and uncoated polymer films, foils, a wide range of papers and boards, and specially designed tie products. Combining these with the range of available processes—such as roll coating, extrusion coating, coextrusion film casting, and laminating—results in a variety of possible structures too numerous to be analyzed in detail here. The methods used to measure these products can only be described in general terms with a few specific examples. However, we have not as yet encountered any structure in which the barrier layers plus total polymer weight could not be measured, with the obvious exception of layers sandwiched between opaque materials.

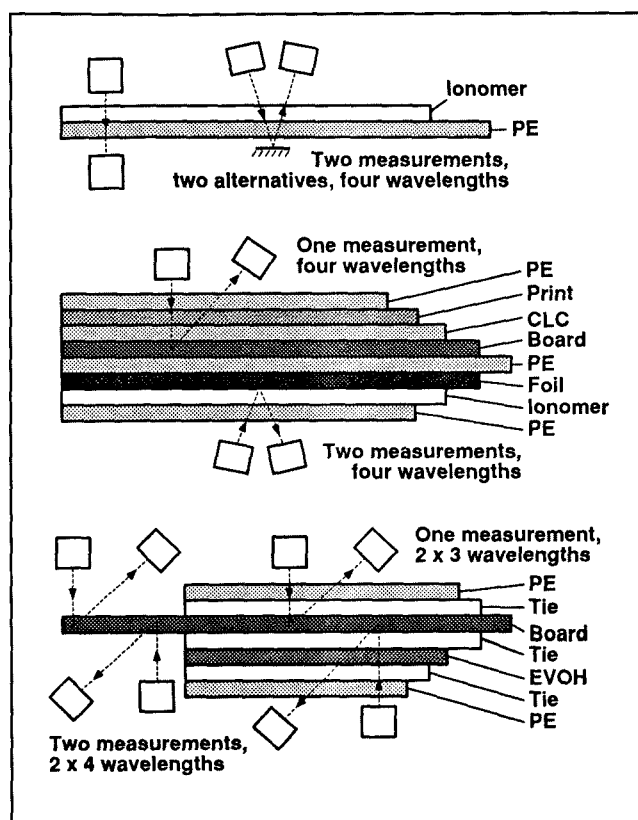
The most common polymer barrier materials are polypropylene (PPL), polyethylene terephthalate (PET), PA, polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), ethylene vinyl alcohol (EVOH), ethylene vinyl acetate (EVA), PE, polystyrene (PS), polycarbonate (PC), ionomer, and ethylene acrylic acid (EAA) (3). **Figure 7** gives some examples of multilayer film structures. All of these polymers can be measured in combinations found in practice, using infrared techniques. PVDC presents special problems when it is used in very thin layers. In these cases, a solution can be found by using low energy nuclear radiation in place of infrared.

For the purpose of measurement, the various structures fall into two categories: transparent films that can be measured in transmission mode and coatings on opaque carriers that require reflection measurement. The distinction is not simply that of using one or two measuring heads. Measurement in reflection involves eliminating the effect of the base material, usually board, which may be clay coated or printed.

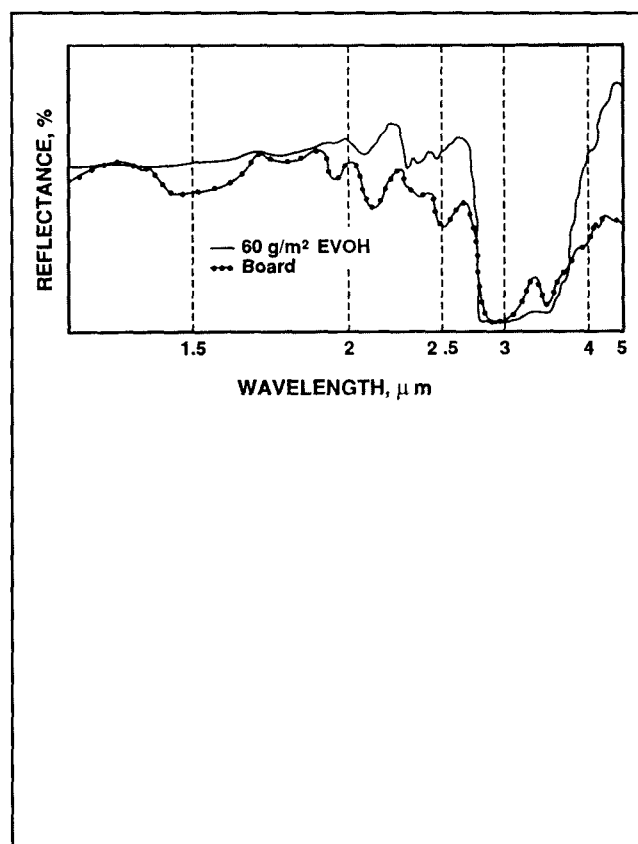
An example of a transparent structure for snack food packaging is shown in Fig. 7. Here HDPE and an ionomer sealant can be measured using two reference wavelengths, one measurement wavelength at the $2.4\ \mu\text{m}$ region and the other at the $3.2\ \mu\text{m}$ sideband. In an alternative arrangement that doubles the available signal, a neutral reflector is placed on one side of the film and a reflection measuring head on the other. This is also very similar to the measurement of the inside layer of an aseptic package in which an aluminum foil acts as the neutral reflector.

Not shown is a meat packaging structure consisting of PVDC-coated PET/tie layer/acid-copolymer. The PVDC coating is first measured using nuclear radiation, and the remaining two coextruded layers are measured as described above. The PET layer is subtracted mathematically when it is known to be uniform, or a measurement

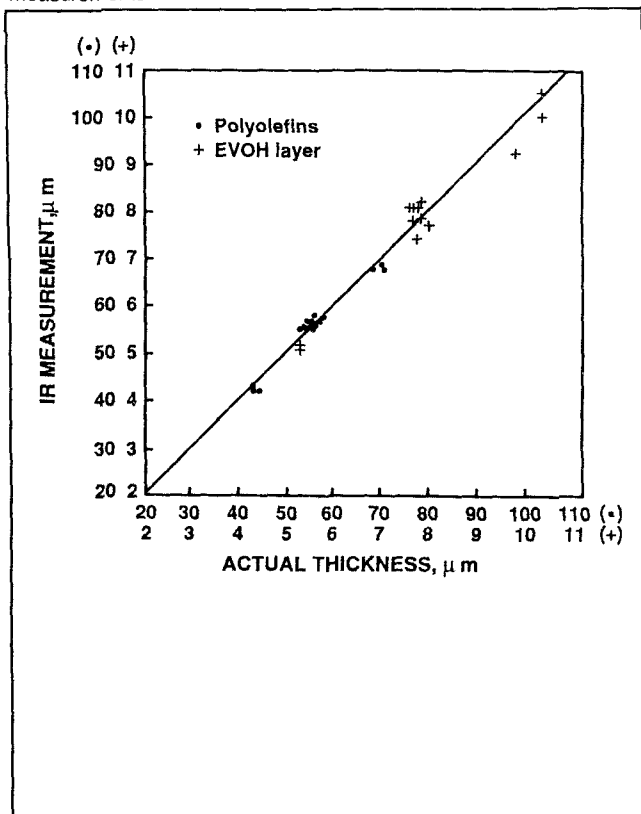
7. Measurement of typical multilayer structures



8. Diffuse NIR and MIR reflection spectra of EVOH and board



9. Comparison of infrared measurements and gravimetric measurements



of the coated film is included before the extruder when the base material is nonuniform.

In the second example shown in Fig. 7, the barrier layers on the inside of a liquid packaging structure are measured in specular reflection against the aluminum foil. The outside PE layer can be measured using the board as a reflector. In this case, an extra measurement is required at a wavelength that is absorbed only by the cellulose to correct the PE measurement for changes in the depth of penetration of the radiation into the board caused by the printing and by changes in the clay coating.

In recent years, the more difficult measurement of coextruded coatings on board has been achieved, principally by study of the NIR and MIR characteristics of all the components, which then leads to the development of a valid mathematical model. Figure 8 shows a spectrum of EVOH, a barrier material currently being investigated as a substitute for aluminum foils in liquid packaging, and a spectrum of board. The overall broad-band absorption of the moist cellulose must be eliminated before the polymer can be measured.

In complex situations such as this, where board is acting as a reflector for coextrusion measurements, changes in the board characteristics (moisture content, filler content, surface conditions, etc.) take on an added importance. It then becomes necessary to measure these changing properties on the base paper, ahead of the extruder, as shown in the third example of Fig. 7. The details of how this is achieved are proprietary information, but the accuracy that can be achieved is shown in Fig. 9.

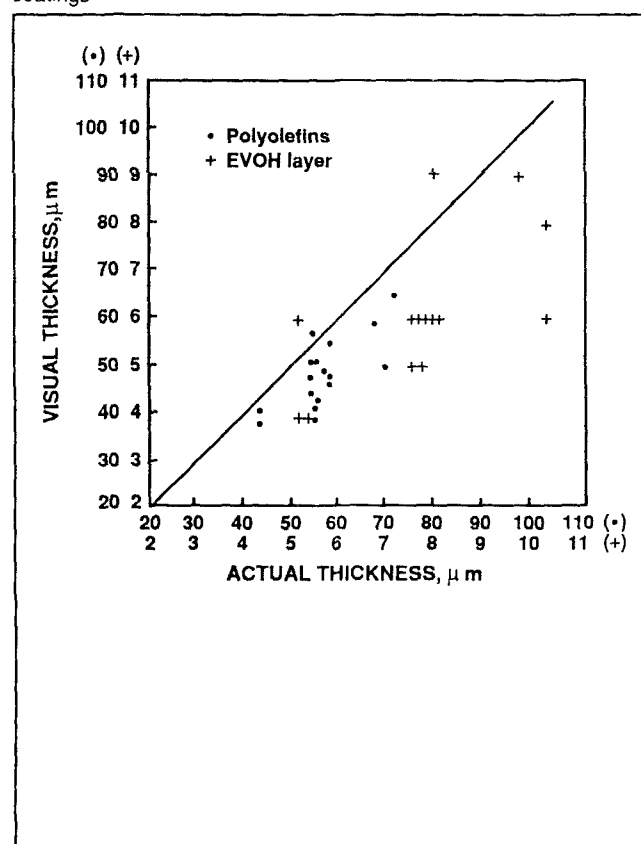
Laboratory checks

The reference to accuracy leads directly into the question of how a user can confirm at any time that the measuring system is reading correctly. Laboratory confirmation of any on-line measurement to within the accuracy specification is difficult under the best conditions; with barrier layer measurement it borders on the impossible. One obvious reason is that the accuracy of most instruments must be in the submicron range to be of any value for on-line control, and the only laboratory technique able to approach this accuracy is precision weighing of a known area. This technique is in common use in measuring total polymer weight. However, the routine separation of a coextrusion into its component parts, followed by the weighing of a known area of each component to within 1%, is beyond the capability of most quality control laboratories. Unless extreme care is taken, the removal of the total polymer from a board substrate results in errors of up to 2 g/m^2 , due to incomplete removal of all the cellulose fibers. Even this level cannot be guaranteed on a routine basis.

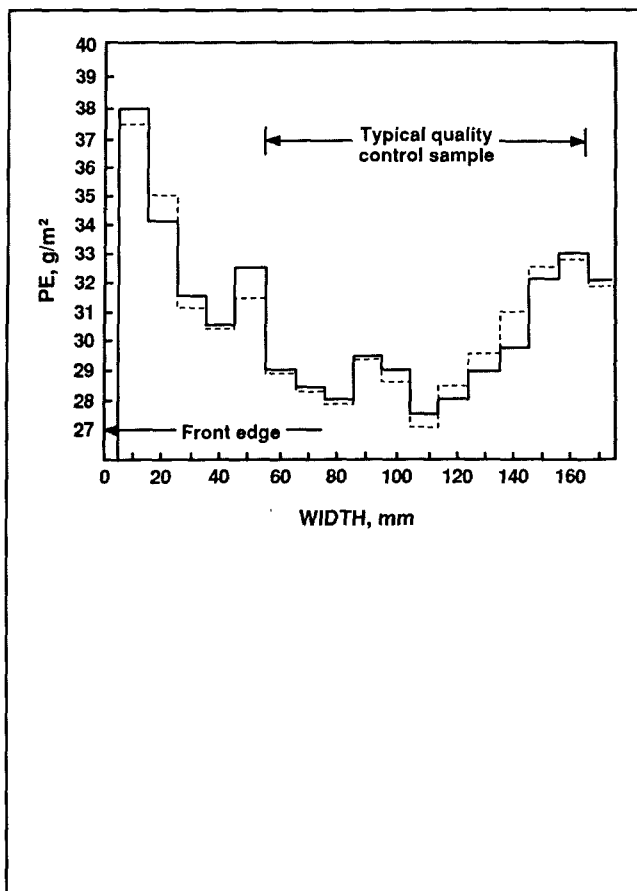
A technique relied upon by many users is the visual inspection and direct measurement of a magnified image of a thin section of the package material, using a combined microtome and phase-contrast microscope. Although the instrument is valuable for a general study of the quality of the extrusion, we have tried different versions and have found that, even in the hands of an experienced user, it cannot achieve the accuracy required to confirm the calibration of an infrared gauge (see Fig. 10).

A less appreciated problem is that almost all extruded

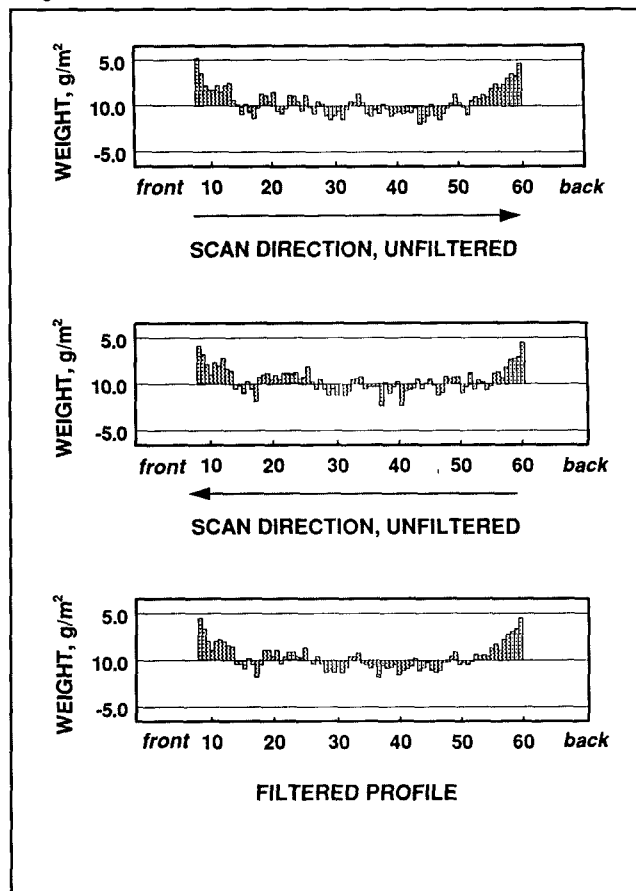
10. Off-line quality control testing of film thickness in multilayer coatings



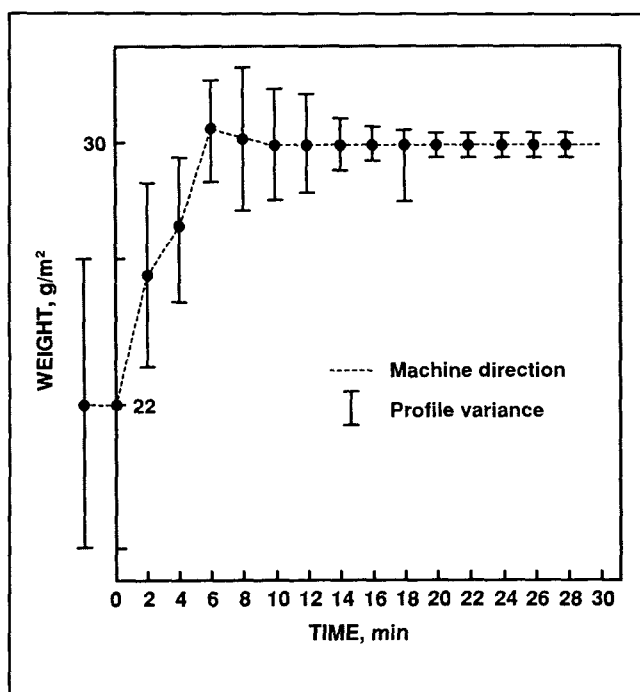
11. High-resolution CD profile for PE extrusion coating on aluminum foil



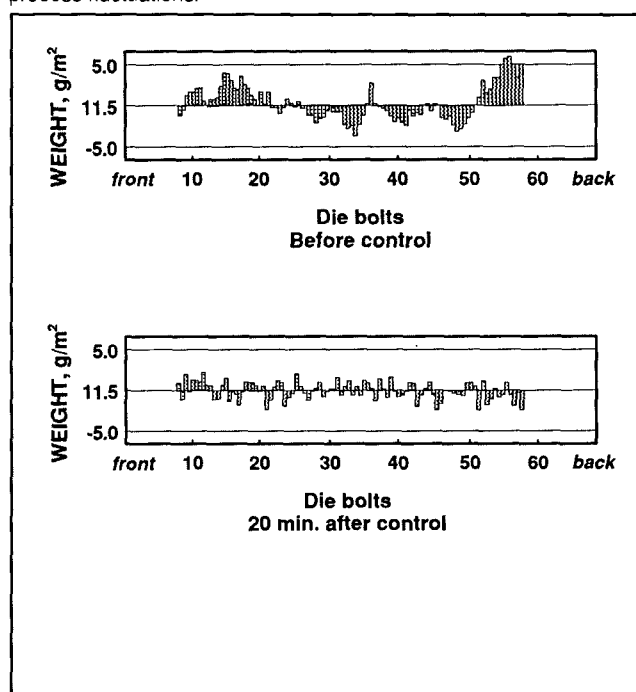
12. Measurement errors can be checked by comparing consecutive unfiltered scans to see if forward and reverse direction displays are congruent.



13. Example of MD and CD automatic control performance. A step change from 22 to 30 g/m² was made at time zero and control was initiated.



14. Typical unfiltered CD profiles for PE extrusion coating on printed clay-coated board. Tolerance limits are 5 g/m² before control and 2 g/m² in the end of control display. Residual deviations are random process fluctuations.



films show a much higher small-scale variation in the cross direction than expected, one too small to be seen with the relatively large sample taken on a routine basis (see Fig. 11). The consequence of this is that the reading from a stationary on-line measuring system can deviate considerably from the laboratory sample taken at the same position. The tests from which Fig. 11 resulted demonstrate that it is possible to cut, separate, and weigh thin strips of polymer (8 mm wide) to within 1% repeatability in order to establish the conformity of the CD profile display. However, the technique is too complex to be used routinely if the results are to be relied on as a calibration check.

At best, a lack of appreciation of these two problems can lead to a lack of confidence in the measurement. At worst, the production manager prevails upon the instrument engineer to adjust the calibration for each new run, eventually destroying the calibration. How then can the accuracy of an on-line measuring system be determined on a routine basis? Briefly, routine sampling of production to determine film thickness is replaced by a one-time intensive effort to establish that the calibration of the on-line gauge is correct, followed by periodic checks of the stability of the gauge as required.

As a start, all visual methods of making routine checks should be abandoned since they lead inevitably to confusion. Instead, a concerted effort should be made to find ways of mechanically or chemically separating the layers of interest. This has been found to be possible, for instance, for PE-ionomer coextrusion coatings by using 1,1,1-trichloroethane, even when the adhesion is well within specification.

There may well be more suitable solvents for this or other structures. Table I (4) is included to assist in identifying them. The technique we have found most effective is to cut lightly around the template through the polymer layer, leaving the base material intact. Next place a drop of the solvent on one corner so that it wets the cut edges. With a sharp knife, lift the upper layer off the second polymer layer and, using a tweezer, peel off by keeping the peel line wet with the solvent. The ionomer layer is then removed with the foil, and the foil etched away with HCl.

Once a method has been established, strips of precisely known width are removed over the full width of the sheet at the end of a reel and the layers are separated and weighed. This is repeated for different coating weights of the same products. The grammage of the layers is then compared with the scan average readings of the measuring system and, if necessary, a correction made to the calibration.

When no further correction is required, a standard reference sample of similar structure should be measured and stored for future reference. This reference sample must be chosen from a region where it has been shown that coating is uniform to assure that slight changes in the position of the sample over the years will have no effect on the reading. The sample should be encapsulated under glass.

There is no need to attempt to prove on a regular schedule that the CD profile of an infrared measurement is correct. Unlike measurements with nuclear gauges, no phenomenon is liable to distort the CD measurement, and

the errors that creep in during sampling are usually much larger than the accuracy in question.

If at any future date the calibration of the gauge is questioned, remeasurement of the standard samples will prove whether or not the gauge is in the same condition as when the calibration was established.

Monitoring the throughput of each extruder is an alternative method of providing a continuous assurance that the measurement has not changed suddenly, causing reject production. Any significant fault occurring suddenly in the measurement will result in a change in the throughput and sound a warning.

Most displays of CD profiles are the average of three or more scans, which can hide measurement errors introduced by the signal handling or by reversing the scan direction, particularly on fast scanning systems. A simple but very effective way of checking for this type of error is to observe individual consecutive unfiltered scans to see if the forward and reverse direction displays are congruent. An example is given in Fig. 12.

Cross-direction control can be applied successfully only after these points have been checked.

Automatic control

Automatic control of machine-direction (MD) changes has been a reality for many years. More recently, techniques have been perfected for the automatic control of the CD profile. The basic requirements for success include the following:

1. A stable measurement of all layers to be controlled, independent of scan direction
2. Fast noise-free measurement that allows high-speed scanning
3. A measuring area that is narrow in the cross direction, allowing measurement right up to the edges
4. Fast and effective separation of the MD and CD components of each scan
5. Stable polymer melt temperatures
6. High-resolution adjustable lip extruder dies
7. An algorithm that relates the point of measurement to the equivalent point across the lip, i.e., correcting for neck-in
8. High-speed computation
9. Algorithms with which the action of a die bolt can be decoupled from that of its neighbor.

Operating personnel often do not understand that a fast-acting MD control can mask any temporary errors caused by short-term changes in either the on-line equipment or in the properties of the base paper. Such errors can seldom be found by routine laboratory sampling.

Again in this case, monitoring of the extruder throughput often can identify changes that can be related to reel changes, scan direction reversals, or automatic standardization cycles. This leads to an understanding of the cause and subsequent correction.

Examples of automatic MD and CD control performance are given in Figs. 13 and 14. Figure 13 shows the progress of the combined controls in response to an offset and a poor CD profile. Both corrections were made

I. Solubility of plastics

Polymer	Solvent	Nonsolvent
Polyvinyl isobutyl ether	Isopropanol, methyl ethylene ketone, chloroform, aromatic hydrocarbons	Methanol, acetone
Polyacrylates and polymethacrylates	Chloroform, acetone, ethyl acetate, tetrahydrofuran, toluene	Methanol, diethyl ether, petroleum ether
Polyacrylonitrile	Dimethylformamide, dimethylsulfoxide, conc. sulfuric acid	Alcohols, diethyl ether, water, hydrocarbons
Polyacrylamide	Water	Methanol, acetone
Polyacrylic acid	Water, dilute alkalis, methanol, dioxane, dimethylformamide	Hydrocarbons, methanol, acetone, diethyl ether
Polyvinyl alcohol	Water, dimethylformamide,* dimethylsulfoxide*	Hydrocarbons, methanol, acetone, diethyl ether
Cellulose	Aqueous cupriammonium hydroxide, aqueous zinc chloride, aqueous calcium thiocyanate	Methanol, acetone
Cellulose diacetate	Acetone	Methylene chloride
Cellulose triacetate	Methylene chloride, chloroform, dioxane	Methanol, diethyl ether
Polyethylene, polybutene-1, isotactic polypropylene	<i>p</i> -xylene,* trichlorobenzene,* decane,* decalin*	Acetone, diethyl ether, lower alcohols
Atactic polypropylene	Hydrocarbons, isoamyl acetate	Ethyl acetate, propanol
Polyisobutylene	Hexane, benzene, carbon tetrachloride, tetrahydrofuran	Acetone, methanol, methyl acetate
Polybutadiene, polysioprene	Aliphatic and aromatic hydrocarbons	Acetone, diethyl ether, lower alcohols
Polystyrene	Benzene, toluene, chloroform, cyclohexanone, butyl acetate, carbon disulfide	Lower alcohols, diethyl ether (swells)
Polyvinyl chloride	Tetrahydrofuran, cyclohexanone, methyl ethyl ketone, dimethyl formamide	Methanol, acetone, heptane
Polyvinyl fluoride	Cyclohexanone, dimethyl formamide	Aliphatic hydrocarbons, methanol
Polytetrafluoroethylene	Insoluble	...
Polyvinyl acetate	Benzene, chloroform, methanol, acetone, butyl acetate	Diethyl ether, petroleum ether, butanol
Methyl cellulose (trimethyl)	Chloroform, benzene	Ethanol, diethyl ether, petroleum ether
Carboxymethyl cellulose	Water	Methanol
Aliphatic polyesters	Chloroform, formic acid, benzene	Methanol, diethyl ether, aliphatic hydrocarbons
Polyethylene glycol tetraphthalate	<i>m</i> -cresol, <i>o</i> -chlorophenol, nitrobenzene, trichloroacetic acid	Methanol, acetone, aliphatic hydrocarbons
Polyamides	Formic acid, conc. sulfuric acid, dimethylformamide, <i>m</i> -cresol	Methanol, diethyl ether, hydrocarbons
Polyurethanes (uncrosslinked)	Formic acid, γ -butyrolactone, dimethylformamide, <i>m</i> -cresol	Methanol, diethyl ether, hydrocarbons
Polyoxymethylene	γ -butyrolactone,* dimethylformamide,* benzyl alcohol*	Methanol, diethyl ether, aliphatic hydrocarbons
Polyethylene oxide	Water, benzene, dimethylformamide	Aliphatic hydrocarbons, diethyl ether
Polydimethylsiloxane	Chloroform, heptane, benzene, diethyl ether	Methanol, ethanol

Appropriate safety measures must be observed when using any of the chemicals listed.

*Often soluble only at elevated temperatures.

simultaneously, resulting in approximately 50% improvement to the profile variance and the offset within 4 min and a further reduction of the variance to 2% in an additional 12 min.

Conclusion

The technology is available now to measure and control any of the packaging structures under consideration. To extract the best performance, however, it is often necessary for the user to obtain a better understanding of some of the fine details of the system, in particular the validity of sampling techniques.

Where sampling techniques cannot be shown to be more accurate than the gauge specifications, it is recommended that regular testing and display of the gauge stability using encapsulated standards be adopted. This approach builds operator confidence and can predict real trends in the calibration.□

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