

In-line composition monitoring of molten poly(ethylene vinyl acetate)

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ABSTRACT: Poly(ethylene vinyl acetate) (EVA) is a very common polymer used in hot melt adhesives. The rheological and thermal-mechanical properties of these adhesives are strongly related to the content of vinyl acetate (VA) incorporated into this random copolymer during polymerization. Results are presented of in-line monitoring of VA content in flowing molten EVA. The method used is fiber optic near infrared spectrometry. This method is discussed in detail and observations are made on how in-line fiber optic monitoring could be extended to quantitatively measure the composition of a flowing melt adhesive, e.g., polymer, tackifier, viscosity reducing diluent, antioxidant, etc.

KEYWORDS: Adhesives, concentration, EVA polymers, hot melts, monitoring, on line measurement, quality control, vinyl acetate.

Poly(ethylene vinyl acetate) (EVA) copolymers are random copolymers that are obtained by the copolymerization of ethylene with vinyl acetate, under high pressure. The incorporation of VA reduces the crystallinity of the polymers which, in turn, improves their flexibility, clarity, and impact strength, and reduces the hardness. Variations in the concentration of vinyl acetate leads to variations in the properties of EVA copolymers, which are used for a variety of applications. Low concentrations of vinyl acetate (VA) (less

than 20 wt%) are primarily used to make extruded film for flexible packaging. The rubber-like properties of the polymers are used in applications such as bumper pads, flexible toys, etc. Concentrations of VA greater than 20 wt% are mainly used as hot-melt adhesives by further mixing the copolymers with waxes and tackifiers. Thus, the properties of the polymers are largely dependent on the concentration of vinyl acetate in the polymer. For quality control purposes, it is therefore imperative that the VA concentration be moni-

tored. In-line monitoring is desired not only for its numerous advantages (such as high-quality products, lower waste, lower developmental cycle time, and lower costs) but also because it eliminates the sample handling concerns associated with molten polymers.

Experimental

The copolymer samples were obtained from two sources and they will be referred to henceforth as Class I and Class II. Class I comprises 16 samples of EVA copolymers and Class II comprises 8 samples of EVA copolymers. The concentration of vinyl acetate in the 24 samples has been tabulated in Table I. The chemical structure of the copolymer is illustrated in Fig. 1. The melting point of the EVA copolymers lies in the 103–108°C temperature range. Processing temperatures range from 150°C to 210°C.

Figure 2 shows the schematic of the system for in-line molten polymer analysis. A variable path length flow cell (Fig. 3) is attached to the exit port of the gear pump of a 3/4-in. single screw extruder. Fiber optic probes are installed in the flow cell such that their separation could be varied by using spacers of different thicknesses. These probes are connected via fiber optic cables to a Guided Wave Model 260 spectrophotometer that uses a tungsten halogen lamp, a lead sulfide detector, and a holographic diffraction grating. The spectrophotometer is inter-

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faced to a computer for data acquisition.

All polymer samples were extruded at a fixed setpoint temperature of 200°C. The screw speed (20 rpm) and flow rate (1.2 lb/h) were kept fixed for all except three (samples 10, 12, and 13 of Class I) of the samples. These three samples had a very high melt index and had to be extruded at a higher flow rate (2.4 lb/h) in order to prevent the polymer flow stream from draining out of the flow cell and forming bubbles in the optical measurement beam. The maximum pressure attained downstream of the gear pump was about 1400 psi. A fixed path length of 2.5 mm was used throughout the experiments. This path length ensured that the maximum absorbance was less than 1.0 absorbance unit (AU). A continuous purge of dry nitrogen gas in the hopper prevented any moisture absorption from the ambient atmosphere. The spectral data for the two sets of polymers were collected on two separate days.

Results and discussion

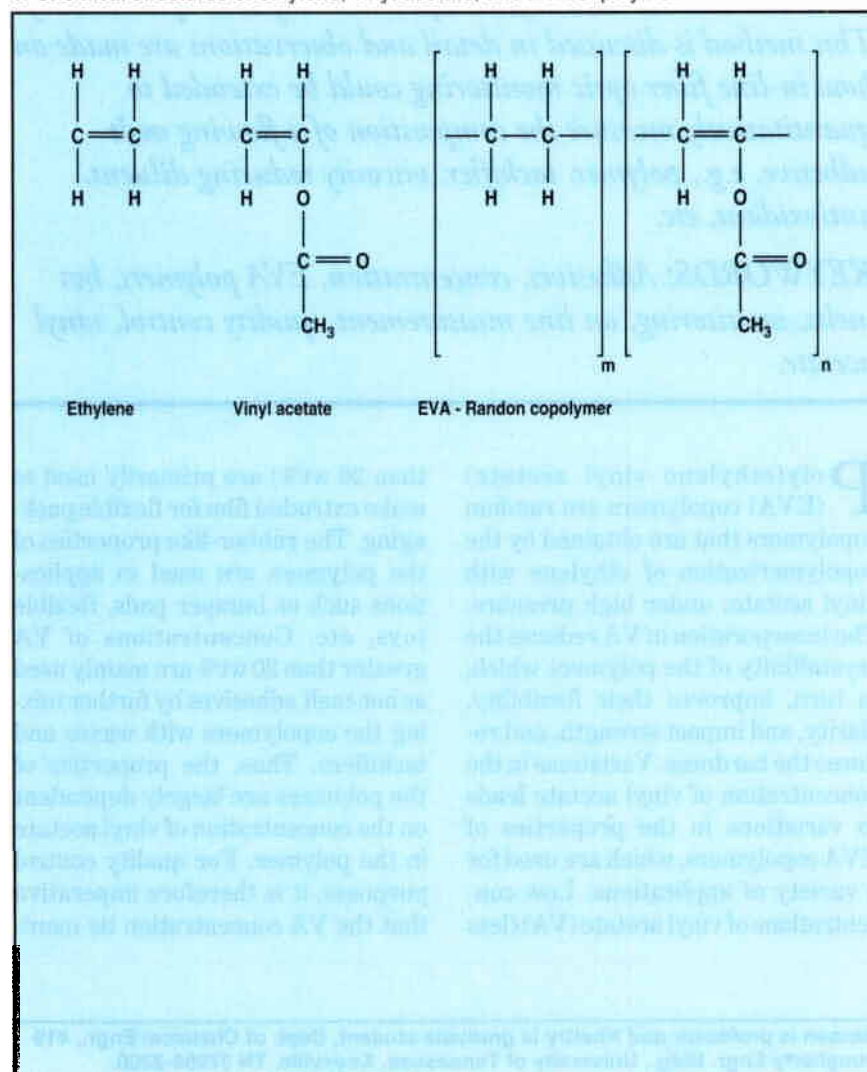
Figure 4 shows the overlaid spectra of polyethylene (PE) and EVA containing 28 wt% VA. The spectrum of pure polyvinyl acetate (PVA) has also been overlaid on the spectra in order to determine spectral features that could be attributed to vinyl acetate. The structure of the copolymer (Fig. 1) shows that although both the comonomers have C-H vibrations, the vibrational overtones and combinations of the C=O stretch, if identifiable and distinct, could be used to quantify the amount of VA present.

A closer look at Fig. 4 shows that there are some changes in two spectral regions: (a) spectral region A, which comprises wavelengths 1600–1950 nm, contains the first overtones of the C-H vibrations (1–3); and (b) spectral region B, which comprises wavelengths 2000–2200 nm, contains combination bands (1–3). These two regions have been enhanced in Figs.

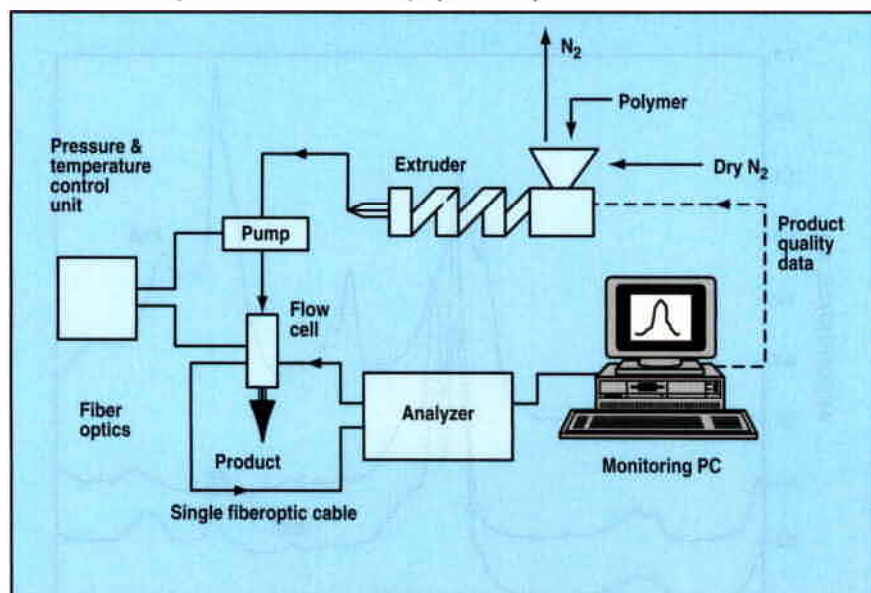
I. Details of 24 EVA samples used in the study

Class I		Class II	
Sample number	Wt.% VA	Sample number	Wt.% VA
1	0	1	18.72
2	9.08	2	18.82
3	9.11	3	21.01
4	12.12	4	20.90
5	12.04	5	26.70
6	15.18	6	26.87
7	17.91	7	34.80
8	18.06	8	34.95
9	24.89		
10	25.22		
11	28.49		
12	27.84		
13	28.59		
14	28.37		
15	32.05		
16	35.57		

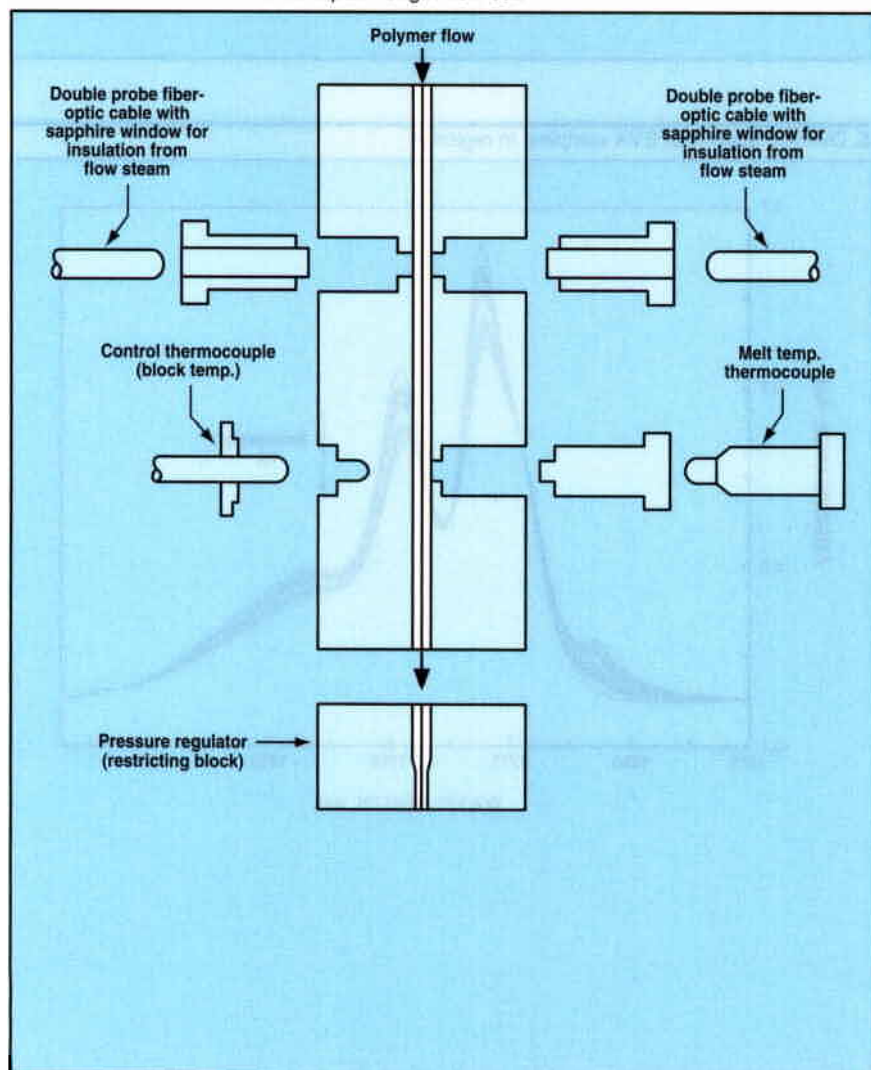
1. Chemical structures of ethylene, vinyl acetate, and EVA copolymer



2. Schematic of system for in-line molten polymer analysis



3. Detailed schematic of variable path length flow cell



5 and 6, respectively. Spectral region A shows that the incorporation of VA leads to a decrease in the intensity of the polyethylene doublet around 1700 nm. This doublet in polyethylene is probably due to the methylene stretch (3). With the incorporation of VA into the chain, there is a decrease in the overall methylene content that leads to a decrease in the intensity of the methylene doublet. The presence of VA also leads to subtle changes in the slope of the methylene doublet. Furthermore, there is a small peak at about 1680 nm that evolves with the increase in VA concentration. This peak is also present in the spectrum of pure PVA and is absent in the spectrum of pure PE. Thus, this peak can definitely be assigned to VA and is probably an overtone of the methyl group in VA (3, 4). The slight variation in the slope of the methylene overtone around 1700 nm is possibly due to the superposition of the VA absorbance in this region.

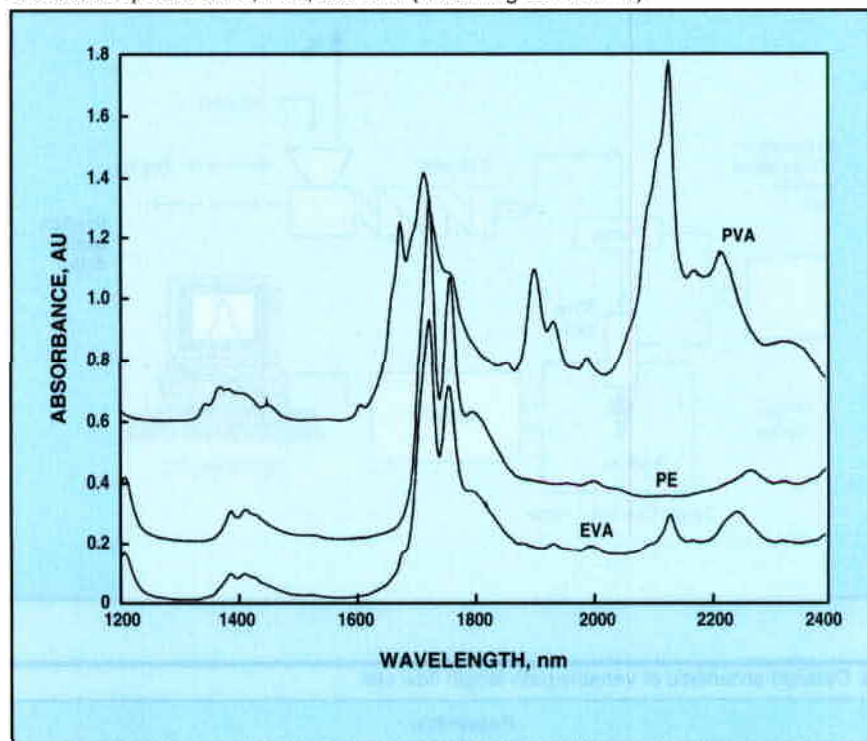
In the spectrum of pure PVA, there are some distinct peaks around 1900 nm and 2100 nm. The second overtone of the carbonyl band is known to exist in the 1900–2000 nm range (3, 5), while a combination band of C–H stretch and C=O stretch is known to exist around 2140 nm (6). In the spectra of EVA samples, there is a peak present at about 2135 nm, which evolves with increase in VA content. Although the intensity of this peak (2135 nm) is much lower than the C–H overtone peaks, it shows the variation in VA content much more clearly. Our conjecture is that this peak (2135 nm) is a combination band of C–H stretch and C=O stretch.

The spectral data of samples in Class I were used for multivariate analysis and for developing calibration models relating the spectral changes to variation in VA content. Ten spectra corresponding to each of the 16 samples were chosen for data analysis. These 160 spectra were divided into two groups comprising 80 spectra each (five spectra for each

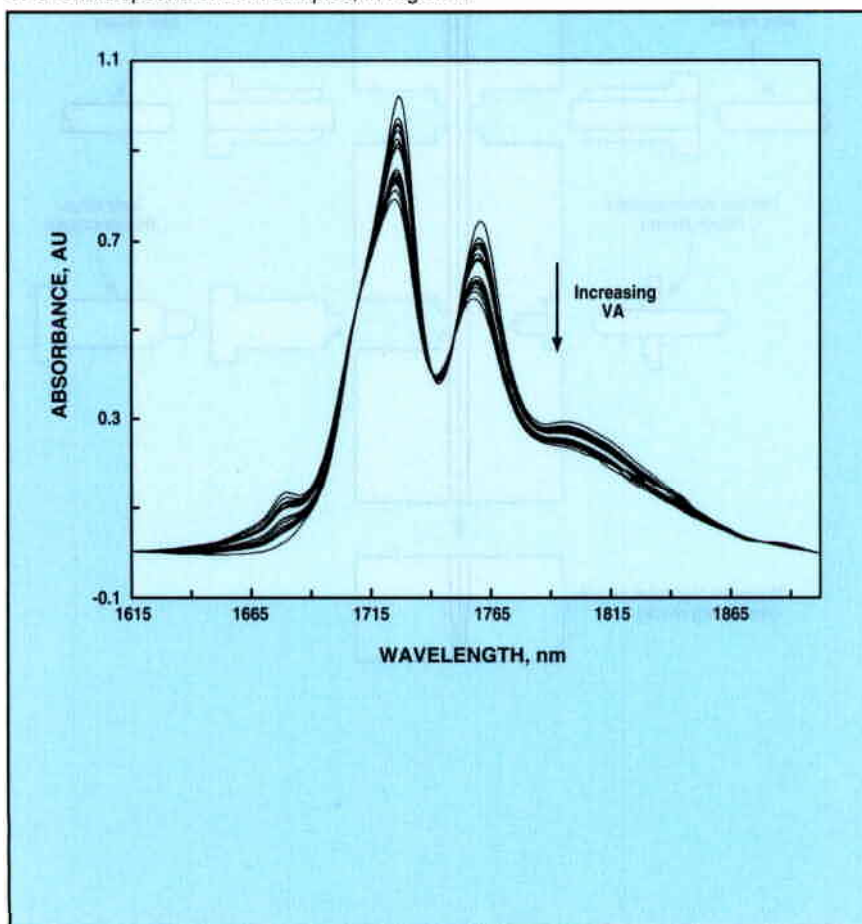
of the 16 samples), one for calibration and the other for validation. Since the number of samples in Class II was not very high, it was decided that the spectral data of the Class II samples will be used to verify the robustness of the calibration models developed on Class I samples. Both of the spectral regions were treated separately for data analysis. Spectral pretreatment consisted of removing baseline offsets by one of two methods: (a) simple 2-pt. baseline correction; and (b) computation of the first derivative of the spectra. The sloping-baseline corrected data are more useful in qualitative analysis, but sometimes they may not be as accurate as the derivative spectra, which not only provide a very flat baseline but also expose many subtle variations in the spectra. On the other hand, derivative spectra are very noisy and have to be repeatedly smoothed before performing any kind of multivariate analysis. In forming the data sets, the 1615–1903 nm wavelength range was used for the first spectral region, while the 2077–2161 nm range was used for the second spectral region. From the calibration data (80 spectra), four data sets, two sets each (derivative and baseline corrected data) corresponding to the two spectral regions, were constructed. The four data sets were then used as calibration sets, and the multivariate technique of partial least squares (PLS) was used. The optimal number of factors was determined using the leave-one-out cross-validation method (4) and was found to be one factor. This result explains that there is one prominent source of variation in the data, i.e., the VA content.

From the validation data (80 spectra), just as from the calibration data, four data sets were constructed for validation purposes. The predictive ability of each of the four calibration models, developed above, was tested by using the corresponding validation set for predictions. By using one factor, the standard errors of pre-

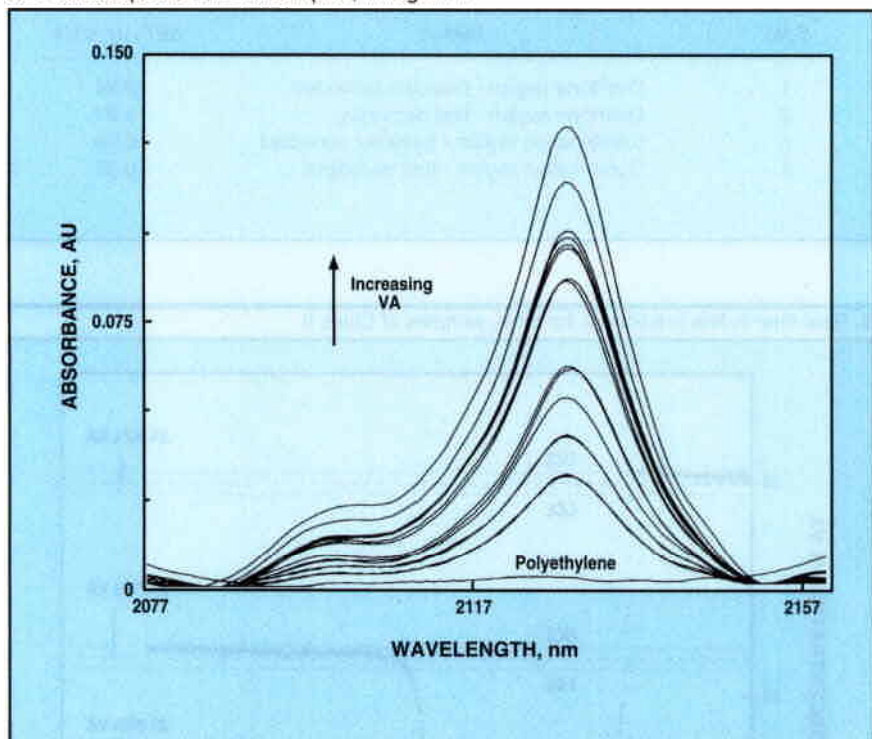
4. Overlaid spectra of PE, PVA, and EVA (containing 28 wt % VA)



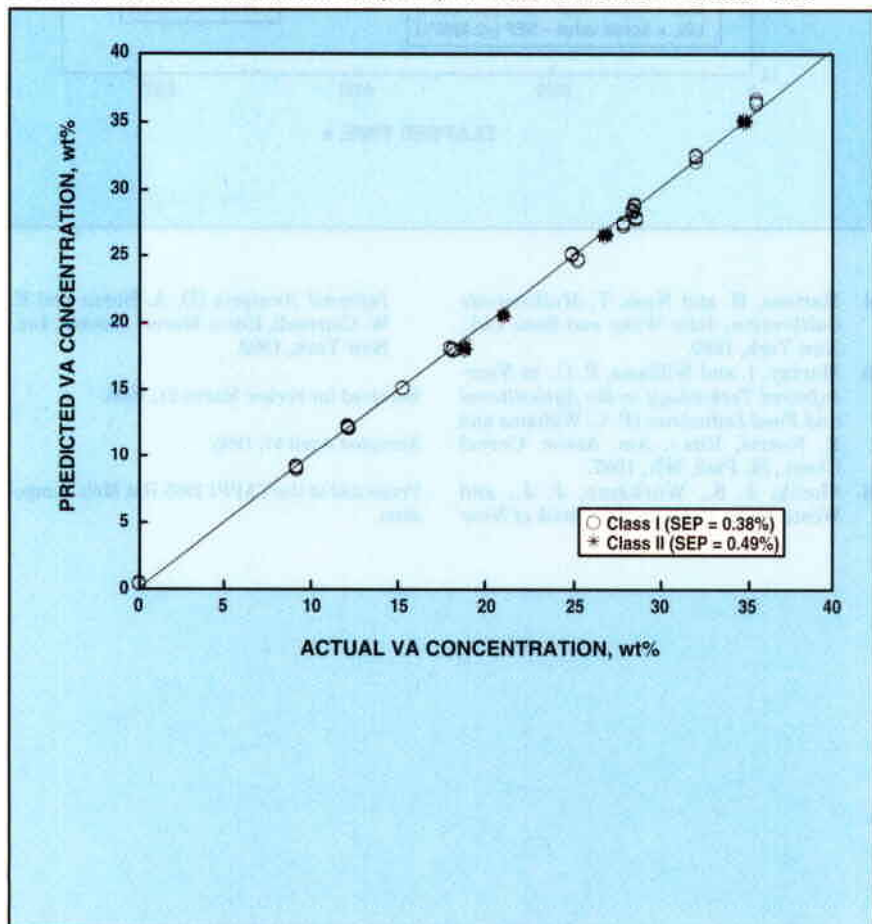
5. Overlaid spectra of EVA samples, in region A



6. Overlaid spectra of EVA samples, in region B



7. Predictions of the calibration model (No. 4) for Class I and Class II validation sets



diction for the four data sets were computed, and they are tabulated in **Table II**. The performance of the combination region was better than that of the overtone region. This is because the peak in the combination region is exclusively a VA peak, and is absent in the spectrum of polyethylene. In both regions, the derivative spectra provided better results than the baseline corrected data. This is because 2-pt. baseline-correction does not remove baseline offsets completely. Moreover, the information content of the near-infrared spectra is quite complex due to the presence of overlapping absorbances. The derivative spectra help to alleviate this complexity by deconvoluting many subtle variations and overlapping peaks in this region.

The multivariate analysis of the EVA spectra leads us to conclude that one-factor calibration models on derivative data in the 2077–2161 nm wavelength range are most ideal for correlating the VA content in the copolymers. The robustness of this calibration model was tested by using the spectral data obtained from Class II samples. Ten spectra corresponding to each of the eight samples were chosen for data analysis. The first derivative data, in the 2077–2161 wavelength range, were used to construct the data set. It was found that one-factor models provided the best results with a standard-error-of-prediction (SEP) as low as 0.49 wt%. This test proved two points: (a) the calibration models are robust; and (b) the optimal number of factors is indeed one. The predictions for VA concentration for both the validation sets (i.e., Class I and Class II) are shown in **Fig. 7**.

Finally, the ultimate test of the robustness of the calibration model was to use the model for real-time in-line predictions. For real-time predictions, the “Monitor” module of the Guided Wave spectral system software was used. This module acquires spectral data in real-time, pre-

processes them as instructed, and then uses an existing model for predictions of the calibrated properties (such as concentration, etc.). Three samples of Class II were used for real-time predictions and the calibration model for derivative data in the combination region was used. Each prediction took about eight seconds. The real-time in-line predictions have been illustrated in Fig. 8. It can be seen that almost all the data points lie within the control limits. The control limits were determined by the SEP value of the model for Class II samples.

Conclusions

In-line monitoring of the VA content in molten EVA copolymers is extremely useful for quality control. The study has demonstrated that near infrared (NIR) spectroscopy, coupled with fiber optics and chemometric data analysis, is ideal for real-time analysis of VA content in molten EVA copolymers. The robustness of the calibration models was tested by using data from two independent sources, and also during real-time in-line predictions. In each case, the results were very promising for implementation in a polymer manufacturing plant. ■

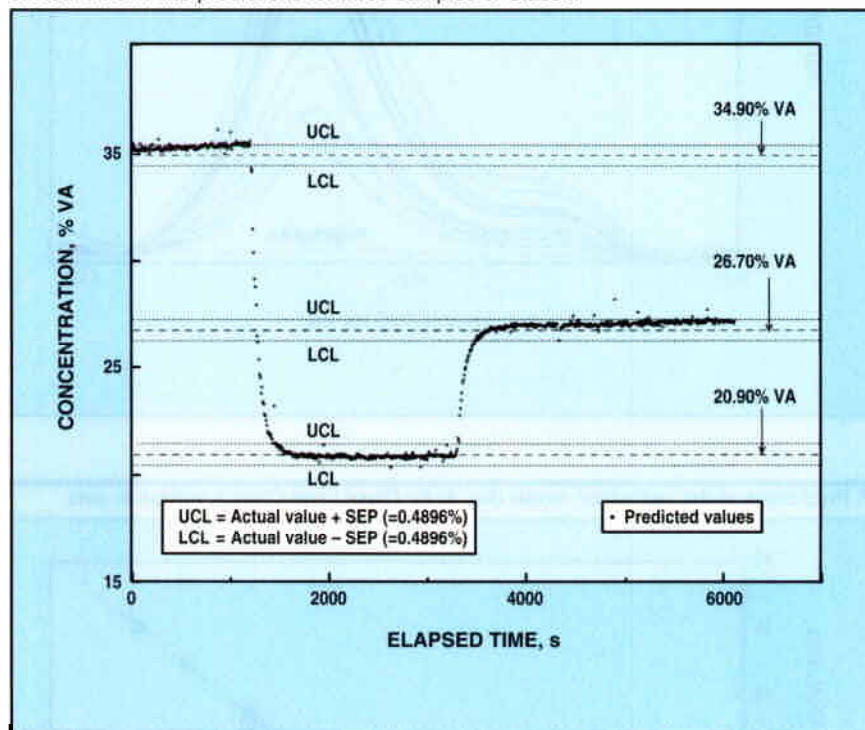
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II. Predictions of the four calibration models for the Class I validation sets

S No.	Method	SEP, wt % VA
1	Overtone region - baseline corrected	0.94
2	Overtone region - first derivative	0.83
3	Combination region - baseline corrected	0.79
4	Combination region - first derivative	0.38

8. Real-time in-line predictions for three samples of Class II



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