

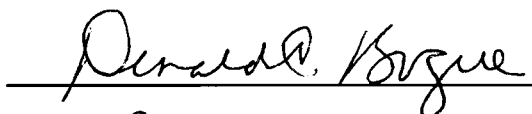
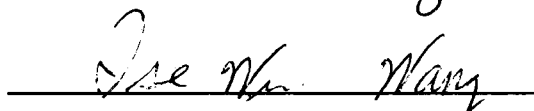
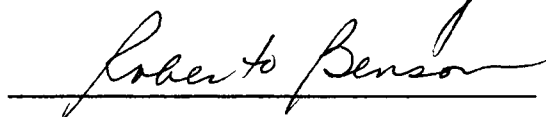
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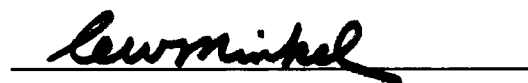
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**IN-LINE FIBER-OPTIC SPECTROSCOPY:
APPLICATIONS TO POLYMER PROCESS MONITORING**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Srinivas Vedula

May, 1997

DEDICATION

To my parents,

Mrs. Nirmala Vedula

and

Mr. Subramanyam Vedula

for their love and sacrifice.

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ABSTRACT

Near-infrared (NIR) spectroscopy has several advantages over conventional mid-infrared (MIR) techniques, such as remote data collection coupled with rapid data analysis methods, availability of fiber-optics, and lack of sample handling problems. These advantages have led to the widespread use of NIR spectroscopy for in-line chemical process measurements. Earlier research studies have addressed problems related to development of fiber-optics, feasibility of in-line monitoring of processes in harsh process environments, data analysis techniques, new process applications, and real-time process control strategies. In the area of polymer process engineering, NIR spectroscopy is being primarily used for measurements of polymer composition in copolymers, polymer blends during extrusion and injection molding; monitoring reaction kinetics; and estimation of physical properties, such as density, relative viscosity, *et cetera*.

In this research, the applicability of NIR spectroscopy has been extended to make simultaneous measurements in an in-line extrusion process of rheological properties and composition of flowing polymer melts. A methodology is proposed and demonstrated for estimating polymer melt index and linear viscoelastic properties for a system of ethylene-vinyl acetate random copolymers. This methodology involved developing calibration models, which were subsequently utilized for real-time monitoring. Qualitative analysis is provided for assignation of spectral regions for the rheological properties and the comonomer ratio. The research also addressed the issue

of in-line polymer additive monitoring using fiber-optic near-infrared and ultraviolet spectroscopy. Predictive calibration models and exploratory data analysis techniques were used as definitive studies for examining the feasibility of in-line trace-level additive monitoring.

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NOMENCLATURE

Symbol	Abbreviation	Description
α		Matrix of regression coefficients, obtained from PLS regression
β		Regression coefficient vectors, obtained from PLS regression
ΔE_m		Energy change, [J]
Δv		Change in vibrational quantum number
Δj		Change in rotational quantum number
ϕ		Phase Angle
η_0		Zero shear viscosity, [Pa.s]
$ \eta^*(\omega) $		Complex viscosity, expressed as a function of ω , [Pa.s]
μ		Reduced mass of two atoms
ν		Frequency of radiation
Σ		Diagonal matrix with singular values as diagonal elements
σ		Singular value
ω		Angular frequency, [rad/s]
A		Absorbance
a		Absorptivity of a chemical species, in Beer-Lambert's law
a		Berry-Fox exponent
B		Matrix of regression coefficients, obtained from PLS regression

C	Concentration matrix
c	Concentration in Beer-Lambert's law
d_{ab}	Euclidean Distance between any two samples
d_{max}	Maximum inter-sample distance within a given cluster
E	Residuals matrix, obtained from PCA, PCR, or PLS analysis
E_p	Energy of a photon, [J]
EVA	Ethylene-vinyl acetate copolymer
F	Residuals matrix, obtained from PLS analysis
f	Effective rank of X
$G'(\omega)$	Storage modulus, expressed as a function of ω , [Pa]
$G''(\omega)$	Loss modulus, expressed as a function of ω , [Pa]
h	Planck's constant
I	Intensity of radiation
I_0	Intensity of radiation incident on sample
j	Index
K	Absorbance matrix of pure analytes
K	Number of nearest neighbors in KNN validation
k	1. Force constant for a harmonic oscillator 2. Index
l	Optical pathlength in Beer-Lambert's law
LAS	Leave-a-sample cross-validation approach

LDL	Lower detection limit
MD	Mahalanobis distance
MI	Melt Flow Index, [g/10 min]
MIR	Mid-infrared
$\overline{M}_w$	Weight average molecular weight of the polymer, [g/mol]
MWD	Molecular weight distribution in the polymer
m	1. Mass of a molecule 2. Index, number of rows in a matrix
NC	Number of samples in calibration set
NP	Number of samples in prediction set
NIR	1. Near-infrared 2. Used as a subscript to denote results from regression with NIR data
NV	Number of samples in validation set
n	1. Discrete energy level quantum number 2. Index, number of columns in a matrix
p	Index
PCA	1. Principal component analysis. 2. Used as a subscript to denote results from PCA analysis
PCR	Principal component regression
PE	Polyethylene
PLS	Partial least squares
PLS-1	PLS regression of one dependent variable

PLS-2	PLS regression of multiple Y data
PP	Polypropylene
PRESS	Predicted residual sum of squares
r	Correlation Coefficient
reg	Used as a subscript to denote a regenerated matrix, after PCA analysis
SEC	Standard error of calibration
SEP	Standard error of prediction
SVD	Singular value decomposition of a matrix
s	Similarity distance
T	Scores matrix
T	1. Transmittance 2. Used as a superscript to denote transpose of a matrix
t	Score vector, column of matrix T
U	Scores matrix or left eigenvector, obtained from SVD analysis
U_q	Potential energy
UDL	Upper detection limit
UV	Ultraviolet
u	Vector of matrix U
V	Right singular vector, obtained from SVD
VA	Vinyl acetate comonomer, in EVA copolymer
W	Matrix containing loading weights, obtained from PLS regression

$\mathbf{X}$	NIR absorbance data matrix
X_e	Anharmonicity constant
x	Displacement for a Hookean spring
$\mathbf{x}$	Independent variable vector
$\mathbf{Y}$	Rheology data matrix
Y_e	Anharmonicity constant
$\mathbf{y}$	Vector, column of $\mathbf{Y}$
$\wedge$	Symbol used to denote estimated values of variables, obtained from regression

CHAPTER 1

INTRODUCTION

Within less than a century of its inception, the field of polymer science has advanced to a stage where polymers have become a part of everyday life. Polymers, or plastics, have numerous applications in diverse markets — clothing, food packaging, transportation, construction, healthcare, *et cetera*. Such applications are brought about by the unique properties of polymers, such as design flexibility, economy, light weight, *et cetera* [1]. With this diversity in polymer uses, comes the need to characterize them in terms of their chemical constitution and their physical properties. Such characterization would allow suitable choice of a polymer with desired, required properties for a given need. Therefore, the growth in the production and usage of polymers can be attributed to the advances in analytical technology that are used for polymer characterization.

Some of the more frequently used analytical techniques for determining useful properties of polymers are as follows: (1) infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) for measuring composition, crystallinity, and structural properties, (2) X-ray diffraction studies for crystallinity measurements, (3) thermal analysis studies for measurements of melting and glass transition temperatures, (4) gel permeation chromatography (GPC) analysis for measurements of average polymer

molecular weight and molecular weight distribution, and (5) rheological measurements for characterizing the mechanical properties. Although most of these techniques provide extremely useful information about polymer physics and chemistry, they require elaborate sample preparation procedures, and can be relatively time consuming. This is especially the case when the thickness of the sample has to be reduced, or when special arrangements have to be made for off-line experimental analysis. Often it is crucial to control material properties in an on-line process for polymer manufacture, such as extrusion, fiber spinning, injection molding, *et cetera*. In such a case, analytical methods are required which can provide rapid analyses. These measurements can then be used for feedback process control to obtain the desired polymer properties.

In the last decade, fiber-optic near-infrared (NIR) spectroscopy has proved to be a viable alternative for such rapid, non-destructive analysis, and it has replaced some of these conventional techniques in real-time process monitoring. Sample preparation for NIR analysis requires minimal technical effort, and is a simple and reliable routine implementation. With the introduction of light fiber-optics, and development of rugged mathematical analysis, NIR spectroscopy has found numerous, successful applications in remote, real-time process control and monitoring in the field of polymer science [2-6].

The success of NIR spectroscopy lies in the ease and speed with which quantitative and qualitative information can be obtained. To address this issue, several

studies have been conducted on development of fiber-optics for the study of polymer melts [7,8], measurement of chemical properties of bulk polymers [9], real-time composition monitoring, *et cetera* [10-13]. Much of the focus in these studies has been on making measurements of chemical composition, and of physical properties directly related to composition, such as density, relative viscosity, *et cetera*. There has been little effort to obtain important information, other than the chemical composition, from the NIR spectra. The rationale behind the current study is to develop a “secondary” methodology using NIR spectroscopy to estimate polymer rheological properties in an extrusion process. Industrially important rheological properties (which give information about the end-use properties of polymers), such as melt flow index (MI), and linear viscoelastic properties, will be considered for study. Another key issue on which very little work has been done before is related to monitoring very low concentrations of additives. This dissertation project aims to address this feasibility problem of utilizing the NIR region for trace-level additive quantification.

The layout of this compilation is summarized below. Chapter 2 provides a brief introduction into the theory of NIR spectroscopy with regard to origin of spectra, typical band assignments, and some common NIR applications to polymers. In this chapter, an overview is presented of data analysis techniques, which are based on multivariate statistical methods. The specific objectives of the current research are outlined in Chapter 3. A detailed description of the experimental system used for this dissertation work will be given in Chapter 4. Chapters 5 and 6 will address the

aforementioned objectives with details of experimental work, data analysis, and discussion of results. Chapter 5 will focus on the problem of simultaneous estimation of polymer rheological properties in conjunction with measurements of polymer composition on a system of random copolymers. Chapter 6 will address the issue of in-line monitoring of polymer additives. Feasibility studies will also be carried out to explore UV spectrometry as a viable alternative for in-line polymer additive monitoring. Conclusions from the above studies and future directions will be discussed in Chapter 7.

CHAPTER 2

NIR SPECTROSCOPY — AN OVERVIEW

INTRODUCTION

The electromagnetic spectrum consists of vibrations ranging from several meters to less than 0.01 nm (nanometers). These vibrations are of several types, for example spin orientations in a magnetic field, molecular rotations, molecular vibrations, electronic transitions, nuclear transitions, *et cetera*. The occurrence of a vibrational mode in a particular wavelength region of the electromagnetic spectrum depends on the type of vibration, as described above. A schematic of the electromagnetic spectrum, as shown in Figure 2.1, indicates the position of the NIR wavelength region of 700–2,500 nanometers (nm) relative to the infrared region of 2,500–25,000 nm. The spectral signatures in the IR and NIR region are attributed to molecular vibrations.

2.1 NATURE AND ORIGIN OF NIR SPECTRA

Organic matter consists of atoms that combine by covalent and electrovalent bonds to form molecules. Because of the nature of these bonds, the molecules vibrate at some characteristic frequencies. In the absence of any external influence, this is termed as the ground state, or the normal mode of vibration, for the molecules.

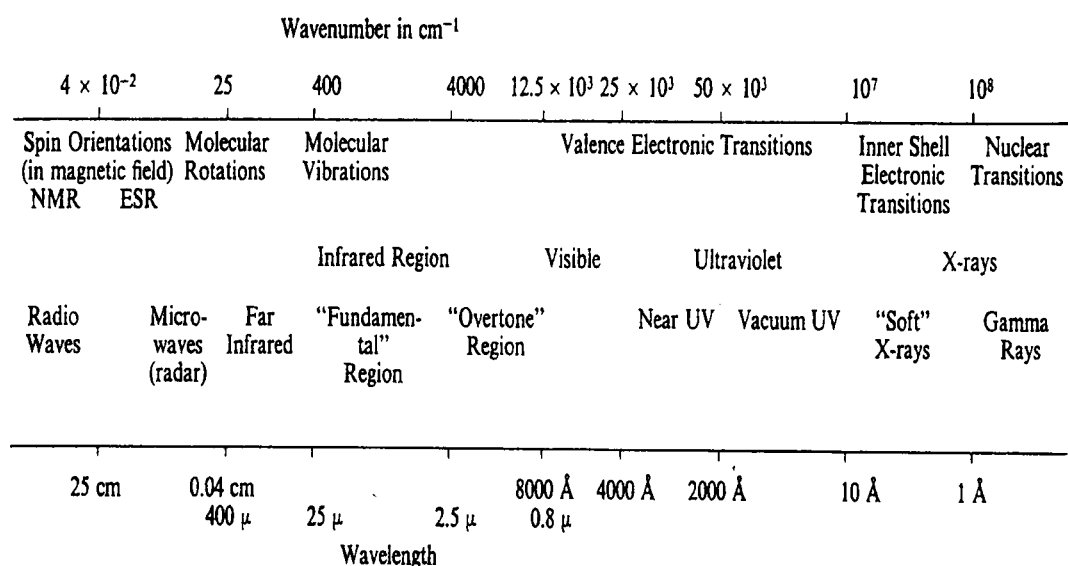


Figure 2.1 Location of the near-infrared (NIR) region in the electromagnetic spectrum.

[Source: R. P. Bauman, *Absorption Spectroscopy* (John Wiley & Sons, Inc. New York, 1962).]

Typically, the normal mode frequencies correspond to the wavelengths in the infrared region of the electromagnetic spectrum. When these molecules are irradiated by an external source of energy, they acquire the potential for energy changes. The energy of a photon (unit of radiation) is related to the wavelength at which it is emitted by the expression:

$$E_p = h\nu \quad \dots(2.1)$$

where

h = Planck's constant

ν = frequency of radiation

The energy of the photon is absorbed by the molecules. This causes an increase in the vibrational, rotational, or electronic energy of the molecule by an amount ΔE_m , which is equal to the energy of the photon. Molecules can only absorb photons that are of an energy coincident with the characteristic vibrations of the molecule and that excite the molecule to a higher energy level. These energy changes, which are marked by changes in the vibrational and rotational quantum numbers, are represented by Δv , vibrational energy changes, and Δj , rotational energy changes [14-16]. A transition from the ground state, corresponding to the lowest energy state, to the next highest energy level, the new energy state, is represented by v_1j_1 and the absorption is called *fundamental absorption*. If the molecules absorb sufficient energy, they reach higher energy levels (v_2j_2 , v_3j_3 , *et cetera*), and these absorbances are called *overtone*s. The intensity of the first overtone (corresponding to energy level v_2j_2) is weaker than the

fundamental absorption, as fewer molecules reach this energy level, and such a trend continues for higher overtones. The intensity of absorption decreases by roughly a tenth in energy for each successive energy level. *Combination bands* occur when the absorbed photon excites two or more vibrational modes simultaneously. Therefore, combinations can be viewed as the average frequency of two adjacent molecular motions in a molecule. For a combination band to occur, the proximity of the atoms is more important than the nearness of the energy levels [17].

Most fundamental molecular vibrations occur in the mid-range infrared, or mid-infrared (MIR), region of the electromagnetic spectrum (2,500 nm - 10,000 nm). This explains the strong “fingerprint” type of spectral signature typically observed in the MIR region [14,15]. The first and second overtones occur at approximately one-half and one-third the wavelength of the fundamental, respectively. As a result, most overtones and combination bands are observed in the NIR region. Often, the overtone and combination vibrations occur at neighboring frequencies. This proximity leads to the formation of broad overlapping absorbance bands in the NIR region [5,6,16].

2.1.1 Anharmonicity and Criteria for NIR Absorption

Infrared radiation absorbed by a molecule causes individual bonds to vibrate in a similar manner to that of a simple harmonic oscillator. Therefore, many of the fundamental frequencies can be roughly calculated by assuming that the molecules exhibit harmonicity. The potential energy, U_q , for the vibrations of an ideal diatomic

harmonic oscillator is given by Hooke's Law, which is described by the equation [5,6,16-18]:

$$U_q = -kx^2 \quad \dots(2.2)$$

where

k = force constant

x = displacement

The frequency, ν , for such an oscillator is given by the expression:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots(2.3)$$

where

μ = reduced mass of the two atoms

The reduced mass can be written in terms of the individual masses of the molecules, m_1 and m_2 , as follows:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots(2.4)$$

This expression would work well for true diatomic molecules, and is not far from the average value of two atoms stretching within a polyatomic molecule. The masses of atoms and the binding forces combine to form harmonic oscillators, which vibrate at frequencies corresponding to infrared radiation. Quantum mechanical treatment of the harmonic oscillator restricts the energy, at any given time, to discrete energy levels. The energy of vibration of a two-particle system is given by the expression:

$$E_n = \left(n + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots(2.5)$$

where

E_n = energy value of a discrete quantum number

n = the vibrational quantum number

For the ideal harmonic oscillator, quantum mechanical selection rules forbid transitions between more than one energy level. The separation between two successive energy levels is given by the expression:

$$\Delta E = E_n - E_{n-1} = h\nu(n - (n-1)) = h\nu \quad \dots(2.6)$$

The ideal potential energy parabola described using Eq. (2.2) is shown in Figure 2.2. In such an ideal case, only fundamental vibrations would be observed, and there would be no NIR spectrum.

In reality, the so-called ideal harmonic oscillator has limitations. At higher vibrational states, the molecules exhibit non-ideal behavior. Again, this can be explained with reference to Fig. 2.2. In the extreme case, when a molecule contains a high level of potential energy, it can no longer return to its equilibrium position and tends to dissociate. Therefore, the ideal potential energy curve is distorted, and becomes asymmetrical. The actual behavior is now explained by adding higher order terms to the potential energy term in Eq. (2.5). This phenomenon can be represented by the expression:

$$E_n = \left(n + \frac{1}{2}\right)h\nu - \left(n + \frac{1}{2}\right)^2 h\nu X_e + \left(n + \frac{1}{2}\right)^3 h\nu Y_e + \text{higher order terms} \quad \dots(2.7)$$

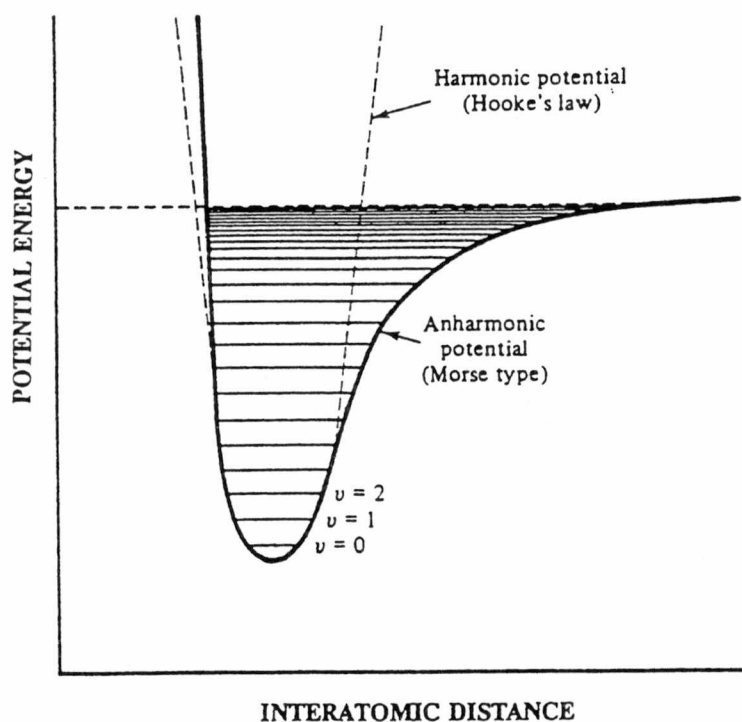


Figure 2.2 Potential energy diagram of the vibrational modes of a harmonic oscillator and an anharmonic oscillator
 [Source: E. W. Ciurczak, *Handbook of Near-Infrared Analysis*, D. A. Burns and E. W. Ciurczak, Eds. (Marcel Dekker, Inc. New York, 1992).]

where

X_e = second-order anharmonicity constant

Y_e = third-order anharmonicity constant.

One of the most important consequences of the anharmonic nature of molecular vibrations is that transitions are allowed between two, or more than two energy levels. These “forbidden” transitions give rise to overtone absorption bands. The separation between any two successive energy levels in an anharmonic oscillator becomes slightly lower with each successively increasing level. Considering only the first two terms in Eq. (2.7), a formula for the separation of the energy levels is derived as follows:

$$\Delta E = E_n - E_{n-1} = (1 - 2nX_e)h\nu \quad \dots(2.8)$$

The above expression implies that the overtones do not occur at frequencies exactly two, or three, times the frequency of the fundamental vibration, but differ by a small amount, which is related to X_e . Also, the transition probability between two energy levels becomes progressively lesser for increasing n , and consequently, overtone and combination band intensities are generally an order of magnitude lower than their lower-term preceding analogs [5,6,16-18].

2.1.2 Dipole Moment , Hydrogen Bonding, and Fermi Resonance

Dipole Moment

As discussed in the previous section, one crucial criterion for the existence of

the NIR region in the electromagnetic spectrum is anharmonicity. Overtones and combination bands, which are forbidden for harmonic molecular vibrations, form the core characteristic of spectral features in NIR. There are two types of anharmonicity that affect the molecular vibrations, namely mechanical anharmonicity and electrical anharmonicity. Mechanical anharmonicity occurs if the potential energy of vibration, as a function of the displacement of vibration, has second and third order terms. Electrical anharmonicity occurs if the dipole moment of the vibrating group is non-linearly related to the displacement of the vibration. (If a pair of atoms has an unequal distribution of electrical charge, a local electric field is created, and it is said to form a dipole. This field interacts strongly with the field of any passing electromagnetic radiation.) Diatomic molecules, such as pure hydrogen molecules have a symmetrical distribution of charge, and consequently, do not form a dipole. Therefore, they do not absorb at infrared frequencies, while molecules such as hydrogen chloride form a dipole and absorb strongly [6,16].

As an example, the typical vibrational motions in a linear triatomic molecule are considered. These are illustrated in Figure 2.3. Of these vibrations, ν_1 represents symmetrical stretching, ν_2 represents asymmetrical stretching, and ν_3 represents the bending motion in a plane perpendicular to the plane of the page. Because there is no effective change in the dipole moment of the system, ν_1 does not lead to any absorption when irradiated by electromagnetic radiation. On the other hand, ν_2 and ν_3 enable changes in the dipole moment. Therefore, these are "active" vibrations that lead

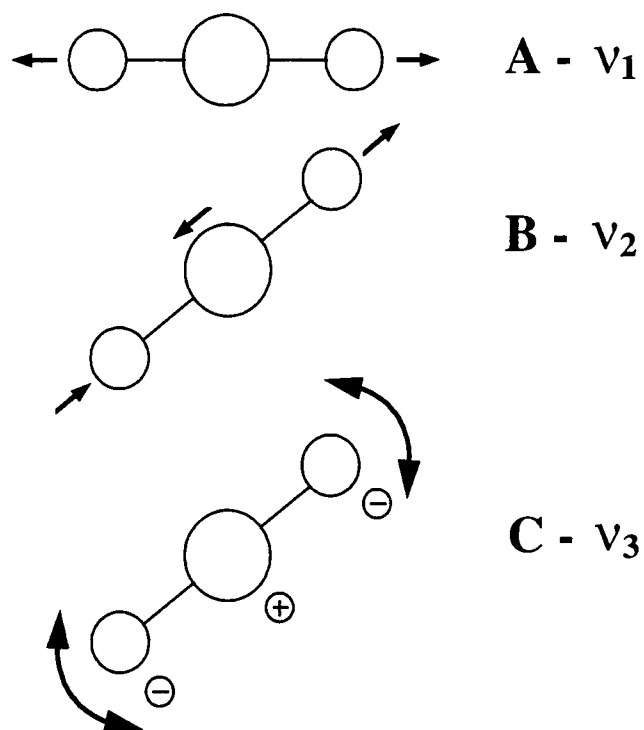


Figure 2.3 Motions for a linear triatomic molecule: (A) ν_1 – symmetrical stretching, (B) ν_2 – asymmetrical stretching, and (C) ν_3 – bending.
 [Source: I. Murray, P. C. Williams, *Near-Infrared Technology in the Agricultural and Food Industries*, P. C. Williams and K. Norris, Eds. (American Association of Cereal Chemists, Inc., St. Paul, MN, 1987.)]

to absorptions in the infrared region. It should also be noted that an “inactive” vibration like ν_1 can couple with an “active” vibration like ν_2 or ν_3 to form an “active” combination band [16].

Hydrogen Bonding

Hydrogen bonding is another feature, which affects overtones and combination bands that form NIR spectra, and a brief description is given here. A hydrogen bond is formed when the s -orbital of the hydrogen atom, from a donor group such as OH or NH, overlaps with the p -orbital of an acceptor atom, such as nitrogen, oxygen, or a halogen. The acceptor group usually has a relatively high electron density. The hydrogen bond modifies the force constant (k in Eq. (2.2)), and thus alters the frequencies of the molecular vibrations. In most cases, hydrogen bonding causes a decrease in band frequency, an increase in band width, and a decrease in band intensity of the overtone and combination bands of the donor group. Several studies were conducted by Miller (1989) that show the effect of hydrogen bonding on donor groups [19].

Fermi Resonance

Another factor that can complicate the interpretation of the NIR spectra is the occurrence of *Fermi resonance* [5,14]. Such resonance can transpire between vibrations of the same symmetry that occur at approximately the same wavelength.

This situation, where two or more energy levels have the same energy, is also referred to as *accidental degeneracy*. When such an interaction occurs, one energy level is moved up in energy and the other downward, by roughly the same magnitude. Also, the wavenumber of the lower frequency band is decreased, while that of the higher frequency band is increased by the same amount. This could lead to false interpretation of the NIR spectra. The effect of Fermi resonance is particularly important for the assignment of bands in the NIR spectra of alkanes. For alkanes, the frequency of the fundamental carbon—hydrogen, or methylene (C—H), stretching vibration is comparable to frequency of the first overtone of C—H bending mode. The symmetric C—H stretch absorbs at about $2,850\text{ cm}^{-1}$, and the overtone of C—H scissoring mode absorbs at $2,920\text{ cm}^{-1}$. Fermi resonance occurs between these two modes [6].

2.2 BAND ASSIGNMENT IN NIR

In order to understand the chemical nature of a process using spectroscopic study, it is essential to identify the functionalities that cause a particular spectral absorbance band. As discussed in earlier sections, the spectra in the NIR region are replete with overlapping absorption bands, and it is very difficult to assign a particular vibrational mode to an absorbance peak. Therefore, unlike the mid-IR region, band assignment in the NIR region cannot be achieved using quantum mechanical calculations. NIR bands are approximately assigned based on the occurrence of MIR fundamental vibrations, using equations involving energy transitions.

The wavelength of an absorption band often reveals the nature of chemical bonds responsible for the absorption. Absorption bands in the upper end of the vibrational spectrum (or the infrared region) involve oscillations of dipoles containing at least one atom with a low mass. These fundamental absorption bands have strong intensity overtones in the NIR region. In organic molecules, hydrogen (the lightest atom) is usually bound to carbon ($\mu = 0.92$), nitrogen ($\mu = 0.93$), and oxygen ($\mu = 0.94$). Therefore, vibrational modes related to carbon—hydrogen (C—H), nitrogen—hydrogen (N—H), and oxygen—hydrogen (O—H) bonds are expected to have strong spectral signatures in NIR. The frequencies of these bands also depend on the strengths of the chemical bonds and on the remaining portions of the molecule [16].

Several review papers carry extensive information about band assignments in the NIR wavelength region [17-22]. In the following sections, assignments of the C—H, the N—H, and the O—H vibrational bands in the NIR region for various organic compounds will be reviewed. Band assignments for specific polymer systems will also be discussed.

2.2.1 Absorption Bands due to Methylene or C—H Vibrations

The fundamental stretching vibrations of most C—H groups lie in the infrared region. In aliphatic hydrocarbons, the overtones and combination bands have strong spectral features in the NIR region and have been widely discussed in the literature. The first overtones of the C—H stretch vibrations are found in the 1,600 nm to 1,800

nm wavelength region. The second overtones are found between 1,150 nm and 1,250 nm. The first set of combination bands is observed in the wavelength region of 2,000 nm to 2,400 nm. Higher order combinations are responsible for weaker bands throughout the lower end of the NIR region. For example, a combination band of lower intensity is observed between 1,300 nm and 1,450 nm [17]. In his review article, Whetsel (1968) included discussions of the absorption bands of various vibrational modes in saturated molecules [20]. In a typical hydrocarbon, the first overtones of the methyl groups occur as doublets at 1,695 nm and 1,705 nm, and the first overtones of the methylene groups occur as doublets at 1,726 and 1,765 nm. The NIR spectrum of a low density polyethylene sample shown in Figure 2.4, indicates the spectral signature of the methylene stretch first overtone vibrational mode, at the wavelengths indicated above. (The transmission spectrum for the molten polyethylene sample was collected at an optical pathlength of 2.5 mm and at a temperature of 200 °C using a Fourier transform NIR spectrometer).

Aromatic hydrocarbons show absorptions at slightly lower wavelengths than aliphatic hydrocarbons. The first overtone is about 1,685 nm, and the second overtone is about 1,143 nm [17]. The second overtone region is used in quantitative analysis of benzene, toluene, *et cetera*.

In olefins, methylene first overtone stretch bands of terminal double bonds are observed at 1,620 nm, and a combination band is seen at about 2,100 nm. The configurational isomers are also identified, with the *cis* unsaturation being observed at

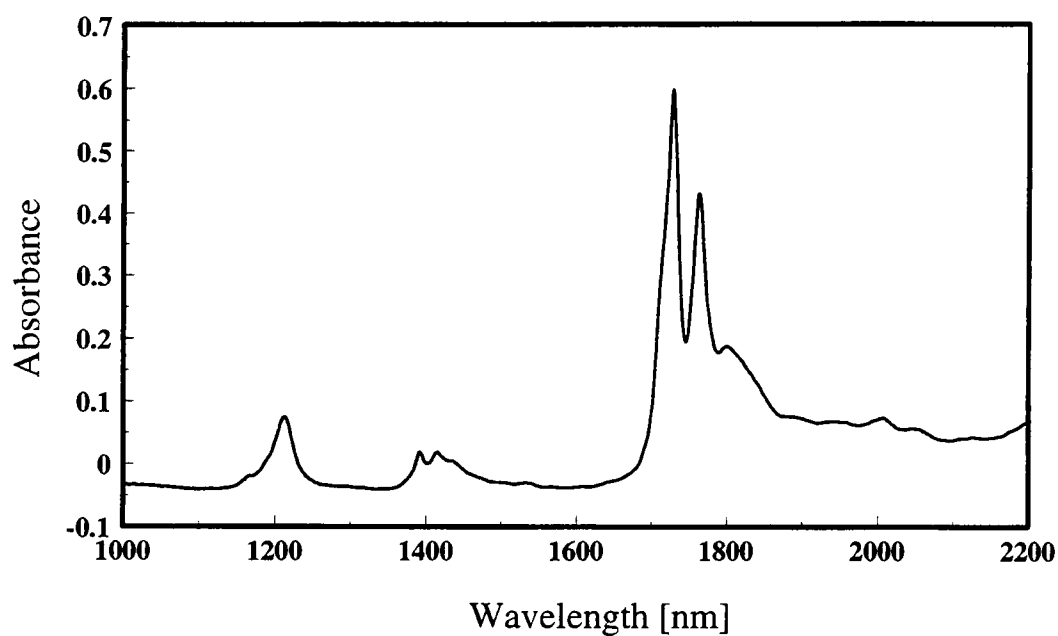
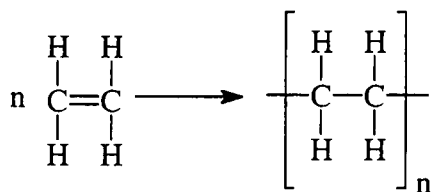


Figure 2.4 NIR spectrum of a low density polyethylene sample showing the methylene stretch first overtone doublets at 1,726 nm and 1,765 nm. The transmission spectrum in the melt at 200 °C was collected using an Analect® Fourier transform NIR spectrometer, at an optical pathlength of 2.5 mm.

the first and second overtones, near 1,680 nm and 1,180 nm, respectively. These bands were used for quantitative analysis [22].

The C—H stretch is important in the study of several properties of polymers. For example, in polymers such as polyethylene, propylene, ethylene—propylene polymers, and poly(vinyl acetate), important composition analyses are carried out by monitoring different types of C—H groups. For example, C—H vibrations have been used to follow the reaction progress of polyethylene from ethylene in the following reaction [23]:



With reaction progress, the absorption peak due to double bonds in the combination region around 2,110 nm decreases in intensity. The relative composition of homopolymers in blends, such as polystyrene (PS) and polyphenylene oxide (PPO), was determined by following the absorbance variation of aromatic C—H stretch first overtone band at about 1,680 nm and a combination region around 2,150 nm [8]. The comonomer ratio in poly(ethylene vinyl acetate) (EVA) random copolymers was studied using the C—H first overtone doublet region, in the wavelengths from 1,620 nm to 1,840 nm, for quantitative analysis [24].

2.2.2 Absorption Bands due to N—H Vibrations

In aliphatic amines, the first overtones have the same orders of absorptivities as their fundamentals. This property can be utilized to analyze the aliphatic amines in the presence of aromatic amines. Primary amines have first overtone bands at about 1,500 nm and a combination band of N—H stretch and NH_2 bending at 2,000 nm. The comparable bands for the NH_2 group exhibit symmetric and asymmetric components, but the asymmetric components of the overtone bands are very weak. Secondary amines have fundamental stretching bands near 2,900 nm and have a first overtone stretch at 1,500 nm. Tertiary amines have no strong bands in the NIR region. Fundamental bands for aromatic amines are stronger than those for aliphatic amines, and therefore, they have been more extensively studied. A combination band of N—H stretch and NH_2 bending is identified at 1,960 nm. Secondary aromatic amines have a single band in the 1,500 nm region. This occurs at a wavelength close to the corresponding primary amine. Goddu (1960) gives an extensive review of the band assignments of the various amines in the NIR region [22]. Weyer (1985) states in a review paper that cyclic amines, such as pyrroles, indoles, and carbazoles, have very intense first overtone bands at about 1,450 nm [17].

Primary and secondary amides absorb in the same spectral region as amines. Some additional bands occur due to *cis* and *trans* configurations. The amides have doublets due to the *cis-trans* configurations. The first overtones of the amides are seen

at about 1,500 nm, and combinations of N-H vibrations, with carbonyl (C=O) and nitrile (C—N) stretching and bending modes, are observed at about 2,000 nm [17].

Vibrations associated with the N—H bond are used in the study of several properties of amide-based and nitrile-based polymers. Because a majority of the polyamides, such as nylon yarn goes into the manufacture of textile fibers, important properties have been studied relating to moisture content, crystallinity, and heat set temperature [25]. Crandall *et al.* (1975) demonstrated the usage of NIR spectra for quantitative analysis of polyurethanes, polyamic acids, and urea-formaldehyde resins [26]. During the production of polyurethane from polyisocyanate and polyol, the evolution of the N—H overtone peak of urethane at 1,492 nm was used to monitor the reaction progress. Hydrogen bonding and dimerization studies have been performed with both amines and amides.

2.2.3 Absorption Bands due to O—H Vibrations

The O—H stretch vibrations of alcohols and phenols have first overtones in the 1,400 nm region [17]. Weak intensity bands of second overtones are observed at 1,000 nm, and combination bands are seen near 2,000 nm. The first overtone region at 1,400 nm is particularly suited for structural studies, especially those of hydrogen bonding. Primary, secondary, and tertiary alcohols have fundamental absorptions near 2,750 nm, 2,760 nm, and 2,766 nm. Goddu (1960) presents a review of studies involving hydrogen bonding, configurations, and integrated absorptivities [22].

The NIR region is ideal for studying the properties of water and for determining the moisture content in various substances. Water has a first overtone due to O—H stretch at 1,440 nm, a combination band at 1,940 nm, and a second overtone at 960 nm. In polymers, water can strongly affect several properties, such as the glass transition temperature, modulus, and the dielectric constant. The presence of water can be monitored in polymerization reactions. Miller (1990) studied the effect of moisture content on the NIR spectra of a reaction-injection-molded block of polyurethane by observation water bands at 1,430 nm and 1,922 nm [27].

2.3 BEER-LAMBERT'S LAW AND TRANSMITTANCE

Beer-Lambert's law relates absorbance at a given wavelength to concentration as follows:

$$A = a l c \quad \dots(2.9)$$

where

A = absorbance

a = absorptivity at a particular wavelength

l = optical pathlength in the measurement volume

c = concentration of the absorbing chemical

Eq. (2.9) states that, in the absence of interactions among absorbing molecules, the absorbance at a particular wavelength is linearly related to concentration. The

absorptivity value is a characteristic of the chemical, and is also a function of processing conditions, such as temperature, pressure, *et cetera*.

Transmittance, T , is calculated from the intensity of light incident on the sample (I_0), and the intensity of light after it passes through the sample (I), by the relation:

$$T = (I/I_0) * 100 \% \quad \dots(2.10)$$

The absorbance is related to transmittance by the expression:

$$A = \log_{10}(1/T) \quad \dots(2.11)$$

Usually, transmittance spectra are collected for melts and solutions.

2.4 QUANTITATIVE ANALYSIS — AN OVERVIEW

The success of any analytical technique lies in the ease and accuracy with which quantitative and the corresponding qualitative information can be extracted from it. As described in the previous sections, the NIR region consists of considerable overlapping absorbance overtones and combination bands in a very small wavelength range of about 1,000 nm. This makes quantitative analysis of the NIR spectra, and its qualitative interpretation, extremely difficult. Despite these drawbacks, the last decade has seen a surge of activity in NIR applications for a variety of research areas. Siesler (1991) attributes this success to two contributing factors: (1) improvement in instrumentation (with long-term wavelength stability), coupled with development of fiber-optics, (2) introduction and development of chemometric evaluation procedures

for quantitative analysis — robust multivariate techniques for calibration [18]. Martens and Naes (1989) define chemometrics as “the science involving the use of mathematics and statistics on chemical data” [28]. The purpose of chemometrics is to develop correlations between experimental data (e.g. NIR absorption spectra) and the property of interest (e.g. polymer composition, polymer relative viscosity, *et cetera*).

In the MIR region, the use of absorbance intensity heights, or peak areas, gives very accurate calibration curves. Usually, a single wavelength, or a few wavelengths, are sufficient for calibrating the property of interest. This requires minimum computational effort, and yet provides the desired quantitative information. However, individual bands in the NIR region are broad and highly overlapping. Usually, no single wavelength can give complete information about the property being calibrated, and several wavelengths are required to determine a particular property. Therefore, quantitative analysis in the NIR region requires multivariate techniques. Because of the inclusion of a large number of wavelengths in the calibration model, the use of conventional multiple linear regression (MLR) techniques for calibration is numerically sensitive to small errors in the data. However, it is noted that the data represented by these wavelength variables are highly intercorrelated, and the essential information is contained in only a few variables. Some multivariate techniques involve data reduction of these highly intercorrelated spectra into a few factors. These factors explain much of the variance in the data, and a detailed description is given in the following sections. The data analysis in this work employed some of these techniques,

such as partial least squares (PLS) [28-35], and principal component analysis (PCA) [28,30,35-37].

In the following section, a brief overview is given of various multivariate methods, commonly used for NIR data analysis. Such methods are classified into two categories: (1) exploratory data analysis methods, which look for similarity patterns in the multivariate chemical data, and (2) regression methods, which correlate the experimental data to the desired property of interest.

2.4.1 Exploratory Data Analysis or Cluster Analysis

Exploratory data analysis pertains to the identification of patterns of association in multivariate data sets, and subsequent display of these patterns in a graphical manner. These patterns, often termed *clusters*, are separable distinct constituent groups of samples in the data sets. The various algorithms for exploratory work are designed to reduce large and complex data sets into a set of best views of the data. Such views provide insight into the structure and correlations that exist among the samples and variables in the data. Two commonly used techniques for exploratory data analysis are heirarchical cluster analysis (HCA) and principal component analysis (PCA).

In spectral data, clusters correspond to one or more physical constituents, which have spectral signatures that are overlapping in neighboring regions. Such data are classified into groups which allow formation of data subsets for subsequent

calibration and modeling. The techniques used in exploratory work also enable identification of “outlier” spectra [Outlier spectra are those spectra which are anomalous in nature and do not fit into the general trend followed by the remaining observations. Usually, such anomalies during data collection are caused by instrumental or manual errors. Including outlier spectra into a calibration model will lead to higher residuals and erroneous predictions. Therefore, it is important to remove these spectra from calibration set.] In this work, both HCA and PCA methods were used to provide qualitative analysis in polymer additive systems (Chapter 6). In this section, some important definitions for HCA and PCA will be furnished in order to enable clearer understanding of the analysis that will be provided in later chapters.

2.4.1.1 Heirarchical Cluster Analysis (HCA)

The primary objective of HCA is to present data in a manner that emphasizes the natural groupings or agglomerations in the data set. In this method, distances between samples (or variables) in a data set are evaluated and compared. If the distances between samples are relatively small, it implies that the samples are *similar*, and such samples are categorized to form a single cluster. Dissimilar samples have larger relative distances. The relative similarity between various samples is used as a measure to identify inherent clusters in the data. HCA provides analysis in the form of an elegant graphical display which helps identification of clusters through

visualization of the correlations among samples. This pictorial description is called a *dendogram*, and a description is given later in this section.

There are a myriad of clustering techniques available in literature, and description of such methods can be found elsewhere [38-40]. These techniques are generally divided into two groups — (a) agglomerative and (b) divisive approaches. In an agglomerative approach, each sample is initially defined as a unique cluster. As HCA proceeds, sample clusters are grouped together to form newer and larger clusters. This procedure is carried on until all samples have been grouped into a single cluster. In contrast, divisive methods begin with a single cluster composed of all samples. Subsequently, division is carried out until each sample becomes a cluster unto itself. In the current research, the algorithms used for HCA (obtained from Pirouette® [41]) will utilize only the agglomerative approach.

2.4.1.1.1 Mathematical

The distance, d_{ab} , between any two given samples, $\mathbf{a}$ ($n \times 1$) and $\mathbf{b}$ ($n \times 1$), is determined by comparing the differences at each of the n variables:

$$d_{ab} = \left(\sum_{j=1}^n \left[(x_{aj} - x_{bj})^{MD} \right] \right)^{1/MD} \quad \dots(2.12)$$

where MD is the order of the distance, and is referred to as the Mahalanobis distance.

The most common metric used in multivariate analysis is an MD value of 2, and this

distance is often called as the Euclidean 2-norm distance, or simply the Euclidean distance [39].

The actual distances between samples in a data set vary with the type and number of data present. Therefore, the Euclidean distances are transformed into a somewhat standard scale called a *similarity*, which is defined as follows:

$$s_{ab} = 1 - \frac{d_{ab}}{d_{\max}} \quad \dots(2.13)$$

where s_{ab} is the similarity between any two given samples, and $d_{\max}$ is the largest distance encountered in the data set. On this scale, a value of 1 implies identical samples, and a value of 0 defines the most dissimilar samples.

After distances between all samples have been computed, the two most similar samples are “linked”. A *link* is a graphical representation for joining any two clusters, and represents the smallest inter-cluster distance. Once a cluster has been linked with another cluster, a new cluster is defined from both. In the next step, the distances between this new cluster and all other existing clusters is computed, the smallest inter-cluster distance is again searched, and another linkage is formed. This process is continued until all samples or clusters have been linked.

The distance between a newly formed link A—B and a previously formed cluster C is defined mathematically using one of several expressions described below:

Single Link

$$d_{AB \Rightarrow C} = 0.5d_{AC} + 0.5d_{BC} - 0.5|d_{AC} - d_{BC}| \quad \dots(2.14)$$

Complete Link

$$d_{AB \Rightarrow C} = 0.5d_{AC} + 0.5d_{BC} + 0.5|d_{AC} - d_{BC}| \quad \dots(2.15)$$

Centroid Link

$$d_{AB \Rightarrow C} = \sqrt{\frac{n_A d_{AC}^2}{n_A + n_B} + \frac{n_B d_{BC}^2}{n_A + n_B} - \frac{n_A n_B d_{AB}^2}{n_A + n_B}} \quad \dots(2.16)$$

Median Link

$$d_{AB \Rightarrow C} = \sqrt{0.5d_{AC}^2 + 0.5d_{BC}^2 - 0.25d_{AB}^2} \quad \dots(2.17)$$

where n_A and n_B are number of samples in clusters A and B, respectively. In general, the choice of any of these aforementioned definitions for a link is arbitrary for a given multivariate data set. If the data set contains clearly distinguishable constituents leading to formation of distinct clusters, any of the above definitions for forming links will produce more or less identical cluster patterns or dendograms. [However, this is not generally true for any data set, wherein the different linkages can lead to formation of different cluster patterns.]

2.4.1.1.2 Clustering Techniques

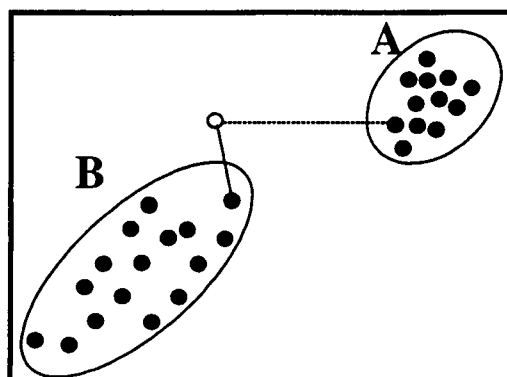
In HCA, a clustering technique is applied to the data, which directs how the samples will be grouped in the resulting dendogram. There are three types of cluster techniques that differ in the manner in which clusters are linked to other clusters — (a) nearest neighbor, (b) farthest neighbor, and (c) cluster centroid.

In the nearest neighbor clustering technique, linking of samples is based on the distance of any one sample point to its nearest neighbor. The sample is assigned to the cluster containing that nearest neighbor. Figure 2.5.a shows this concept on a schematic, where an unknown sample is allotted to cluster B based on comparative distances to the nearest neighbor in clusters A and B. In the farthest neighbor technique, a given sample is assigned to a cluster whose farthest neighbor is closest to that sample. This concept is illustrated in Figure 2.5.b. In contrast to nearest and farthest neighbor clustering, centroidal clustering assigns a sample to the cluster whose center is nearest to the sample, as depicted in Figure 2.5.c. Of the various definitions for links introduced earlier, a single link is based on the nearest neighbor clustering technique, a complete link relates to the farthest neighbor approach, and the centroid (which uses the average position within the cluster as the cluster center) and median (which uses the median point within the cluster as the cluster center) definitions are based on the centroidal approach.

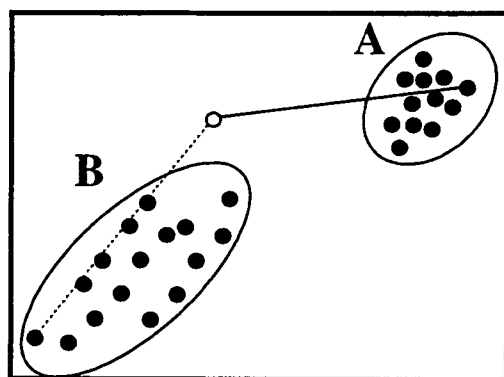
2.4.1.1.3 Dendogram

The dendogram is a pictorial representation of sample clusters and is a tree-shaped distance map, which is constructed using the entire set of inter-sample distances. A typical dendogram is illustrated in Figure 2.6. A *tree* is formally defined as a connected graph made up of links on a similarity scale. It consists of short and long *branches*, whose relative lengths are decided by the similarity values of the inter-

a)



b)



c)

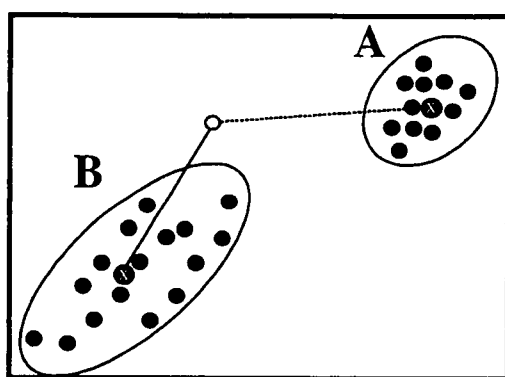


Figure 2.5 Figure illustrating the various clustering techniques a) nearest neighbor approach, b) farthest neighbor approach, and c) centroidal approach.

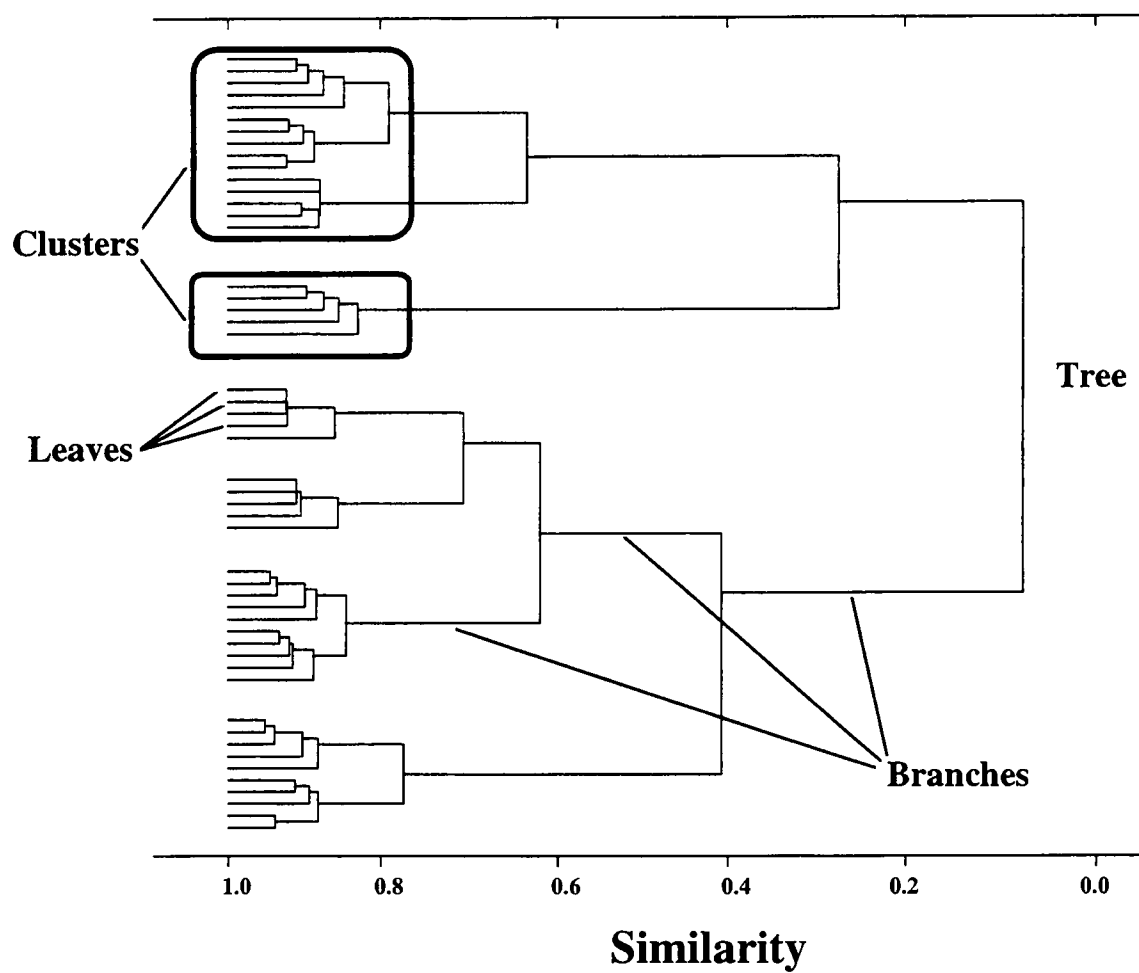


Figure 2.6 Schematic representation of a dendrogram

sample distances. Longer branches have lower similarity values and therefore, constitute dissimilar samples. Conversely, the shorter the branch, the smaller is the distance separating the samples. Each of the short branches on the extreme left of the similarity scale (similarity ~ 1.0) represents a single sample and is called a *leaf*. Thus, a given set of leaves which are connected to a short branch will represent identical samples. A dendrogram can be interpreted in terms of the number of distinct clusters that are formed using HCA.

In general, if random noise is added to a data set, the leaves become longer in length, and the branches shorten. For a data matrix consisting of strictly random data, the leaf lengths are as long as or are longer than the branch lengths, and no clusters are observed.

2.4.1.2 Classification using K-Nearest Neighbors (KNN)

Classification techniques aim to categorize a large set of samples into different groups based on their similarity values [42,43]. The KNN method uses a Euclidean distance comparison among samples; where an N-dimensional distance between all samples in the data set is calculated (N is the number of variables in the measured data). The KNN method is a validation-prediction type of approach. In this approach, a calibration model is originally developed using standard representative samples and variables (e.g. samples and their NIR spectra).

The methodology is described as follows. The standard sample properties (e.g. concentrations) are defined as *class variables*. Next, Euclidean distances are evaluated using Eq. (2.12). Each sample in the data set is compared to all others by evaluating the multivariate distances or similarity values among the samples. After all inter-sample distances are computed, a distance matrix is created. In the next step, each sample in the training set is compared to all other samples, by evaluating the Euclidean distance measures. These distance measures are evaluated for each sample with respect to K nearest neighbors. Based on these measures, the resultant matrix formed contains elements, which have the estimated class values for each sample at every level of K . Such a matrix is called a *votes matrix*.

The values in the votes matrix are converted into an errors matrix of ones and zeros, where the ones are assigned only to erroneous classifications. A representation of the classification errors is obtained by summing each column in the errors matrix. The resultant vector is termed a *misses vector* and is a representation of the total erroneous classifications at each K value. This vector is utilized as a criterion for the choice of optimal number of nearest neighbors, K value, to be used for future classifications of unknown samples. Another diagnostic introduced in KNN modeling is the *misclassification matrix*. For a given K value, a matrix is generated which tabulates how many samples known to be in one class were predicted to each of the classes included in the training set. The diagonal values in the matrix indicate samples

that were correctly classified; off-diagonal values represent the number of samples misclassified by the procedure.

KNN Validation and Prediction

The choice of optimal size of K is very critical while developing a KNN model. If too few neighbors are polled, a sample may be erroneously assigned to a class whose samples have a large variability and spread into the range of the true class for the test sample. In contrast, if the number of nearest neighbors chosen is too large, a sample may be erroneously assigned to a class which has more number of samples. This highlights the importance of the misses vector in deciding the K value for a KNN model. The K value is optimized using a leave-a-sample (LAS) cross-validation technique [19] which will be discussed in Chapter 5.

Once a KNN model has been built, samples with unknown class variables are predicted based on the samples used in the training set, and the optimal K size.

2.4.1.3 Principal Component Analysis (PCA)

The algorithms designed for a PCA analysis involve reduction of a large data set (e.g. a matrix containing the absorbance spectral data) to a smaller data set that explains most of the variance in the data. Thus, a few variables (which are linear combinations of the original variables) account for intercorrelations in the original variables and are used to avoid redundant information in the calculations [28-30,36].

This kind of analysis also provides insight into the relationships that exist between the samples and the variables in the data set.

In PCA, the matrix $\mathbf{X}$, (of size $m \times n$, with $n \gg m$ usually), which contains the response values (e.g., NIR absorbance values for m samples at n wavelengths), is expressed as follows:

$$\mathbf{X} = \mathbf{T}\mathbf{P}^T + \mathbf{E} \quad \dots(2.18)$$

where

$\mathbf{T}$ = matrix of size $(m \times f)$ with orthogonal columns

$\mathbf{P}$ = matrix of size $(n \times f)$ with orthonormal columns

$\mathbf{E}$ = matrix of size $(m \times n)$ containing the residuals

According to Eq. (2.12), if the NIR spectra have only f inherent factors of variation, then $\mathbf{X}$ can be reduced to a product of two smaller matrices, $\mathbf{T}$ and $\mathbf{P}$, each with f number of columns. These matrices still explain most of the variance in $\mathbf{X}$ and the residuals matrix, $\mathbf{E}$, contains random experimental noise. This form of matrix rank reduction also resolves the information in terms of the contributions from the individual inherent factors of variation. Often, these factors can directly reflect the combination of the actual physical parameters which affect the system response [28]. As an example, in compositional analysis of a ternary system, one might expect two factors ($f = 2$) to sufficiently explain most of the data variance (there are two physical factors of variation in the system because the compositions of two samples can vary independently). In such a case, the makeup of the reduced matrices would show the

contribution of the two independent physical factors. Each of these factors, which explains significant variance in the data, is called a *principal component*, or *factor*, or *eigenvector*. These terms will be used interchangeably in the sections on data analysis. Mathematically, this decomposition into principal components involves maximizing the covariance of the matrix $\mathbf{X}^T\mathbf{X}$, where $\mathbf{X}^T$ is the transpose of $\mathbf{X}$. The columns of the matrices $\mathbf{T}$ and $\mathbf{P}$ are related to the eigenvectors of $\mathbf{X}(\mathbf{X}^T)$ and $\mathbf{X}^T\mathbf{X}$, respectively [44].

The decomposition of $\mathbf{X}$ can be carried out by several algorithms. These algorithms differ in the manner in which the eigenvectors are evaluated. There are two methods which are commonly used: (1) Non-linear iterative partial least squares (NIPALS) — a modified version of this algorithm is used for PCA. The eigenvectors are evaluated in an iterative fashion. (2) Singular value decomposition (SVD) [45] — the matrix is decomposed in a manner, such that the singular values (the square root of the eigenvalues of $\mathbf{X}^T\mathbf{X}$) are put in a diagonal matrix and the lower magnitude singular value components are rejected. The current research uses the SVD algorithm (written in Matlab® platform) for most calculations, wherein the $\mathbf{X}$ matrix after preprocessing of mean-centering and scaling is decomposed as follows:

$$\mathbf{X} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T \quad \dots(2.19)$$

where

$\mathbf{U}$ = left singular matrix of size $(m \times f)$ with orthonormal columns

$\mathbf{\Sigma}$ = diagonal matrix of size $(f \times f)$, containing positive singular values in decreasing order

$\mathbf{V} = \mathbf{P}$ (above), right singular matrix of size $(n \times f)$ with orthonormal columns

f = effective rank of $\mathbf{X}$

The first f principal components can be defined as follows:

$$\mathbf{T} = [\mathbf{u}_1\sigma_1, \mathbf{u}_2\sigma_2, \dots, \mathbf{u}_f\sigma_f] \quad \dots(2.20)$$

where the subscripts on $\mathbf{u}$ and σ imply the column number of matrices $\mathbf{U}$ and Σ , respectively.

Scores and Loadings

In this section, scores and loadings matrices are introduced as analysis parameters which aid in *qualitative* interpretation of multivariate analysis. By definition, each principal component is associated with a “score” and a “loading” vector. The loading vectors constitute the columns of matrix $\mathbf{P}$, which is obtained by SVD decomposition. These vectors display the clustering of the independent variables into classes which are used in explaining the variance in the data. Thus, the loading values can be viewed as “weights” associated with each independent variable, and they describe the *relative importance* of the independent variables in regression. The i -th member of the j -th score vector indicates the projection of the i -th sample or the j -th loading vector, or principal factor.

2.4.2 Regression Methods

In this section, various algorithms for multivariate regression are described.

2.4.2.1 Classical Least Squares (CLS)

The CLS regression method [19,46,47] is based on the Beer-Lambert's law and is employed for calibration of a system which satisfies the following criteria: (1) all of the possible analytes in the calibration samples are known, (2) there exist no spectral interactions between the analytes in the samples. This relation can be expressed in matrix notation as follows:

$$\mathbf{X} = \mathbf{C}\mathbf{K}^T + \mathbf{E} \quad \dots(2.21)$$

where

$\mathbf{X}$ = matrix of size $(m \times n)$, usually containing the NIR absorbance spectra of m samples at n wavelengths

$\mathbf{C}$ = matrix of size $(m \times p)$, containing the response matrix (e.g., concentrations of the m pure analytes)

$\mathbf{K}$ = matrix of size $(n \times p)$, containing the spectra of the p pure analytes

$\mathbf{E}$ = matrix of size $(m \times n)$, containing the residuals

CLS calibration is carried out by calculating the least-squares estimate of $\mathbf{K}$, which can be expressed in the form provided $\mathbf{C}$ is of full rank:

$$\hat{\mathbf{K}} = \mathbf{X}^T \mathbf{C} (\mathbf{C}^T \mathbf{C})^{-1} \quad \dots(2.22)$$

where

$\hat{\mathbf{K}}$ = matrix of size $(n \times p)$, containing the least-squares estimated values of $\mathbf{K}$.

The concentration of a future sample, $\hat{\mathbf{c}}_p$, can be estimated from its spectrum,

$\hat{\mathbf{x}}_p$, by using the value of $\hat{\mathbf{K}}$ estimated in Eq. (2.21) as follows:

$$\hat{\mathbf{c}}_p = \hat{\mathbf{x}}_p \hat{\mathbf{K}} (\hat{\mathbf{K}}^T \hat{\mathbf{K}})^{-1} \quad \dots(2.23)$$

CLS has advantages that include: (1) increased precision in calibration as compared to methods that are restricted to a small number of wavelengths, (2) availability of qualitative interpretation of the pure analyte spectra, and (3) ability to predict concentrations from spectra with additive and multiplicative effects [19,46]. One major disadvantage of CLS is that knowledge is essential prior to calibration of all the analytes present in the samples, and implication of when $(\mathbf{C}^T \mathbf{C})^{-1}$ does not exist.

2.4.2.2 Inverse Least Squares (ILS)

The ILS method [46] is based on the inverse Beer's law, which assumes that concentration is a function of absorbance. Though this method is rarely used in calibration, it forms the basis for other widely used bilinear methods, such as principal component regression (PCR) and PLS that also use inverse Beer's law. According to the inverse Beer's law, the concentration of m calibration standards is expressed as follows:

$$\mathbf{C} = \mathbf{X}\mathbf{B} + \mathbf{E}_c \quad \dots(2.24)$$

where $\mathbf{C}$ and $\mathbf{X}$ are defined as before, and

$\mathbf{B}$ = matrix of size $(n \times p)$, containing the unknown calibration, or regression, coefficients

$\mathbf{E}_c$ = matrix of size $(m \times p)$, containing the calibration residuals, or the errors in explaining the concentration values.

The unknown coefficients are estimated from the calibration by using the following relation:

$$\hat{\mathbf{B}} = (\mathbf{X}^T \mathbf{X})^{-1} \mathbf{X}^T \mathbf{C} \quad \dots(2.25)$$

The concentration of a future sample, $\hat{\mathbf{c}}_p$, can be estimated from its spectrum, $\hat{\mathbf{x}}_p$, by using the value of $\hat{\mathbf{B}}$ estimated in Eq. (2.25) as follows:

$$\hat{\mathbf{c}}_p = \hat{\mathbf{x}}_p \hat{\mathbf{B}} \quad \dots(2.26)$$

One advantage of ILS is that calibration can be performed even if the concentration of only one component is known in the samples. The major disadvantages are the following: (1) analysis has to be restricted to a small number of wavelengths. This is because of the singularity in the matrix $\mathbf{X}^T \mathbf{X}$, which makes matrix inversion in Eq. (2.19) very difficult. This means that the dimension of the matrix (or, the number of wavelengths included) cannot exceed the number of calibration mixtures used in the analysis, (2) if the number of wavelengths included becomes very large, collinearity (near linear relationships of NIR absorbances at multiple wavelengths) can become significant. This reduces the effective dimension, or *rank*, of the matrix $\mathbf{X}^T \mathbf{X}$ and makes the matrix singular [46].

2.4.2.3 PCR and PLS Models

The general goals of the PLS and PCR algorithms are similar, and this section

discusses their similarities and differences. The idea of decomposing the highly correlated NIR data into fewer principal components, which still describe most of the inherent data variation, was discussed earlier. Both PCR and PLS incorporate similar ideas of data reduction, such as that in PCA, in their algorithms.

The regression equation for calibrating the response matrix, $\mathbf{Y}$ (of size $m \times p$), (containing the concentration values or any property being calibrated) against $\mathbf{X}$ can be written as below:

$$\mathbf{Y} = \mathbf{XB} + \mathbf{E}_e \quad \dots(2.27)$$

PCR is simply PCA followed by a regression step [46,48,49]. The $\mathbf{X}$ matrix, containing the NIR absorbance data, can be decomposed into two smaller matrices according to Eq. (2.18). The response matrix, $\mathbf{Y}$, is regressed against the reduced scores matrix, $\mathbf{T}$, instead as follows:

$$\mathbf{Y} = \mathbf{TB}_v \quad \dots(2.28)$$

where it is assumed that SVD-type decomposition of $\mathbf{X}$ has been carried out, as detailed in Eq. (2.19) and Eq. (2.20), and

$\mathbf{B}_v$ = matrix of size $(f \times p)$, contains a set of reduced regression coefficients and

is related to the original set of regression coefficients as:

$$\mathbf{B}_v = \mathbf{V}^T \mathbf{B} \quad \dots(2.29)$$

where $\mathbf{V}$ is as defined in Sec. (2.4.1.3).

This accounts for any collinearity problems that frequently occur during calibrations involving a large number of wavelengths. During PCR, the matrix

decomposition is performed by finding the loading vectors that individually account for the largest amount of spectral variance in the spectral data of the calibration set. This can be viewed as a transformation into a coordinate system where the basis vectors are the loading vectors [46-49]. Linear combinations of these basis vectors, (the weights of which are obtained from the scores matrix), can be used to reproduce the original calibration spectra to within spectral noise and calibration error. The number of significant loading vectors, required to explain the data variance, is equal to the number of independent factors of variation in the data. The noise is distributed throughout all loading vectors, with more noise in the latter loading vectors, and therefore, including fewer significant principal components in the calibration results in noise reduction.

The PLS algorithm is a similar methodology with one difference. PLS performs analysis by both accounting for the variance in the spectral data while simultaneously finding the loading, or basis, vectors that have the greatest relevance for prediction. In other words, matrix decomposition in PLS involves maximizing the covariance in $\mathbf{X}^T\mathbf{Y}$ while matrix decomposition in PCR involves maximizing the covariance of $\mathbf{X}^T\mathbf{X}$. The loading vectors are found by performing a coordinate transformation such that a rotation of $\mathbf{X}$ -data variance in the direction of $\mathbf{Y}$ gives a maximum. The $\mathbf{X}$ and the $\mathbf{Y}$ matrices are decomposed in the following manner:

$$\left. \begin{aligned} \mathbf{X} &= \mathbf{TP}^T + \mathbf{E} \\ \mathbf{Y} &= \mathbf{UW}^T + \mathbf{F} \end{aligned} \right\} \quad \dots(2.30)$$

where **X**, **Y**, **T**, **P**, and **E** are as defined previously and

U = scores matrix of size $(m \times r)$, for r principal components

W = loadings matrix of size $(n \times r)$, for r principal components

F = residuals matrix of size $(m \times n)$, containing the **Y**-residuals.

The PLS method makes no *a priori* assumption about the relationship between the NIR absorbance spectra and the property of interest. Therefore, it can be used to calibrate physical properties to the NIR spectra.

The various available PLS algorithms differ in the manner in which the decomposition is carried out. The NIPALS algorithm, introduced by Wold *et al.* (1983), is based on an iterative method for evaluating the principal components in succession [50]. Many earlier studies on quantitative analysis of NIR spectra used this algorithm, and this has been included in many commercial softwares, such as Unscrambler® [51], Pirouette® [41], *et cetera*. The SVD-based algorithm [45] is supported by the Matlab® environment, and uses a non-iterative methodology for evaluating the eigenvectors. In general, the NIPALS algorithm is faster if only a few of the principal components need to be evaluated, while the SVD-based algorithm usually takes less computational time if all components are to be calculated.

This research will use the SVD-based algorithm for most computations. For the sake of comparison, some studies have been conducted using both commercial softwares listed above.

2.4.3 Calibration Procedures

2.4.3.1 Cross-Validation

The cross-validation procedure is used to determine the optimal number of factors for a PLS calibration [28,37,47,52]. Using fewer principal components in the calibration model would mean excluding important information from the model, and this would lead to an insufficient calibration model. Using too many factors would mean incorporating redundant information and random noise, and thus, higher residuals in the predictions. Therefore, the choice of an optimal calibration model with minimum residuals is critical.

In a cross-validation modeling procedure, a subset of samples is removed from the calibration sample set, and is used for internal validation. The calibration model is built on the sample set (excluding the removed samples), and the developed model is used to predict the properties of the samples in the extracted subset. These samples are then included in the calibration model and a different subset is removed from the calibration, which is used for internal validation. Thus, a series of PLS calibration models is built till all the samples have been used for internal validation at least one time. Also, for a given calibration and validation set, a number of PLS models are also built over a number of principal components.

A residual error term, Predicted Residual Sum of Squares (PRESS) value, is then evaluated with the following definition:

$$\text{PRESS}_j = \sum_{i=1}^N (y_i - \hat{y}_{i,j})^2 \quad \dots(2.31)$$

where

j = number of factors included in the model

y_i = actual property value of the i -th sample

$\hat{y}_{i,j}$ = predicted property of the i -th sample for a calibration model built with j
factors

N = number of samples used for cross-validation

After predictions from all PLS models have been made, the PRESS value is plotted against the number of factors. From this plot, the optimal number of factors is to be decided by the one which yields the minimum PRESS value. This optimal number is then used to form the final calibration model.

2.4.3.2 Calibration Model Error Estimates

In a typical calibration procedure, a calibration model is developed on a set of samples with known properties (called *calibration set*), and subsequently, this model is used to predict the properties of a different set of samples with unknown properties (called *prediction set*). The residual errors in the predictions of the samples in the calibration set are “averaged” statistically, and this calibration model error is termed as the Standard Error of Calibration (SEC). Similarly, the model error in the predictions of the samples in the prediction set is termed as the Standard Error of Prediction (SEP).

For samples in the calibration set, the SEC is defined as follows:

$$SEC = \sqrt{\frac{\sum_{i=1}^{NC} (y_{i,c} - \hat{y}_{i,c})^2}{NC - 1}} \quad \dots(2.32)$$

where $\hat{y}_{i,c}$ and $y_{i,c}$ are the predicted and the actual property values of the i -th calibration sample, and NC is the total number of samples in the calibration set.

For samples in the prediction set, the SEP value is defined as

$$SEP = \sqrt{\frac{\sum_{i=1}^{NP} (y_{i,p} - \hat{y}_{i,p})^2}{NP}} \quad \dots(2.33)$$

where $\hat{y}_{i,p}$ and $y_{i,p}$ are the predicted and the actual property values of the i -th calibration sample, and NP is the total number of samples in the calibration set.

The SEC and SEP values are quantitative estimates of the accuracy of the calibration models. It is expected that predictions for an unknown sample using the calibration model would lie within $\pm SEP$ limits of the true value. The SEP limits can be utilized for setting control limits, or detection limits, in a real-time process.

2.5 NIR SPECTROSCOPY — APPLICATIONS

Improvements in NIR instrumentation, availability of fiber-optics, and development of chemometric tools for quantitative analysis, have led to a meteoric rise in NIR related applications. Extensive literature is published each year in key areas of agriculture, biotechnology, textiles, pharmaceuticals, and polymers. Such applications include monitoring product purity, identifying trace level impurities, moisture determination in processes, *et cetera*. Physical properties such as density, relative

viscosity, molecular weights of polymer end groups, have also been successfully measured by NIR spectroscopic techniques.

2.5.1 Applications Related to Polymers

The literature has excellent review papers which discuss various applications of NIR spectroscopy to polymeric systems [3,4,17,18,25,53]. Before the advent of robust chemometric tools, very little quantitative analysis of the NIR spectra was done, and the studies usually focused on peak assignments.

One of the earliest papers [54] involving the application of NIR spectroscopy for the study of polymer properties was the determination of acrylonitrile-butadiene-styrene (ABS) terpolymer content in PVC compounds. The amount of terpolymer was determined in unknown samples by comparing the absorbance data with those of some standards of known ABS composition. Takeuchi *et al.* (1969) studied the NIR spectra of ethylene-propylene copolymers [55]. The differences in the NIR spectra of random ethylene-propylene rubbers, isotactic polypropylene, high-density and low-density polyethylenes, and physical blends of the homopolymers were studied. Calibration curves were obtained without any elaborate quantitative analysis methods. A combination region of a symmetrical and a rotational methylene mode was identified at 2,466 nm. This band was ratioed with a reference band at about 2,350 nm. This absorbance ratio was used to distinguish between the physical blends of the homopolymers with the ethylene-propylene polymers. Another band at 2,310 nm was

found to shift for the physical blends, and this shift was observed to be a monotonic function of the composition of the physical blends. This band was also used to distinguish between random copolymers and blends.

Work was reported by Crandall *et al.* (1975) on the NIR spectra of polyamic acids [26]. The resins were prepared under various reaction conditions, and the NIR spectra were used to follow the amidization and imidization processes. For this purpose, a combination band of the amines at 1,950 nm was used along with another band at 2,300 nm which was assumed to be a function of the amide group. The reaction of bis(4-aminophenyl) methane with 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) was carried out, and spectra were collected once a month after preparation of the resins. Spectra were collected again after four months to measure changes in the chain length and hydrolysis. It was shown that the absorption intensity at 2,300 nm, of the amide N—H group in the polymer, decreases as curing progresses. The effects of concentration, reaction and storage temperatures, were studied by comparing the amine and amide overtones with the C—H overtones.

Crandall *et al.* (1977) conducted another study on the NIR spectroscopy of polymers [56]. In this work, a series of step-growth reaction polymers were prepared, and studied as melt films, and in solution. Specifically, the various polymers used for the study were polyesters, polyamides, and urea-formaldehyde polymers. First overtones of C—H, N—H, and O—H vibrational modes were used for analysis. Urea-formaldehydes, polyamides, and polyurethanes were observed in their strong N—H

overtone in the 2,000 to 2,100 nm wavelength region. The C—H first overtone band in the 1,600 to 1,700 nm wavelength region was used as an internal standard. Polymers with aryl rings were also studied which showed a doublet in the 2,130 nm to 2,160 nm region. The polyamide (Nylon 66) was identified with an N—H overtone at 1,420 nm, and a weaker carbonyl overtone at 1,940 nm. The urea-formaldehyde resin was shown to absorb at the O—H overtone at 1,340 nm. These polymers were compared in a quantitative manner, both with respect to reaction conditions and heat curing.

Another study was conducted to measure the combined vinyl acetate concentration in poly(vinyl chloride)/poly(vinyl acetate) copolymer [57]. A comparison of NIR photo-acoustic and diffuse reflectance spectrometries was made, with specific reference to particle size and sample distribution. The C—H stretch first overtone band at 1,700 nm in the ester and the second overtone of the carbonyl vibrational mode at 2,100 nm were used for quantitative analysis. Calibration curves were prepared using the intensity ratios of the bands at 2,100 nm and 1,700 nm. Calibration curves were compared for samples with different particle sizes. It was shown that for diffuse reflectance spectrometry, a decrease in the particle size led to an increase in specular reflectance, and this led to poorer sensitivity. Particle size was shown to be important for photoacoustic spectrometry as well.

Schirmer (1986) demonstrated the feasibility of using an on-line, fiber-optic-based spectroscopic system for making NIR measurements [58]. Fiber optics were shown to withstand high pressures up to 3000 psi, and temperatures up to 350 °C. The

fiber-optic probes were directly inserted into a flowing melt stream. Because polymer extruders and other such equipment operate under such extreme conditions, fiber-optics were shown to be of great use. Composition of comonomer vinyl acetate in poly(ethylene vinyl acetate) (EVA) random copolymers was determined using this analysis, and real-time monitoring of the process was demonstrated in this work. A similar study was conducted on on-line analysis of extruded polymers via fiber-optic coupled Fourier Transform NIR spectrometry [59]. This setup was used to obtain the NIR spectra of similar materials on-line at an extruder exit port.

In the context of fiber-optic probes, definitive work was done by Khettry (1994) in developing, and evaluating, a fiber-optic probe set-up for remote in-line polymer analysis in an extrusion system [7,8]. These probes were developed with focus on certain issues: (1) maximum transmission efficiency of the probe after losses due to spectral attenuation in the fiber, (2) variation in the intensity of collimated beam with distance, and azimuthal orientation, and (3) durability of the probes in withstanding high temperature and high pressures. Griesser and Sahagen (1995) developed in-line analytical probes for operation at pressures up to 30,000 psi and temperatures of up to 1000 °F [60]. A patented silicon-on-sapphire technology was employed for the probe windows, which gave the probes desired temperature and pressure resistance.

Weyer (1986) demonstrated the use of NIR reflectance technique for the analysis of polymer pellets and films [61]. In this study, derivative spectroscopy was

used to minimize scattering effects and the enhancement of spectral features. The effect of zero crossover points in minimizing interferences at the measuring wavelengths was studied in a mixture of three structurally similar hydrocarbon polymers. This method was also used to determine composition of methyl ethyl ketone (MEK) in an acrylic resins.

Paputa Peck *et al.* (1987) made NIR measurements of terminal epoxides in polymer resin systems [62]. The terminal epoxides show a group specific combination band near 2,300 nm. This band was found to be reasonably free of interferences and was employed to measure oxirane ring concentrations for epoxy coating resin systems during synthesis and crosslinking. The resins were prepared in chloroform for epoxide equivalent weight, and correlated with results obtained by perchloric acid titrations. A simple regression analysis was carried out, which involved integrated areas in the combination region, and the technique was found to give a linear calibration for epoxy concentrations.

Many polymer-related applications using NIR spectroscopy were studied by Miller (1989), which are compiled in his Ph.D. dissertation [19]. At a time when chemometric techniques were still in a rudimentary stage of development, Miller presented in a series of articles [9,19,25,27,63-68], numerous new applications of NIR spectroscopy to specific polymeric systems. Some of these results are reviewed here.

Miller (1989) used multivariate calibration methods for the NIR analysis of ethylene-propylene-diene monomer (EPDM) terpolymers [67]. The terpolymers

samples were made with two types of diene monomers: 1,4-hexadiene (HD) and ethylidene norbornene (ENB). The scattering effects in the NIR spectra were removed by using multiplicative scattering correction (MSC) methods. Three spectral regions were identified and used for quantitative analysis: region 1 – C—H stretch second overtone in 1,100-1,300 nm wavelength region, region 2 – C—H stretch first overtone in 1,570-1,850 nm, and region 3 – combination band in 1,950-2,500 nm. CLS and PLS regression methods were used for developing separate calibration models in the three regions, and their results were compared. It was observed that PLS had better prediction capabilities than CLS. This was attributed to unknown interaction effects in the polymer spectra, and PLS outperforms CLS in the presence of such effects. In PLS, second derivatives of the spectra were used which remove baseline offsets and improve spectral resolution. However, the second derivatives increase spectral noise and make qualitative interpretation of spectra difficult. The presence of interchain and intrachain interactions, which were known before to affect the mid-infrared spectral region, was observed in the CLS reconstructed spectra. This study was first of its kind in that NIR measurements were made on bulk polymer samples (earlier measurements were made in solutions). The low absorptivities in the NIR region were found to be an advantage as thicker samples could be used for non-destructive analysis. Spectral residuals were used for outlier sample detection, and for determination of unknown spectral effects.

Miller *et al.* (1990) used transmission NIR spectroscopy to determine the microstructure and composition in butadiene and styrene-butadiene rubber (SBR) polymers [68]. Multivariate analysis involving CLS was used to analyze the NIR spectra of polymers with predetermined microstructures and composition. It was observed that although the NIR spectra of the pure analytes, namely *cis*-1,4-butadiene, *trans*-1,4-butadiene, 1,2-butadiene, and styrene, were highly overlapped, CLS gave accurate predictions for the compositions. The C—H stretch first overtone region was used to quantify 1,2-butadiene and 1,4-butadiene in the polymers with very small prediction errors. The study demonstrated the sensitivity of NIR spectroscopy to intermolecular interactions and neighboring group effects in these polymers. It was also concluded that the prediction ability of the CLS method depends a lot on the NIR spectral region, optical pathlength, spectral data pretreatment, and the sample state. In a related work, Miller and Naes (1990) developed a path length correction method to account for the additive effects (caused by baseline effects) and multiplicative (caused by sample thickness variation) in NIR diffuse reflectance spectra [63]. This method was found to be more suitable than MSC correction technique in case of large spectral variability. This correction technique was successfully tested on the second derivative spectra of the SBR polymers.

In another study, Miller and Eichinger (1990) conducted crystallinity and morphology tests of poly(ethylene terephthalate) (PET) by diffuse reflectance spectroscopy in the NIR region [67]. SAXS-determined crystallinity values and NMR-

determined amorphous structure in PET yarns were correlated with NIR spectra using multivariate techniques. PCA was used to study the differences in the NIR bulk PET samples that were crystallized at different temperatures. The principal components of variation in the NIR spectra contained contributions from structural variations in the samples. In this analysis, temperature was introduced as an extraneous variable. It was concluded that NIR analysis could detect changes in both intermolecular and intramolecular interactions. The presence of moisture was also detected in bulk PET using principal components. The ability of NIR spectroscopy to distinguish between orientation and crystallinity in PET was also demonstrated.

In another study, diffuse reflectance spectroscopy was used to determine thermal properties and compression of rigid polyurethane foams [27]. Polyurethane samples were prepared with different polymeric formulations (varying polyol component), and PCA was used to discriminate between these foams. Several physical properties, which are related to the chemical formulation, were calibrated using PLS. These properties included compression modulus, strength, deformation at failure, and the thermal conductivity factor (K-factor). The compression modulus was predicted, using NIR calibrations, to within 63.6 psi, compression strength within 2.63 psi, deformation at failure to within 1.29%, and K-factor to within 0.0089 Btu-in./°F-h-ft². The studies indicated that the effect of using different polyols to form the foams could be measured by NIR spectroscopy.

In other studies, Miller *et al.* (1990) used NIR diffuse reflectance analysis of bulk composition of poly(ether urethane urea) (PEUU) block copolymers [64,65]. Calibration models were built on a set of PEUU samples, which had varying soft-segment and hard-segment compositions, using CLS. The experimental hard-segment composition was determined from a calibration curve with known mass percent nitrogen values. MSC and baseline corrected spectra in the 1,650-1,800 nm region (C—H stretch first overtone) and the 1,900-2,100 nm region (N—H stretch first overtone) were used for quantitative analysis. Second overtone carbonyl bands in the NIR spectrum at 1,918 nm and 2,036 nm wavelengths were used to monitor the phase separation of PEUU block copolymers. The absorbance spectra of these bands were found to vary with increasing annealing time. This study also led to development of feasibility criteria for hydrogen bonding measurements using NIR spectroscopy.

In-line real-time measurements of chemical composition in polymeric processes using NIR spectroscopy have been studied extensively [7,10-13,24]. These studies involved polymeric systems, such as physical blends and terpolymers [7,10,11], copolymers [24], and varying modifier-matrix composition in polymers [11]. Measurements of physical properties, such as yellowness index in polymer melts [10], have also been made successfully. Qualitative information about the polymeric process was obtained from PLS scores and loadings [24]. Another study monitored the progress of a reaction of isocyanate and polyol in the production of polyurethane [12]. Second derivatives of absorbance bands relating to polyol and isocyanate signatures

were used for building the calibration models. In all these studies, the use of fiber optic cables and appropriate fiber-optic probes enabled remote measurements of the properties of interest with minimum delay times. In a recent work, van Uum *et al.* (1995) used NIR spectroscopy to estimate the number of carboxylic end groups and relative viscosity in PET chips and PET extrusion melt [69,70]. These values were found to be dependent on the average molecular weight, chemical stability, and the processability of the material. A methodology was described using PCA and *z*-transformation for sample selection to form the calibration model. These physical properties were measured in-line in a real-time process [70].

Miller (1993) demonstrated the ability of NIR spectroscopy to make non-destructive estimates of the blend ratio of high density and low density polyethylenes in polyethylene blend films [71]. This work demonstrated the use of chemometric techniques, such as PCR, for making these estimates. It was shown that the NIR spectrum in the 2,100-2,500 nm region could be used to determine HDPE mass percent of about as low as 2.5%. Differences in molecular orientations in the samples with varying blend ratios were used to correlate the blend ratios with NIR spectra. Work was done by Miller (1993) on food packaging laminates of polyethylene, polyamide-6 (Nylon-6), and ethylene vinyl alcohol (EVOH) layers [72]. Multivariate techniques were used for outlier detection, identification, and characterization of unidentified samples. Path length correction methods were employed to estimate the laminate thickness, and to estimate the thickness percentages of polyethylene, and

EVOH in the laminates. Non-destructive analysis of bulk polymer systems, such as polyurethanes, and PET, was demonstrated [9].

Hansen and Khettry (1994) carried out in-line monitoring studies of molten polymer blends, with particular attention to development of robust fiber-optic probes [8]. Temperature effects on the NIR spectra of blends of polystyrene and poly(phenylene oxide) were studied and the blend composition estimated using PLS. This research group also reported work involving measurements on hot melt adhesives system of poly(ethylene vinyl acetate) (EVA) copolymers [7,24]. In another study, Batra *et al.* (1994) estimated the filler content (titanium dioxide) in PET extrusion, by using consistent and systematic baseline shifts as a criterion for PLS calibration [73].

Several systems have been analyzed in the mid-IR and NIR region to make comparative studies. An excellent review article is available which gives a detailed analysis of the information available from both mid-IR and NIR regions [53]. Bunding Lee *et al.* (1993) used the mid-IR and NIR region to determine the hydroxyl number in polyesters, and outlined the advantages and disadvantages of both approaches [74]. Spectroscopic measurements were made on ethylene-propylene copolymers, with comparisons of qualitative and quantitative information obtained from the NIR and mid-IR regions [75].

Some other studies of importance have been conducted on polymeric systems, such as epoxy resins [76], composition measurements on ethylene oxide—propylene oxide block polymers [77], polymerization kinetics [78], composition and

particle diameter in styrene/methyl methacrylate copolymer latex [79], and study of specific interactions in blends [80].

A lot of work has been reported on NIR spectroscopy of both synthetic and natural polymers (such as cellulose esters, *et cetera*) with emphasis on robust, non-destructive measurements of chemical compositions, and other physical properties related to the composition. Though some of these measurements are system specific (for example thermal properties in polyurethane foams [27]), NIR spectroscopy, combined with chemometric techniques, serves as a generalized methodology for making remote, in-line measurements of polymer properties.

CHAPTER 3

RESEARCH OBJECTIVES

INTRODUCTION

The status of NIR technology has changed drastically over the two decades. The once so-called "sleeping giant" [81,82] has now found numerous applications in a variety of research areas — such as polymers, textiles, analytical chemistry, pharmaceuticals, and agriculture. NIR instrumentation is now-a-days accepted for rapid, non-destructive analysis of in-line processes in near real-time. When compared with mid-IR, or the traditional infrared spectroscopy, NIR spectroscopy has distinct advantages. The absorbance bands in the NIR region are very low in intensity as compared with the sharp intensities typically observed in the mid-IR region. This feature in the NIR region is used to an advantage as it allows larger sample thickness in the optical beam path (Beer's law). Therefore, problems related to sample preparation, which is an elaborate process in the mid-IR region, are more or less non-existent. This feature also enables usage of fiber-optics in the NIR region, thereby remote process monitoring is made possible which saves the time required for an off-line analysis. With the development of rugged multivariate techniques for data analysis, NIR fiber-optic spectrometry has proved to be viable in many applications.

In the field of polymer science, several key issues have been addressed relating

to development of fiber-optics for the study of polymer melts [7], measurement of chemical properties of bulk polymers [9], and real-time composition monitoring [10-13,24]. Studies have also been conducted on correlating physical properties to the NIR spectra which are directly related to the chemical composition (for example relative viscosity, density, polymer morphology, *et cetera*). There are still several issues relating to polymer process control which have been largely unexplored, and this research will address some of these issues.

3.1 PROBLEM STATEMENT

The general objectives of the current research can be classified into the following broad categories:

(1) To demonstrate feasibility of in-line monitoring of polymer rheological properties, such as melt index and complex viscosity response during polymer extrusion, in conjunction with measurements of chemical composition.

(2) To estimate trace level polymer additive concentrations, and conduct feasibility studies for utilizing fiber-optic near-infrared and ultraviolet spectrometric techniques for in-line additive monitoring.

3.1.1 Estimation Of Rheological Properties During Extrusion

In this research, a robust methodology will be proposed to estimate the rheological properties in an in-line polymer extrusion process. This technology will

utilize fiber-optic NIR spectroscopy for real-time measurements. The methodology involves correlating polymer rheological properties of interest with the NIR absorption spectra. In the NIR absorption spectra of flowing melting polymers, there are two independent factors of variation — (1) polymer composition and (2) polymer molecular weight parameters. The effect of composition on the NIR absorbance spectra is a *strong, primary* factor and has dominant features in the spectra. In addition to these primary effects, there are *secondary* effects, which are attributed to rheological flow effects during polymer extrusion. These secondary effects are lower-order magnitude effects and are functions of molecular weight parameters. These effects are used to correlate polymer rheological properties to the NIR spectra. The specific rheological properties of interest for the current research are polymer melt flow index (MI) and linear viscoelastic functions, namely complex viscosity response.

The objective of this study was to independently estimate the rheological properties and polymer composition, thus separating the subtle, secondary features from the strong primary effects on NIR spectra. The polymeric system chosen for study was a random copolymer of ethylene and vinyl acetate (EVA). This system provided an excellent data set of samples in terms of wide variations in both composition (comonomer ratio) and rheological properties (MI values). Another objective was to outline criteria for developing multivariate calibration models for simultaneous in-line monitoring, which can be extended to other polymeric systems.

3.1.2 Monitoring Polymer Additive Levels

Another study, which is of interest to the current research, is in the area of polymer additive monitoring. This is a challenging task, primarily because of the presence of low concentrations of additives in polymer resins. The research will focus on experimental studies on two additive systems, with intent to address the following issues:

(1) To set quantitative limits of detection for a set of EVA copolymer samples with varying erucamide content. In these samples, the erucamide concentration varied in *ppm* levels. The study will demonstrate that suitability of fiber-optic NIR spectroscopy for such applications can be improved by judicious use of both qualitative and quantitative data analysis tools.

(2) To estimate hindered amine additive concentrations (low percent levels) in polypropylene. This system was chosen with aim to address two issues: (a) feasibility of fiber-optic spectroscopy for additive monitoring and (b) qualitative deconvolution of overlapping spectral peaks and identifying unknown spectral effects. A methodology is demonstrated, which uses correlation NIR—UV spectrometry for such analysis.

CHAPTER 4

EXPERIMENTAL SETUP

Figure 4.1 shows a schematic of the system for in-line fiber-optic spectrometry of molten flowing polymers. Molten polymer is produced by a 3/4-inch single-screw extruder, which has an L/D ratio of 25:1. The polymer from the extruder is pumped to a gear pump. A uniform mass flow rate of the polymer is supplied from the gear pump to a variable pathlength flow cell. A temperature gradient is maintained in the extruder to produce homogeneous melting and proper conveying of the polymer along the screw. The temperature of the flow cell is set at the value desired for collecting the NIR spectra. The temperature and pressure conditions are regulated by a temperature and pressure control unit. Dynisco[®] pressure transducers are used to measure the upstream and downstream pressure readings. The fiber optic probes are connected *via* 500- μ fiber optic cables to an analyzer-detector system which records the intensities obtained at different wavelengths.

Figure 4.2 illustrates a detailed schematic of the flow cell which houses the fiber-optic probes. This flow cell is located at the exit port of the gear pump and provides a rectangular flow channel. The cross-section of the flow channel is 20 mm long and 9.5 mm wide. Dual transmission type fiber-optic probes commercialized by Sensotron, Inc.[®] [83] are used to transmit light through the polymer flow stream. The

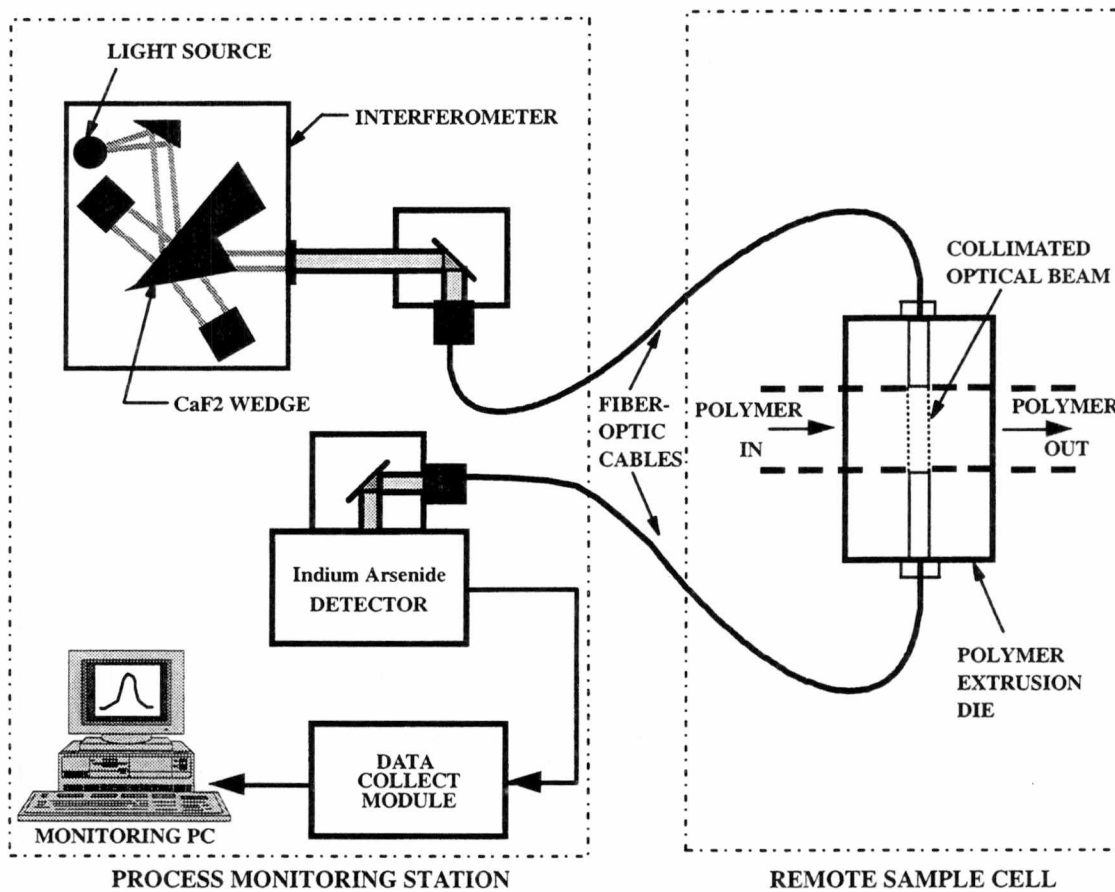


Figure 4.1 Schematic of the experimental setup for in-line Fourier transform Near-Infrared spectrometry of molten, flowing polymers.

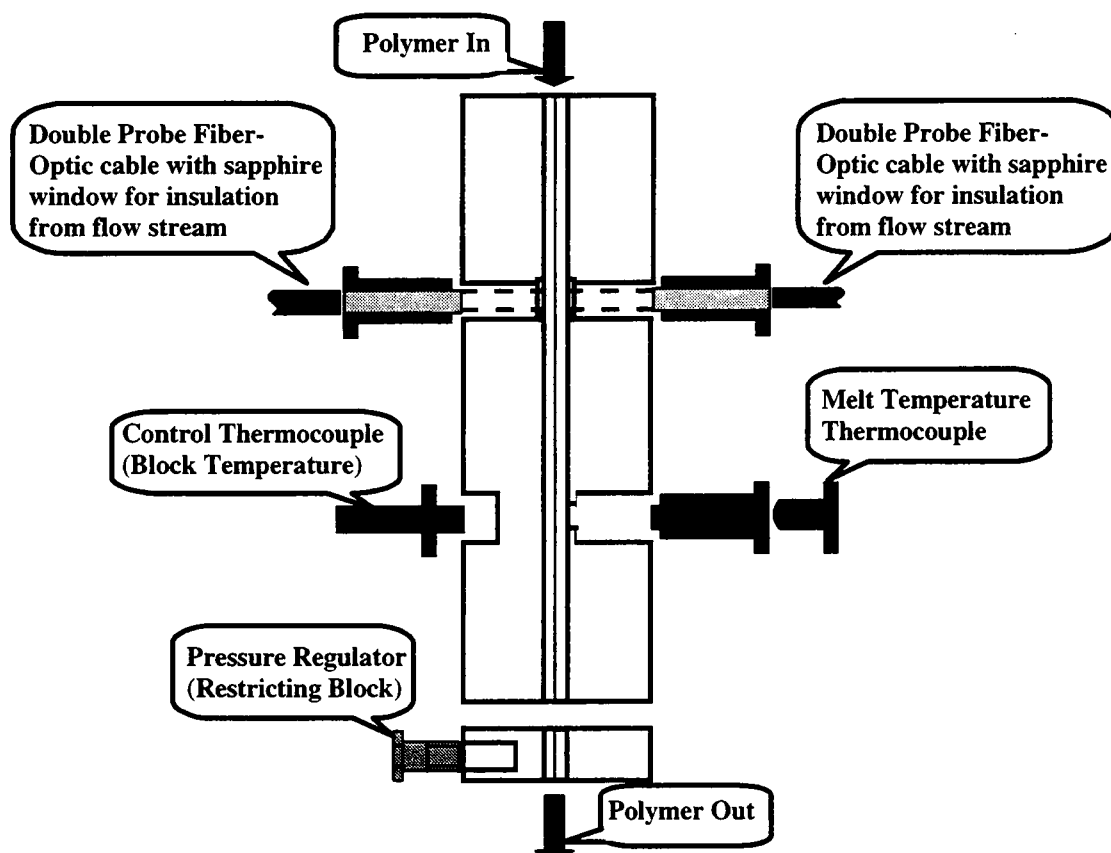


Figure 4.2 Detailed schematic of variable pathlength flow cell. This flow cell houses dual transmission fiber-optic probes. Optical pathlength between the probes can be altered between 1 mm and 9.5 mm by using mechanical spacers. The transverse dimension of the flow channel is 25.0 mm. The axial length of the die is approximately 200 mm.

optical pathlength between the probes is altered using ring shaped spacers of varying thickness. In the current setup, the pathlength can be varied from 1.0 mm to 9.5 mm. The pathlength is optimally set for each polymeric system such that the maximum absorbance is less than 1.0 unit. This ensures the validity of Beer's law (linear relationship of absorbance to concentration) to the spectra. Also, absorbance values greater than 1.0 mean that less than 10% of the incident light is reaching the detector, and that implies very low signal-to-noise ratio. Sensotron[®] fiber-optic probes are manufactured using a patented silicon-on-sapphire technology which gives them excellent resistance towards extreme operating conditions of pressure and temperature. The sapphire diaphragm of these probes can withstand temperatures as high as 400 °C and pressures as high as 30,000 psi. Khettry (1995) conducted a detailed study on the performance of these probes with specific attention to the following problems [7]: (1) maximum transmission efficiency of the probes, (2) intensity variation of the collimated beam with distance and azimuthal orientation, (3) fouling effects, (4) resistance to temperature and pressure, and (5) secondary containment of the probes, i.e. the maximum pressure that the probe can withstand before failure, if the sapphire is accidentally knocked off. Figure 4.3 shows a schematic of the specialized housing developed by Sensotron for the fiber-optic probes, and Figure 4.4 shows the composite assembly of the probe with the housing.

The analyzers used for various studies in the current research are primarily of two types: (1) interferometric (Fourier Transform based) spectrometer, and (2)

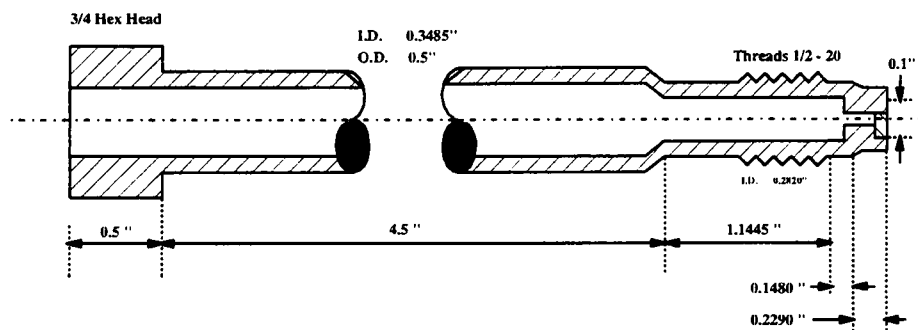


Figure 4.3 Schematic representation of Sensotron[®] dual transmission fiber-optic probe housing.
 [Source: A. Khettry, In-line Monitoring of Molten Polymeric Processes. Ph.D. Dissertation (1995). University of Tennessee, Knoxville.]

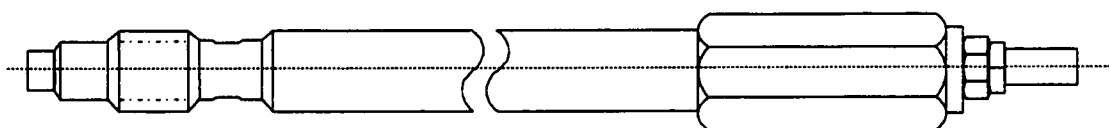


Figure 4.4 Composite diagram of Sensotron[®] fiber-optic probes with housing.
[Source: A. Khettry, In-line Monitoring of Molten Polymeric Processes.
Ph.D. Dissertation (1995). University of Tennessee, Knoxville.]

dispersive spectrometer. The Diamond-20™ (DS-20) Fourier Transform near-infrared (FT-NIR) spectrometer from Analect, Inc.[®] [84] consists of an interferometer that works on the moving-wedge principle. For measurements in the NIR region, the wedges are made up of calcium fluoride (CaF₂). The spectrometer uses a quartz halogen lamp as the source and an Indium Arsenide (InAs) detector with CaF₂ windows. The spectral range covered by this instrument is 12,000 cm⁻¹ (~834 nm) to 1,200 cm⁻¹ (~8,334 nm). The wavenumber resolution used for the experiments is typically 8 cm⁻¹. The dispersive spectrometer is a Guided Wave[®] [85] model 260 spectrometer which has capabilities to make measurements in both the NIR and the ultraviolet (UV) region. A quartz halogen lamp is used as the NIR source, and a deuterium lamp is used as the UV source. Lead sulfide (PbS) and photo-multiplier tube (PMT) detectors are used in the NIR and UV regions, respectively. Separate diffraction gratings are utilized for measurements in the two regions. The NIR grating is grooved at 300 lines/mm of the surface. For the UV region, the grating is grooved at 1,200 lines/mm of the surface. The slit widths are 0.5 mm and 0.25 mm for the NIR and UV regions, respectively.

For the current research, the FT-NIR spectrometer was used for most measurements in the NIR region, and the dispersive spectrometer and a linear-array based detector were used for measurements of polymer additives in the UV region.

CHAPTER 5

ESTIMATION OF POLYMER RHEOLOGICAL PROPERTIES AND CHEMICAL COMPOSITION IN AN EXTRUSION PROCESS

INTRODUCTION

The numerous advantages of NIR spectroscopy over conventional MIR spectroscopy, such as remote data collection coupled with rapid data analysis methods, availability of fiber-optics, and lack of sample handling problems were detailed in the previous chapters. Because of these advantages, NIR spectroscopy has proved to be an ideal analytical technique for in-line process monitoring. Measurements of chemical composition, polymer relative viscosity, and polymer morphology have been carried out in earlier studies [7,19]. Feasibility studies have been conducted for composition measurements under extreme process conditions, for example molten flowing polymers in an extrusion process, with focus on development of fiber-optics, optical probes, and near real-time measurements [7,10-13,24]. This technology is now employed in the commercial industry and is no longer restricted to measurements made using off-line laboratory instrumentation.

The primary objective of the current research is to extend the applicability of NIR spectroscopy in making in-line measurements of industrially important processing parameters, such as polymer rheological properties in an extrusion process, in addition

to measurements of chemical composition. Earlier, not much work has been done to address this problem. Marrow [86] attempted correlation of polymer melt flow index (MI) with NIR absorption spectra. In this study, data analysis was performed for MI-absorbance correlation, under the assumption that the rheological properties of a molten polymer were functionalities of chemical composition. However, this assumption does not follow from the theories of polymer science. Also, suitable data preprocessing techniques were not utilized, and hence, the model results had limited success. Because the rheological properties of polymers are indicators of end-use mechanical characteristics, in-line measurements of these properties are desirable during polymerization and processing. In the current research, a methodology will be described for simultaneous in-line measurements of rheological properties and comonomer composition for a system of random poly(ethylene vinyl acetate) (EVA) copolymers. The rheological properties of interest are polymer MI and linear viscoelastic material functions, namely complex viscosity response, or $|\eta^*(\omega)|$ response (ω , angular frequency), which is obtained from sinusoidal, oscillatory shear experiments. The methodology will be demonstrated for near *real-time* measurements in an in-line extrusion process, and will use fiber-optic NIR spectrometric techniques coupled with mathematical tools of multivariate statistical data analysis.

The specific objectives of the current research are detailed as follows:

- (1) To develop quantitative calibration models for correlating MI with the NIR absorption spectra for molten flowing EVA copolymers. In conjunction with models

for estimating vinyl acetate (VA, comonomer) concentration, these models will be used for simultaneous predictions of MI and composition during a real-time extrusion process.

(2) To develop quantitative calibration models for correlating $|\eta^*(\omega)|$ responses, (obtained over several decades of angular frequency values), with the NIR absorption spectra. The analysis will also focus on theoretical considerations for the origin of rheological response in NIR absorption spectra of flowing, molten polymers.

In the following section, a brief introduction will be given of EVA copolymers and polymer rheology with specific attention to definitions of linear viscoelastic functions and polymer melt index.

5.1 THEORY

5.1.1 Poly(ethylene vinyl acetate) (EVA) random copolymers

EVA copolymers are random copolymers that are produced by the polymerization of ethylene and vinyl acetate using one of the following processes [1,87]: (1) continuous bulk polymerization, (2) solution polymerization, or (3) emulsion polymerization. The chemical structures of the comonomers and the random copolymer are shown in Figure 5.1. At the end of the polymerization process, the molten polymers are compounded with lubricants and antioxidants and pelletized for use in subsequent processes. The VA comonomer results in PE-like resins with randomly distributed, pendant acetoxy groups. The incorporation of VA into the copolymer increases its

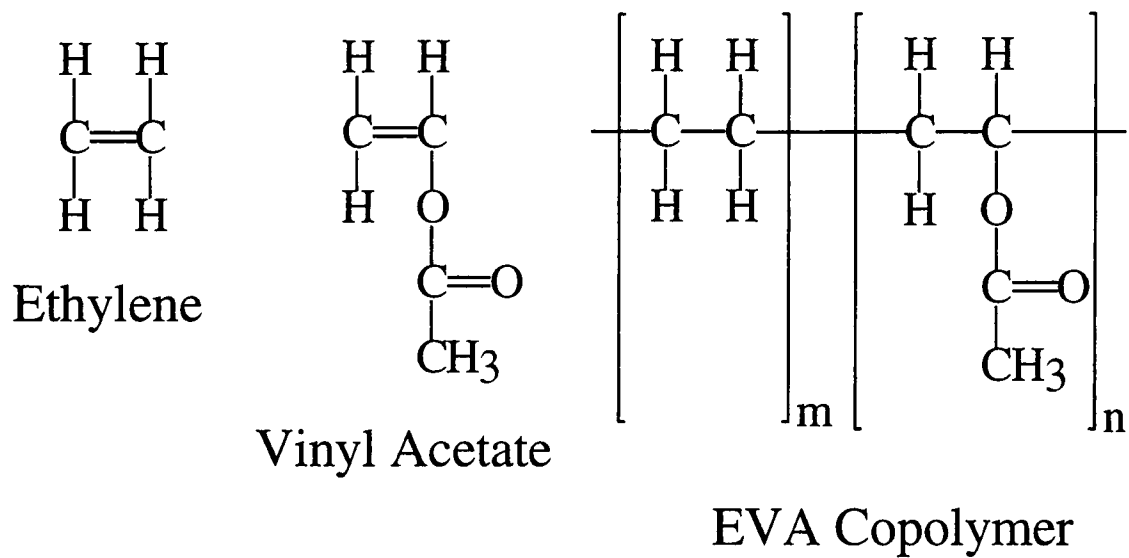


Figure 5.1 Chemical structure of ethylene and vinyl acetate monomers and poly(ethylene vinyl acetate) (EVA) copolymer.

rubber-like properties, and controls the elasticity and amorphous character of the copolymer. Also, the crystallinity of the copolymer decreases and the density increases with VA content. With increasing VA concentrations, the plastic becomes tougher and feels tackier. The VA content also enhances environmental stress-cracking resistance, tolerance for fillers, increases polarity, and improves compatibility and blending properties. Thus, the comonomer greatly influences the mechanical properties of these copolymers.

In addition to the comonomer content, other polymer properties that are controlled during polymerization are related to the molecular weight parameters. As the molecular weight increases, the viscosity, and the softening point increase. The polymer solubility, adhesion, and paintability decrease with increase in molecular weight. For EVA copolymers with similar weight average molecular weight, $\overline{M}_w$, those with narrower molecular weight distribution (*MWD*) will flow faster and set in a mold rapidly. EVA copolymers find numerous applications including use as hot melt adhesives and are compounded with other materials to produce a variety of color concentrates, coatings, and textile products [1,87].

The EVA copolymers differ from each other primarily in their VA content and their molecular weights. The typical values for the comonomer content for these polymers is usually between 0 wt.% VA and 50 wt.% VA.

5.1.2 Polymer Rheology — Melt Index and Linear Viscoelastic Properties

Melt index is an important parameter that is widely used in the polymer industry

as an indicator of the melt viscosity of a molten polymer. The experimental apparatus for measuring MI is a standardized equipment (ASTM D 1238-73 [88]) that provides a single numerical quantity (units: g/10 min), which is used as a rough estimate of the “flowability” of the polymer. A schematic of this apparatus is provided in Figure 5.2. The variables for MI measurements are the temperature and the input load on the piston, and these values depend on the particular polymer under study. For PE based resins and copolymers, the common operating condition is termed “condition E”, which involves a temperature of 190 °C and 2.16 kg load on the piston [89].

In addition to the MI parameter, there are other important properties that are used to characterize polymer flow behavior under applied stress or deformation, and some of these properties are discussed below. For most polymeric materials, the rheological response to deformation is *time-dependent* [89-92]. This behavior is attributed to the fact that the exhibited response lies between that of an ideal solid (obeys Hooke’s law of elasticity) and an ideal liquid (obeys Newton’s law of viscosity). In other words, the rheological response for polymeric materials is a combination of both elastic and viscous natures. This phenomenon is called *viscoelasticity*, and it governs the flow behavior of most polymers. When the applied stress-strain relationship is linear, (i.e. the modulus is independent of the applied stress), the response is termed *linear viscoelastic*. The particular response of a sample during a deformation experiment depends on the time-scale of the experiment in relation to the natural response time of the material under deformation. Thus, if an experiment is relatively slow, the material will appear to be elastic rather than viscous, and *vice versa*. At

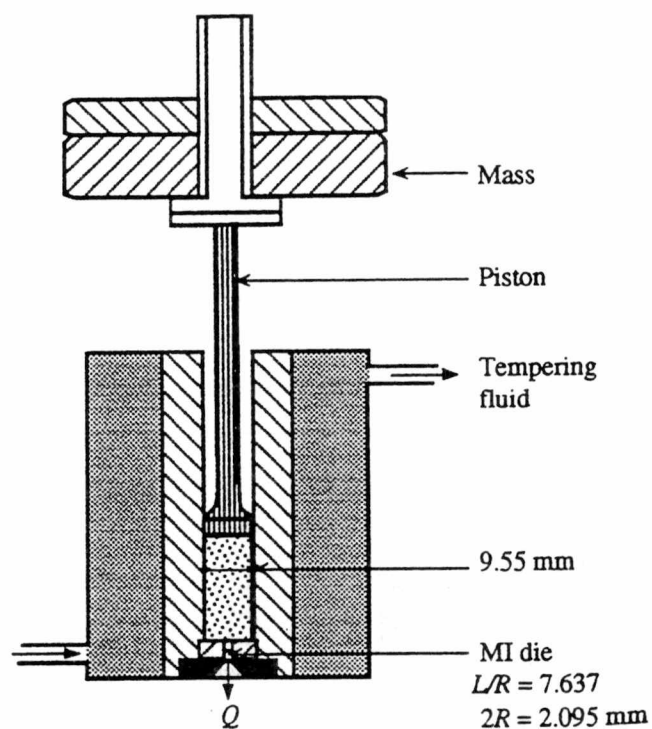


Figure 5.2 Schematic of an ASTM standardized melt index (MI) measurement apparatus

[Source: C. W. Macosko, *Rheology - Principles, Measurements and Applications* (VCH Publishers, Inc. New York, 1994)]

intermediate time-scales, a mixed viscoelastic response is observed. Such time-dependent responses are derived from experiments in which the overall response is expressed as a combination of the elastic and viscous responses. These dynamic experiments involve subjecting the material to constant amplitude sinusoidal stress at varying angular frequencies in order to suitably represent the time-dependent behavior.

These experiments yield measured material functions, which are functions of shear rate, frequency, or time. For an ideal solid, small amplitude, oscillatory shear experiments result in a response, such that the resulting shear stress oscillates with the input frequency and is exactly in phase with the input shear strain. On the other hand, for an ideal liquid, these experiments result in a shear stress that oscillates with the input frequency, but exhibits a phase shift of 90° (out-of-phase) with the shear rate.

For viscoelastic materials, the response behavior is intermediate such that the resulting shear stress exhibits a phase shift of $0^\circ < \phi < 90^\circ$ with both input shear strain and strain rate. For such experiments, the response can be resolved into two components, a real part, that is in phase and represents the elastic nature of the material, and an imaginary part, that is out-of-phase and represents the viscous nature of the material. These material functions are defined as follows: (1) storage modulus, $G'(\omega)$ — a measure of the elastic energy storage that takes place during deformation; (2) loss modulus, $G''(\omega)$ — a measure of the viscous energy dissipation that occurs in flow; and (3) complex viscosity, $|\eta^*(\omega)|$ — a combined measure of the real (elastic) and the imaginary (viscous) terms. The real part of the complex viscosity is related to the

dynamic viscosity (viscosity of an ideal liquid) and the imaginary part is related to the storage modulus. This quantity is related to the storage and loss modulus by the expression:

$$|\eta^*(\omega)| = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \quad \dots(5.1)$$

Small amplitude oscillatory measurements are made using a parallel plate, cone-and-plate, or a couette type of viscometer [89,91]. A typical cone-and-plate type viscometer is shown in a schematic representation in Figure 5.3.

5.1.3 Correlation of Rheological Properties with NIR Absorption Spectra

In the current research, in-line measurements of the rheological properties, for example the MI and the $|\eta^*(\omega)|$ response are carried out on flowing, molten EVA polymers in a single-screw extrusion process. During polymer extrusion, the rheological flow behavior of molten polymers is anisotropic. The extent of anisotropic nature of flow is governed by the level of molecular orientation and the orientation distribution of flowing polymer melt. Under nominal extrusion operating conditions involving more or less constant shear rates, these anisotropic effects will be strong functions of polymer weight-averaged molecular weight ($\bar{M}_w$), *MWD*, chain length, entanglements, and branching parameters. It is expected that these varying levels of orientation and orientation distribution in the optical measurement volume would affect the NIR absorption spectra in some manner. These rheological effects on the NIR spectra, which are attributed to anisotropic rheological flow, are *lower-order magnitude* effects.

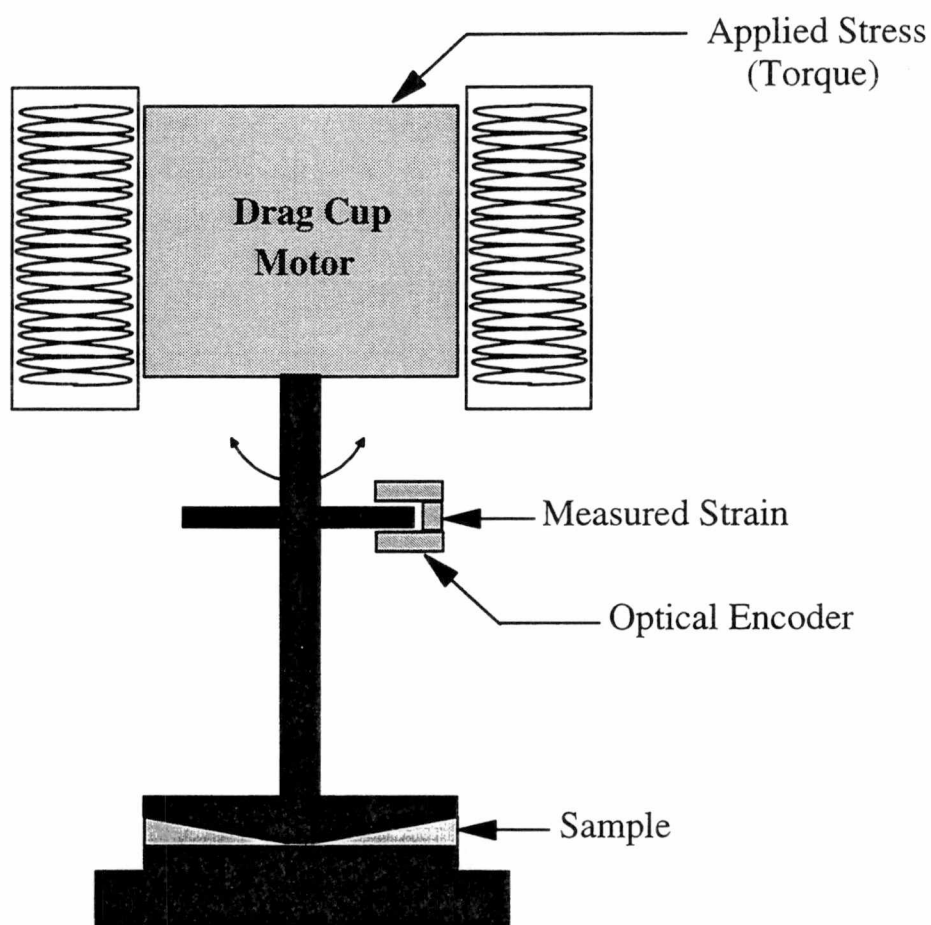


Figure 5.3 Schematic representation of experimental setup for rheological measurements using a Rheometrics[®] Dynamic Stress Rheometer. A cone-and-plate viscometer arrangement was utilized for small-amplitude, oscillatory shear experiments. The experiments were performed over four decades of angular frequency values.

In the NIR absorption spectra, variations in chemical composition are *dominant* effects, and in this study, the variations of comonomer concentration are termed as the *primary factors of variation*. Compared to the strong, primary effects of chemical composition, the rheological flow effects are only subtle variations in the NIR spectra, and such variations are termed as *secondary factors of variation*. It is noted that these rheological effects contain important information about physical properties that directly correlate with the molecular weight parameters. Some of these properties are polymer MI and linear viscoelastic properties. In a very generic sense, MI is inversely related to the polymer molecular weight parameters, such as the $\overline{M}_w$ values. At moderately low stress values, the MI resembles an “inverse” viscosity, and a high MI value implies a low zero-shear viscosity, η_0 , or a low $\overline{M}_w$ value [89]. Because this parameter is so widely used in the industry, there is considerable interest in relating it quantitatively to other rheological material functions, such as the complex viscosity response. In a similar manner to MI, the $|\eta^*(\omega)|$ responses are also functions of polymer molecular weight parameters, such as $\overline{M}_w$ and *MWD*. In general, for EVA random copolymers, these rheological properties are *not related to* the comonomer ratio of ethylene and VA. (Only at very high VA concentrations (> 30 wt.% VA), the incorporation of VA favors increased branching in the copolymer, and subsequently, affects rheological behavior to some extent.)

Therefore, the primary (due to chemical composition) and secondary (due to rheological flow) effects on the absorption spectra are independent; and these effects

can be separated to give simultaneous information about the chemical composition and rheological functions. In the following sections, experimental studies will be described, and results will be detailed for quantitative analysis of the MI-absorbance and $|\eta^*(\omega)|$ -absorbance relationship.

5.2 EXPERIMENTAL

The EVA copolymer samples were obtained from two independent sources and will be, henceforth, referred to as Group I and Group II samples. Group I comprises of fourteen samples of EVA copolymers from one manufacturer, and Group II comprises of five samples of EVA copolymers, which were made available from a second manufacturer. The existence of two separate sets of polymer samples provided the advantage of preparing calibration models on one set of polymer samples and using the second set as an independent test set to validate the precision of the calibration models. This would also test the ability of the calibration models to predict the desired properties in light of external variations, such as processing differences during polymerization, *et cetera*.

For the MI calibration model, only Group I samples could be used for analysis, because the primary analysis for MI values were not made available for Group II samples. The primary MI analysis for Group I samples was performed using ASTM standardized analysis procedure and equipment [88] at the laboratory facility of the company that provided the Group I samples. The primary analysis for the $|\eta^*(\omega)|$

values was performed in our laboratory for both sample sets, and Group II samples were utilized to validate the calibration model developed on Group I samples. The laboratory measured concentration values of VA for both Groups I and II, and MI values for Group I samples have been tabulated in Table 5.1. The system of EVA samples chosen for this study consists of primarily two factors of variation, namely the comonomer ratio or the concentration of VA in the copolymer and the molecular weight parameters. As mentioned earlier, the melt viscosity, or melt index, of the polymer is governed by the molecular weight parameters. The VA content varied from 0 wt.% to 34 wt.% and the MI values varied from 0.34 g/10 min to 370 g/10 min.

In-line NIR transmission spectra of molten EVA samples were collected in a flow cell at the exit port of the single-screw extruder. Earlier, the experimental apparatus was detailed in Figure 3.1. In the current setup, the nominal flow rate of molten polymer through the extruder is ~ 1.2 lb/hr. For the rectangular flow channel in the extruder flow cell, the nominal shear rate was estimated at ~ 25 s⁻¹. All EVA samples were extruded at more or less constant shear rates. The temperature of the flow cell was maintained at 200 °C throughout the experiments. An average temperature fluctuation of about 1-3 °C was observed while the spectral data were being recorded. The NIR spectra were collected in the wavelength region of 1,000 nm to 2,500 nm. The analyzer used for measurements in the NIR region was the Analect® FT-NIR spectrometer. Ten replicate spectra were collected for each sample, and each spectrum was averaged over 64 scans. The optical pathlength, or the distance between the two

Table 5.1: Laboratory measurements for EVA samples in Group I and Group II

Group I			Group II	
Sample Number	VA Concentration (wt.%)	Melt Index (g/10 min)	Sample Number	VA Concentration (wt.%)
1	0	1.89	1	18.72
2	9.08	6.45	2	20.90
3	12.12	7.79	3	21.01
4	12.04	0.34	4	26.70
5	15.18	7.84	5	34.95
6	17.91	0.64		
7	18.06	6.92		
8	24.89	17.54		
9	25.22	370.0		
10	28.49	6.07		
11	27.84	143.0		
12	28.59	368.0		
13	28.37	23.68		
14	32.05	37.8		

fiber-optic transmission probes, was maintained at 2.5 mm. This pathlength was chosen to keep the maximum absorbance at less than 1.0 unit.

5.3 BAND ASSIGNMENT

Figure 5.4 shows the overlaid absorbance spectra of EVA samples in the NIR wavelength range of 1,620 nm to 1,840 nm. The absorbance band in this wavelength region corresponds to the first overtone vibrational mode of methylene (C—H) stretching [17,20,22], and is a common feature for all macromolecules. (Note the presence of methylene in EVA copolymers). With the incorporation of VA into the copolymer, the number density of the C—H stretch vibrations in the optical measurement volume (2.5 mm long and 1.5 mm in diameter) decreases. This leads to a decrease in the intensity of the polyethylene doublet around 1,725 nm and 1,765 nm. This difference in the absorbance values allows for the quantification of VA. Subtle changes are observed in the shoulders of the methylene stretch doublet. A second region (not shown in Fig. 5.4), tentatively assigned to a combination band of carbonyl (C=O) and C—H stretches, occurs in the wavelength range of 2,000 nm to 2,200 nm, with a peak at 2135 nm. This peak increases with an increase in the VA content.

5.4 MELT INDEX CALIBRATION MODEL

5.4.1 Data Analysis

The objective of quantitative analysis of NIR absorbance spectra is to simultaneously, and independently, estimate VA content and MI, thus separating the

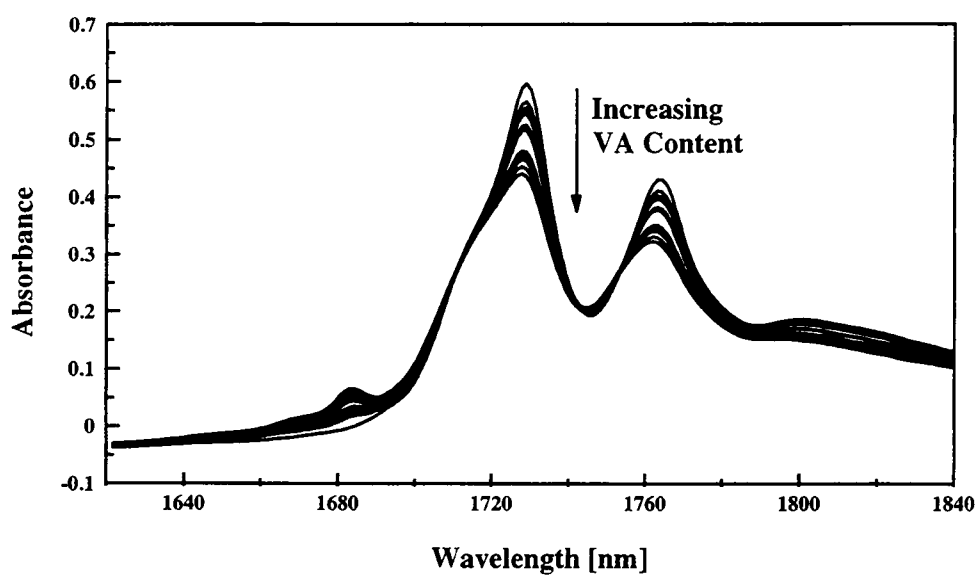


Figure 5.4 Overlaid absorbance spectra of EVA samples in the NIR wavelength region of 1,620-1,840 nm. The absorbance band is attributed to methylene (C—H) stretch, first overtone vibrational mode.

primary and secondary sources of variation. Thus, separate calibration models were developed for estimating VA content and MI for EVA samples. Because VA content is the dominant factor of variation in the absorbance spectra, a multivariate regression analysis can be carried out easily to develop a model for estimating VA concentration. Khettry [7] demonstrated that a robust regression model could be developed to quantify VA content using spectral data in either of the two regions of first overtone or carbonyl combination region.

In attempts to correlate the MI with the absorbance spectra, it was observed that the range of MI values in the available set was very large. Samples were available with a wide range of MI values, from very high viscosity (MI ~ 0.34 g/10 min) to very low viscosity (MI ~ 370 g/10 min). This implies that there is significant variation in the $\overline{M}_w$ parameters among the samples. Because such large variations lead to only subtle effects of lower order magnitude on the NIR spectra, it is assumed that a *first-order response* from the $\overline{M}_w$ parameters-absorbance relationship can be obtained by expressing the $\overline{M}_w$ parameters in terms of their natural logarithms. Such data preprocessing also amounts to “linearizing” the variables used for regression.

Therefore, in conjunction with the above assumption, any rheological function, such as MI or $|\eta^*(\omega)|$ response, must be processed before regression using the same correlation of natural logarithms. The theoretical justification for using the natural logarithms for these rheological properties comes from the definition of material functions, such as zero-shear viscosity in dynamic rheological experiments. For

polymer melts with molecular weights greater than the critical molecular weight M_c , the zero-shear viscosity is given by the proportionality:

$$\eta_0 \propto \overline{M}_w^a \quad \dots(5.2)$$

where η_0 is the zero-shear viscosity, and a is a constant exponent. Berry and Fox [93] observed that for linear homopolymers of narrow molecular weight distribution, $a = 3.4$. The above expression implies that the relationship of $\overline{M}_w$ with most rheological material functions is non-linear. Taking the natural logarithm of the expression on both sides, the following “affine” relationship is obtained:

$$\ln(\eta_0) = \ln(K) + a \ln(\overline{M}_w) \quad \dots(5.3)$$

where K is a constant of proportionality. In the previous section, it was mentioned that the MI variation with $\overline{M}_w$ parameters and η_0 was of an inverse proportionality. This relationship could be expressed as follows:

$$\ln(MI) \propto -k \ln(\eta_0) \quad \dots(5.4)$$

Therefore, in the multivariate data analysis for melt index, the $\mathbf{Y}$ matrix consists of $\ln(MI)$ values, and similarly, $\ln(\eta^*(\omega))$ values. Linearity is retained by mean-centering the $\mathbf{Y}$ columns, such that the $\ln(K)$ term vanishes after subtraction.

In order to separate the lower-order, secondary rheological effects from the strong primary features of chemical composition in the NIR spectra, it was essential to choose a random sample set, where the two variables of VA content and $\ln(MI)$ values had low correlation in their numerical entries. Therefore, care was taken to avoid

inadvertently capturing any information about VA content, while developing a calibration model for $\ln(\text{MI})$. In this context, a statistical term called the correlation coefficient, r , is introduced, which is defined as follows [94]:

$$r = \frac{\text{cov}(\mathbf{x}, \mathbf{y})}{\sqrt{\text{var}(\mathbf{x})\text{var}(\mathbf{y})}} \quad \dots(5.5)$$

where for any given variables $\mathbf{x}$ (for example VA content) and $\mathbf{y}$ (for example MI), $\text{var}(\mathbf{x})$ and $\text{var}(\mathbf{y})$ are the variances of $\mathbf{x}$ and $\mathbf{y}$, respectively, and $\text{cov}(\mathbf{x}, \mathbf{y})$ is the covariance of $\mathbf{x}$ and $\mathbf{y}$.

An r value close to 1.0 implies very high correlation between the two variables, while an r value close to 0 implies that the distribution of the two variables is random. To obtain a strict random distribution, a very large sample set is required. Unfortunately, such a large sample set is rarely commercially manufactured, and only a limited set of fourteen Group I samples were available for analysis. Therefore, from the available sample set, a subset of sample spectra was chosen for which the VA concentration values and $\ln(\text{MI})$ values had very low correlation, to develop a *trial* calibration model for $\ln(\text{MI})$. A successful MI-calibration for this sample subset would mean that the melt index is an independent physical factor of variation, which is inherent in the absorbance spectra of these samples. Because the MI and VA content variations were random for this subset, it would ensure that a “false” relationship is not extracted between the two variables due to numerical collinearity.

For the *trial* subset, EVA samples were selected in the VA content range of 24 wt.% VA to 32 wt.% VA and $\ln(\text{MI})$ values in the range of 1.8 (MI ~ 6 g/10 min) to 6

(MI ~ 370 g/10 min). In effect, while developing the *trial* model, large VA variations were suppressed, and significant variations in the MI values were incorporated. The correlation coefficient was a low value of 0.10 for the *trial* set, which implied a fairly random set.

Once a successful relationship between the $\ln(\text{MI})$ values and the absorbance spectra was established using the *trial* calibration model, a new calibration model will be developed with an enlarged sample set. This sample set will include a wide range of variation in both VA content (wt.% VA ~ 0 to 32) and $\ln(\text{MI})$ values ($\ln(\text{MI})$ ~ 0.34 to 6). The *final* calibration model will be tested for MI predictions of EVA samples belonging to two categories: (1) EVA samples with similar MI values but widely varying VA content, and (2) EVA samples with widely varying MI values but similar VA composition. A detailed analysis of the development of both the *trial* and the *final* calibration models is given below.

5.4.2 Results and Discussion

Ten replicate spectra for each sample were included in the analysis. First derivatives of the spectra were taken to build the *trial* calibration model. Differentiated spectra, as shown in Figure 5.5, are free of any baseline offsets. They also resolve spectral peaks better and expose any subtle variations in the spectra. However, such spectra are noisier and have to be smoothed before multivariate analysis. The smoothed data were standardized by mean-centering as a part of pretreatment. Mean-centering involves subtracting the mean of each column in the **X** and **Y** matrices from the data

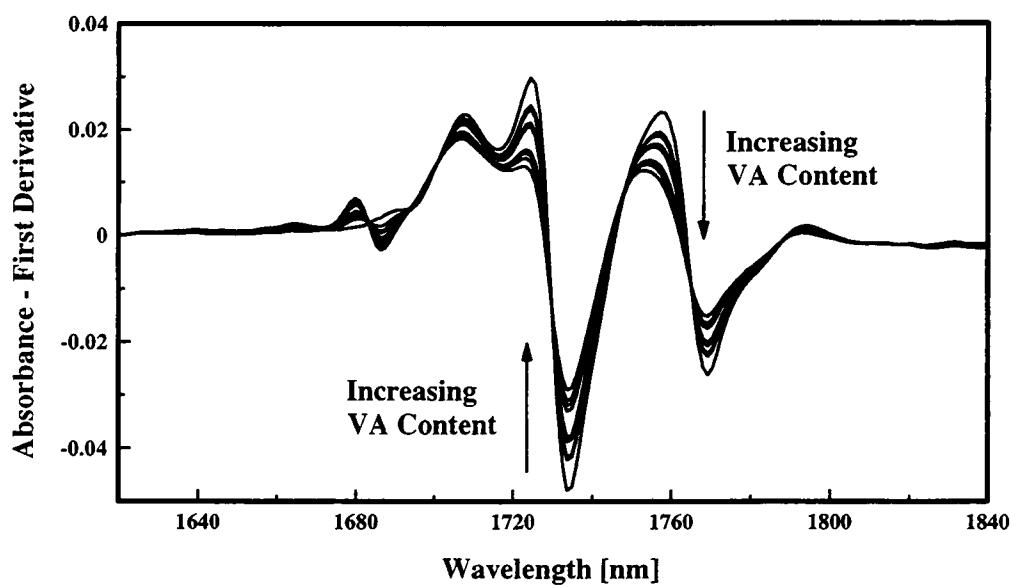


Figure 5.5 Overlaid plot of absorbance-first derivative spectra of EVA samples in the NIR wavelength region of 1,620-1,840 nm. The absorbance band is attributed to methylene (C—H) stretch, first overtone vibrational mode. Differentiated spectra are free of baseline offsets and provide better spectral resolution.

points, such that the mean of each mean-centered matrix is zero [95]. One spectrum, the average of the ten replicate spectra, for each sample in the subset was included to form the calibration set.

For the MI *trial* calibration model, the Y matrix consisted of one column, of size $(m \times 1)$, with the $\ln(MI)$ values corresponding to each sample. A leave-a-sample (LAS) cross-validation technique was used to build the PLS regression model [7,19]. A general description of the cross-validation techniques was provided in Chapter 2. The LAS cross-validation procedure was essential because the sample set was not large enough for two separate calibration and prediction subsets. According to this approach, one sample was left out from the calibration model every time and chosen as an internal validation set. This sample was predicted from a calibration model developed on the remaining samples. Several such calibration models were developed, with additional principal components being incorporated each time. The residual errors for the predictions of this excluded sample were evaluated from the actual values and the NIR predicted values, as a function of the number of principal components. In the next step, this sample was included into the calibration set and another sample was removed; and a similar procedure was followed. This process was continued until all samples in the original calibration set were left out from the calibration at least once and used for internal validation.

The optimal number of principal components, or factors, was decided by evaluating a cumulative PRESS term. For every principal component, this term was calculated by summing the individual PRESS values for each sample (according to Eq.

2.31). The number of factors retained in the final calibration model corresponded to a *minimum* cumulative PRESS value. In addition to the PRESS value, an *F-statistic* criterion was used to decide the optimal number of principal components required for calibration [46,47]. This criterion is a statistical method, which takes into account the relative importance of incorporating additional factors into the calibration model.

The cross-validation procedure is also advantageous in that it highlights sample outliers. Outlier samples are those samples that do not fall in the linearity range decided by the calibration model, and these are identified by unusually large prediction errors, or PRESS values. If there are far too many outliers, it means the existence of either a nonlinear relationship or lack of any relationship between **Y** and **X**.

The PLS algorithm used singular value decomposition (SVD) to evaluate the principal factors. The cumulative PRESS plot *versus* the number of principal factors is illustrated in Figure 5.6. In combination with the F-statistic criterion, this plot suggested that a model with three factors was required for optimal MI predictions. Using Eq. 2.32, the standard residual error for the model, or the SEC value, was found to be 0.14 (on a natural log scale). Figure 5.7 shows the predictions for samples in the calibration set, with a calibration model based on three factors. This plot shows excellent agreement for the NIR predictions of MI with the actual MI values obtained from primary analysis.

A qualitative interpretation is obtained from an analysis using the first loading vector. As was discussed in Chapter 2, loading vectors define the effect of the independent variables, (or the responses at individual wavelengths), on the variance in the data. In Figure 5.8, the first loading vector is plotted against the NIR wavelengths. In

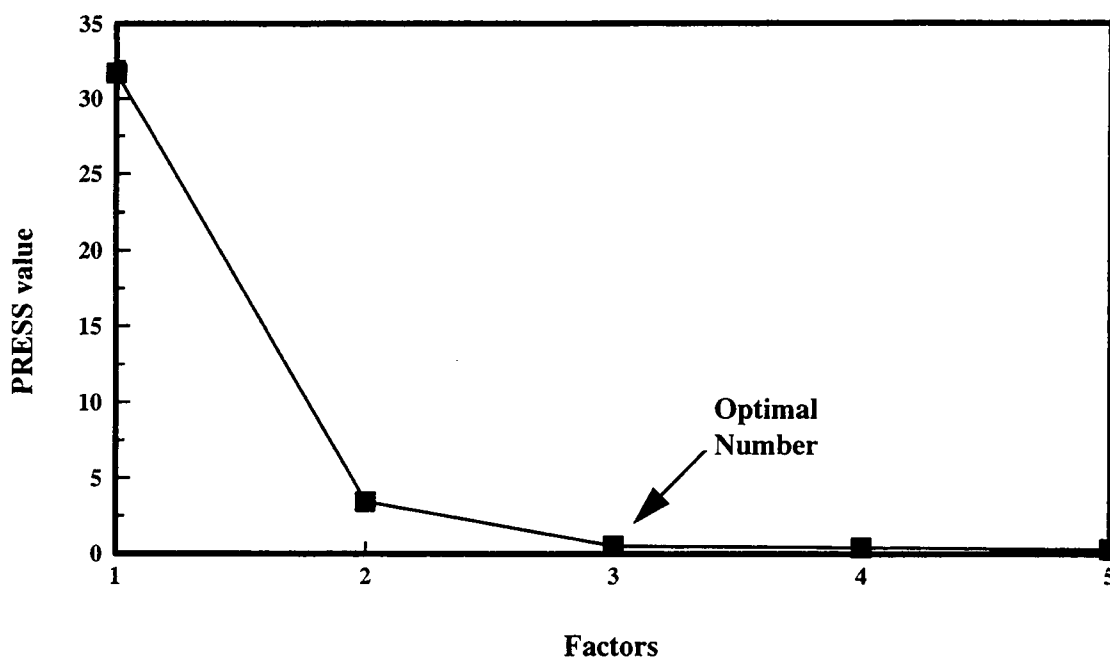


Figure 5.6 PLS calibration of $\ln(\text{MI})$: PRESS plot for five factors obtained from LAS cross-validation. The optimal number of factors was chosen using the PRESS criterion coupled with an F-statistic criterion

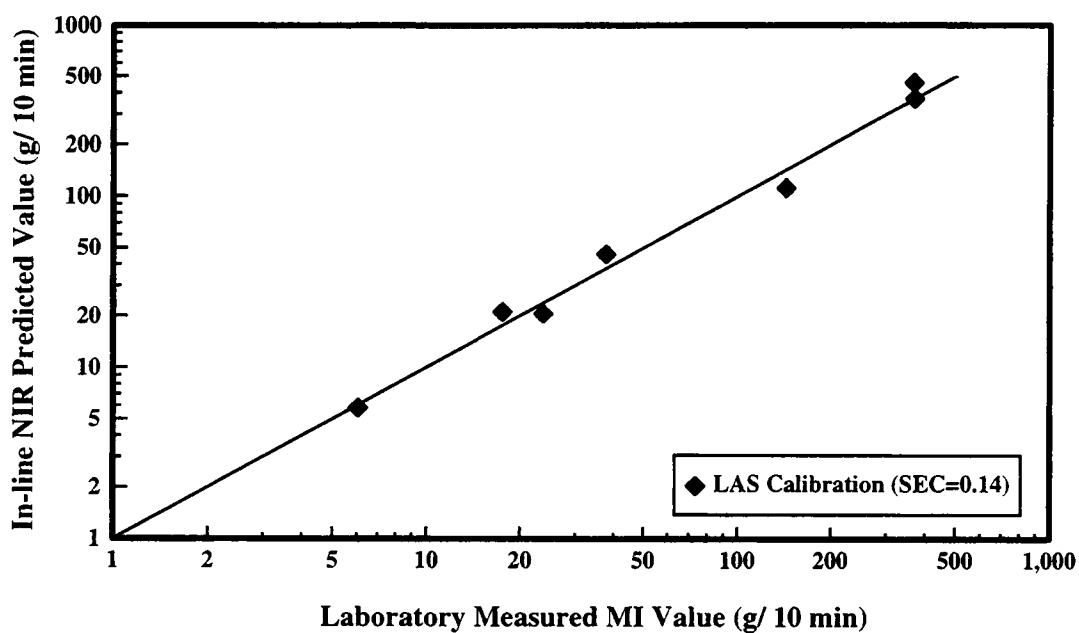


Figure 5.7 LAS cross-validation results: MI predictions for samples in the calibration set. In this figure, it is observed that the NIR predicted MI values show excellent agreement with the laboratory measured MI values.

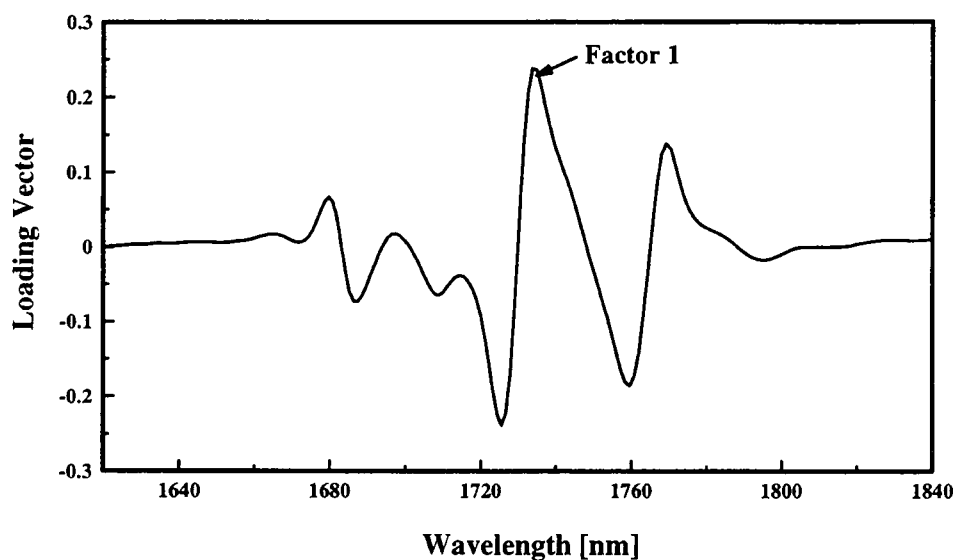


Figure 5.8 Plot of the loading vector for the first principal component *versus* NIR wavelengths. From this figure, the first loading imitates the *average* first-derivative spectrum (Fig. 5.5).

comparison with the absorbance-first derivative plot in Fig. 5.5, it is observed that the first loading vector typically mimics the profile of an *average* first derivative spectrum. Because VA content is the dominant feature in the NIR absorbance spectra, it is expected that the first principal component contains information about the VA content. Therefore, the first loading vector explains the strong contribution of VA variation in the absorbance spectra. In conjunction with results obtained from the PRESS criterion, it is observed that the higher principal components explain information pertaining to MI-absorbance correlation. A thorough qualitative analysis using score and loading vectors will be presented in later sections on $|\eta^*(\omega)|$ -calibration. Such interpretation will focus on identifying spectral regions in the absorbance spectra correlating individually with VA content and rheological response.

The above *trial* model established that there is independent information about the rheological response in NIR absorbance spectra. With suitable data preprocessing in the form of natural logarithms, multivariate techniques can be used to correlate physical properties, such as MI with the absorption spectra. With the success of the *trial* model, the sample set was enlarged to include a larger variation in both variables, namely the VA content and the MI values. This sample set was used to develop the *final* calibration model that would be used for real-time monitoring during polymer extrusion. As before, one spectrum for each sample, corresponding to the average of ten replicate spectra, was utilized in the model. A separate, independent calibration model was built to predict the VA concentration. Using the PRESS and the F-statistic criteria, a one-factor model was developed for predicting VA content and a three-factor model was developed for

predicting $\ln(\text{MI})$. Table 5.2 shows the variance explained in the y -blocks for the two calibration models. From Table 5.2, it is observed that three factors are required to explain about 99.6% variance in the MI data, while only one factor is sufficient to account for about 99.7% variance in VA content. For MI-calibration, the inclusion of a second principal component explains an additional variance of 59.1%. Hence, the second principal component is most significant during MI-calibration and contains maximum information about MI variance.

An external prediction set was formed using spectra of samples, which were not included in the calibration set. The calibration models developed above were used to predict the samples in the prediction set. The SEP values, as evaluated from Eq. 2.33, for the two models were 0.46 for MI predictions (three-factor model) and 0.62 wt.% for VA predictions (one-factor model). A plot of the standard errors in the calibration and prediction set for the MI-calibration model is shown in Figure 5.9. The SEP curve in this figure reiterates the fact that three principal components give minimum residual error for MI. Therefore, three factors should be used to build the calibration model for MI. The in-line predictions for $\ln(\text{MI})$ and VA concentration for the final calibration and prediction sets are shown in Figures 5.10.a and 5.10.b, respectively. Excellent agreement is observed between the actual, laboratory primary analysis and the in-line, NIR predicted MI and VA values.

5.4.3 Real-time Predictions in In-line Extrusion Process

Finally, the stability of the predictions using the calibration models was tested

Table 5.2: Total y-block variance explained for different factors.

From the MI calibration model, it is observed that the second factor explains maximum information about rheological response.

Number of factors retained	VA calibration model Total y-block variance explained (%)	MI calibration model Total y-block variance explained (%)
1	99.7	36.5
2	99.9	95.6
3	99.9	99.6

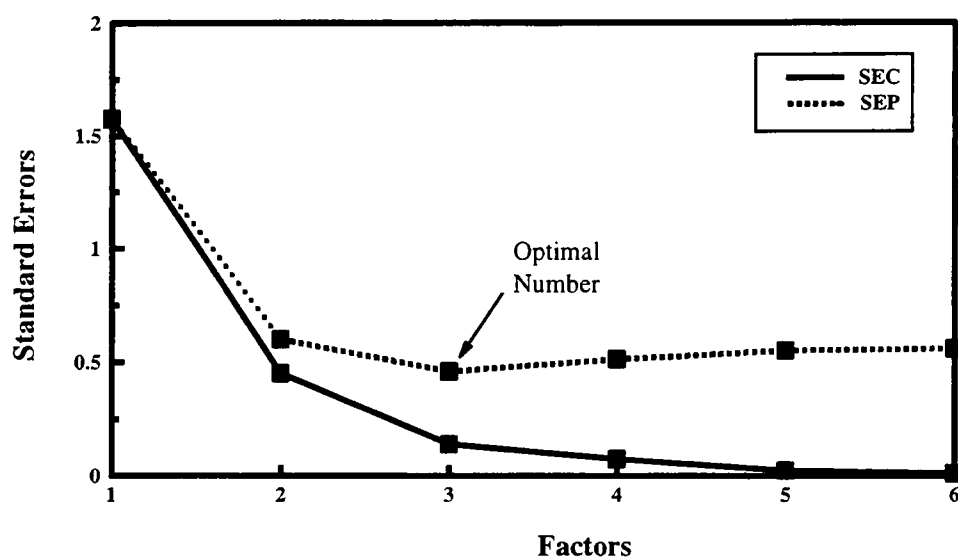
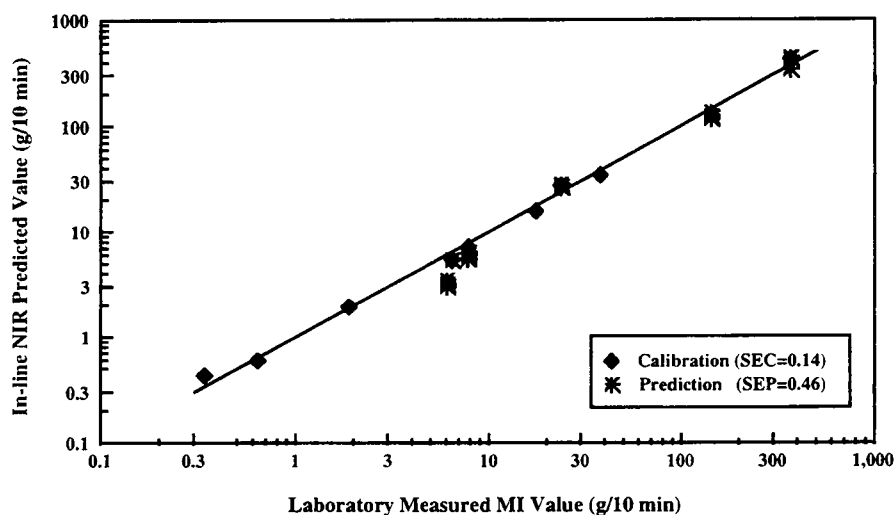


Figure 5.9 Standard Errors plot for PLS models with different principal components. As expected, the SEC curve shows a decreasing trend with increasing number of factors. The optimal number of factors is decided by the minimum PRESS value and an F-statistic criterion.

a)



b)

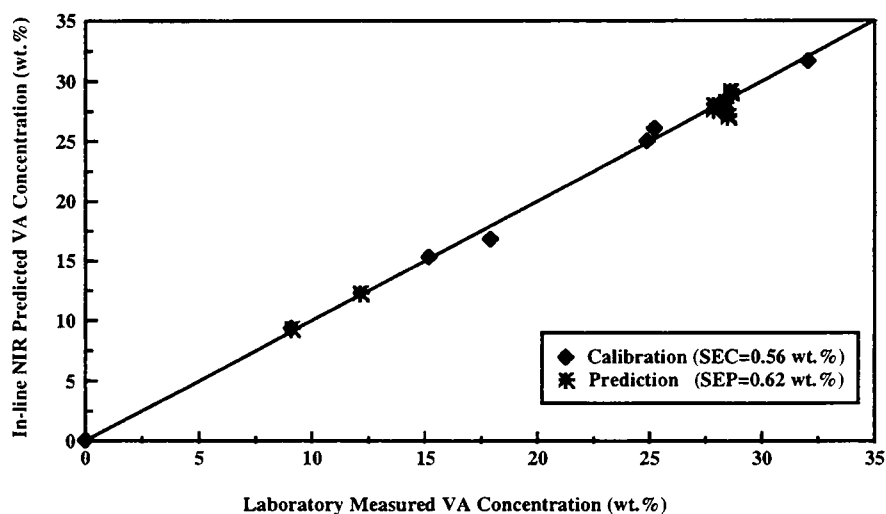


Figure 5.10 Plot illustrating the NIR predictions for a) melt index, MI and b) vinyl acetate, VA concentration (wt.%). The MI calibration model was built using $\ln(\text{MI})$ values. A three-factor model was used for optimal predictions for $\ln(\text{MI})$ and a one-factor model was developed for predicting the VA content.

for simultaneous, real-time predictions of MI and VA concentration during extrusion. A generic schematic of the methodology for real-time monitoring is presented in Figure 5.11. EVA samples were continuously fed through the extruder, and test scans were taken. Data preprocessing of these spectra (such as first-derivative, mean-centering, *et cetera*) was carried out in a similar manner to the sample spectra used for calibration. Each spectrum was averaged over sixteen scans and every fifth spectrum was saved. One spectrum was saved after approximately every forty seconds. The two calibration models built earlier were then used to estimate the desired properties of VA content and MI. The real-time process monitoring modules, PC80[®] and FSP6802B[®] available in the Analect[®] calibration software [84], were used for spectral data collection during extrusion. Six samples belonging to two different classes were used for real-time predictions. Class A consisted of EVA samples with widely varying VA concentrations, but similar MI values. These constituted the first three samples in Table 5.3. Four EVA samples were included in Class B. These samples consisted of ~ 28 wt.% VA and had very different MI values. The samples in the two classes, (one sample overlaps in the two classes), were continuously fed through the extruder in the order in which they are presented in the table.

The real-time predictions for VA content and MI for Class A and Class B samples are illustrated in Figure 5.12. It is observed that most predictions lie within the limits set by the SEP values. This implies that the predictions for both VA concentration and $\ln(\text{MI})$ lie between the actual laboratory value $\pm$ SEP. The calibration models can

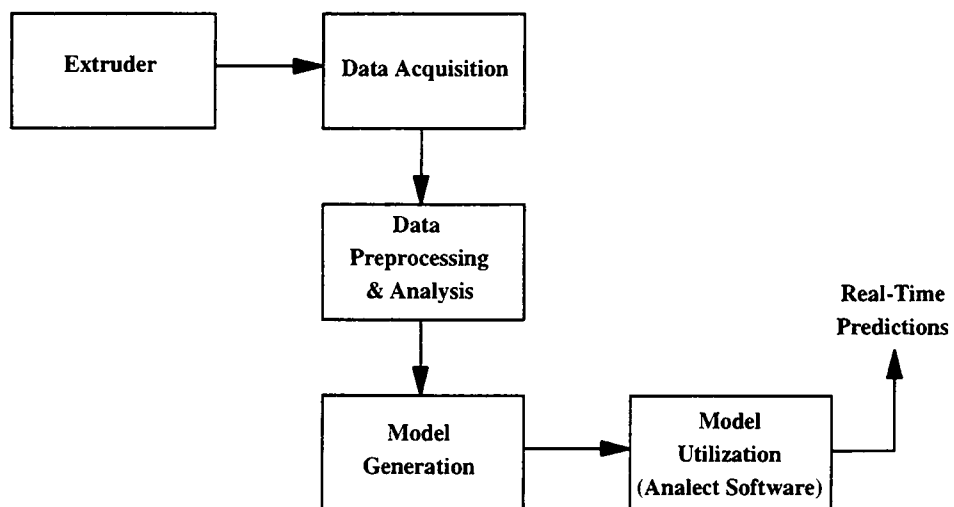


Figure 5.11 Schematic for real-time monitoring of VA content and melt index in EVA copolymers.

Table 5.3: EVA samples for real-time monitoring

Sample Number	Class Identity	VA Concentration (wt.%)	$\ln(\text{MI})$ values
1	A	9.11	1.86
2	A	12.12	2.05
3	A & B	28.49	1.80
4	B	27.84	5.91
5	B	28.59	4.96
6	B	28.37	3.16

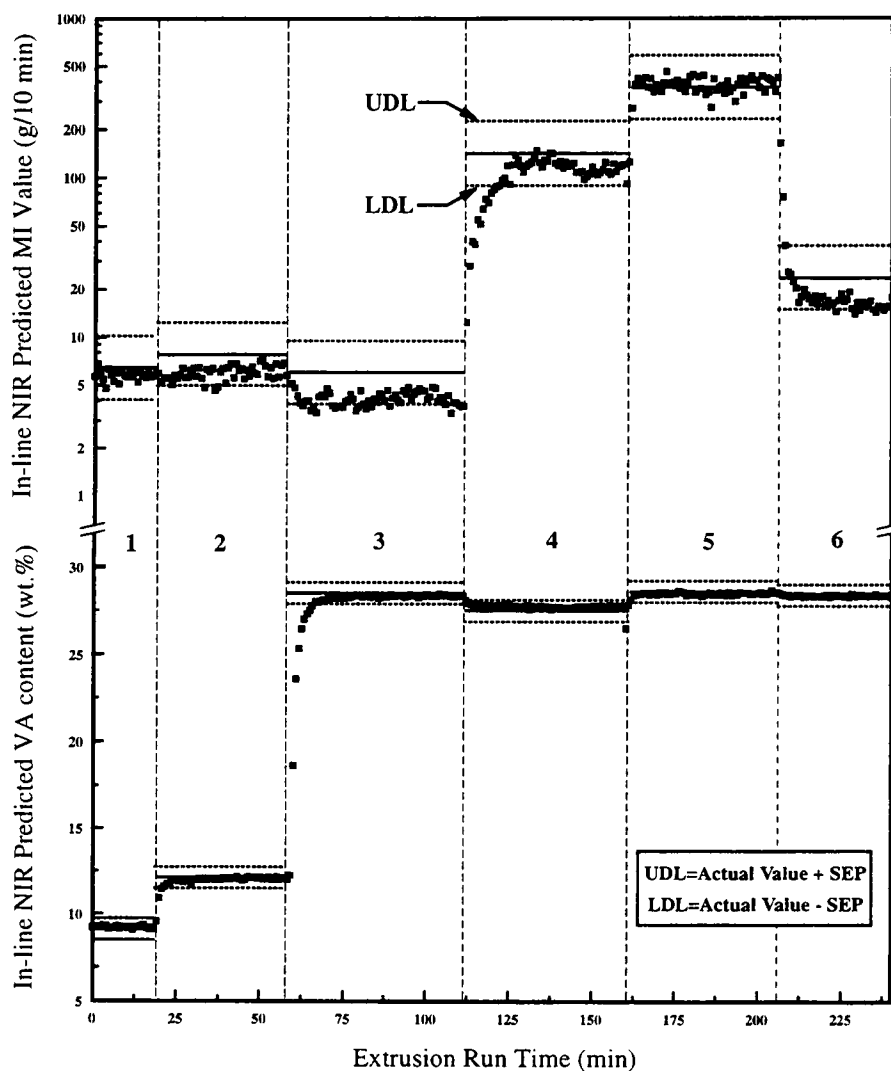


Figure 5.12 In-line, real-time predictions for MI and VA content in Class A (samples numbered 1, 2, and 3) and Class B (samples numbered 3, 4, 5, and 6) EVA samples. The predictions for both primary (VA content) and secondary (MI) variables lie within SEP limits associated with the calibration models. [SEP for VA-calibration model = 0.62 wt.%; SEP for MI-calibration model = 0.46 on a natural log scale]. The transition region between successive samples exhibits intermediate properties of VA content and MI. This region is also an indicator of the *average* sample residence time in the extruder. [UDL: upper detection limit; LDL: lower detection limit]

successfully estimate samples belonging to both classes. This reiterates that the PLS calibration models can *separate* the two independent factors of variation in the EVA samples, namely VA concentration and MI. Another observation is made in the smooth transition region between any two successive samples. In this region, a “blend” of the two samples is expected in terms of both VA content and melt viscosity conditions. This “blend” would progressively change in both VA composition and MI from the previous sample to the new sample. In Fig. 5.12, it is observed that the calibration models capture the expected behavior in the transition region, with regard to intermediate properties of VA content and melt viscosity in the blend. The transition region is also an indicator of the average residence time of the sample in the extruder, gear pump and flow cell. According to the figure, the MI values seem to take a longer time to stabilize to steady values than the VA concentration values.

5.4.4 Conclusions

Simultaneous in-line monitoring of both VA content and MI values in molten EVA copolymers is extremely useful for polymer quality control. The above study has demonstrated that the application of NIR fiber-optic spectrometry can be extended to estimate polymer MI during extrusion, in addition to composition measurements. It is established that the variation of MI in EVA copolymers is independently observed in the NIR absorption spectra. The robustness of calibration models was tested by real-time predictions. The predictions for both VA concentration and MI lie within detection limits decided by the SEP limits (0.62 wt.% and 0.46, respectively). The calibration

models were tested on EVA samples belonging to two categories: (1) EVA samples with similar MI values but widely varying VA content, and (2) EVA samples with widely varying MI values but similar VA composition. The ability of the models to estimate samples in these two distinct groups further validated the robustness of calibration.

5.5 COMPLEX VISCOSITY CALIBRATION MODEL

5.5.1 Experimental

The primary analysis for the complex viscosity response, $|\eta^*(\omega)|$, was carried out for EVA samples from both manufacturers, namely Group I and Group II samples. Linear viscoelastic measurements were performed on molten EVA samples at 200 °C with a Rheometrics[®] Dynamic Stress Rheometer. A schematic of this apparatus was shown in Fig. 5.3. The samples were compression molded into disks, 25 mm in diameter, which were melted in the rheometer at the desired temperature. A 25-mm diameter cone-and-plate viscometer with a gap angle of 0.1 radians (rad) was used for these measurements. Constant amplitude, sinusoidal shear stress at 200 Pa was applied to the molten sample, and rheological measurements were made over a wide range of angular frequencies, ω , from 0.01 to 500 rad/s. At a stress of 200 Pa, the EVA samples exhibited rheological responses in the linear viscoelastic region over several decades of frequency. The properties of interest were measured at twelve frequency values per decade. A continuous purge of dry nitrogen gas prevented any sample degradation, or

moisture absorption, from the ambient atmosphere. The properties obtained from these experiments are the storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and $|\eta^*(\omega)|$ as a function of ω . Figure 5.13 illustrates a typical plot of the linear viscoelastic response for an EVA sample with 9.08 wt.% VA concentration and $\overline{M}_w$ of 228,000. (The $\overline{M}_w$ value was measured at the laboratory facility of the company that provided Group I samples.)

Large experimental scatter was observed in the $G'(\omega)$ measurements for samples with low $\overline{M}_w$ (low melt viscosity or high MI values) at small ω values ($\omega < 0.3$ rad/s). This is due to limitations in instrument accuracy for measurements of low $G'(\omega)$ values ($G'(\omega) < 0.0001$ Pa). Similarly, sample losses were observed at higher frequencies ($\omega > 150$ rad/s), and the actual applied shear stress differed from the control stress. This led to some noise in the measurements. Therefore, only data in the frequency range, $\omega = 0.38$ rad/s to $\omega = 122$ rad/s, were considered for analysis. Figure 5.14 shows an overlaid plot of the complex viscosity, $|\eta^*(\omega)|$, response, with varying ω , for the EVA samples. These measurements were used as the reference values for the data analysis.

5.5.2 Data Analysis

Quantitative analysis for predicting the complex viscosity response from NIR absorption spectra is a challenging task, and mathematical modeling involves a combination of multivariate techniques, such as PCA and PLS. A schematic

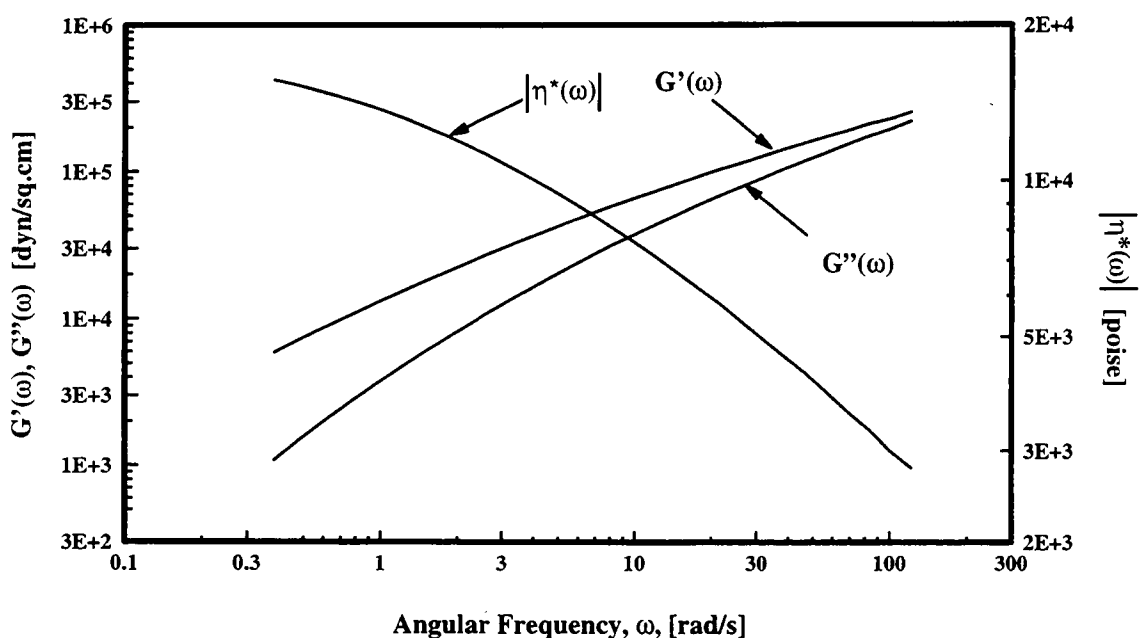


Figure 5.13 Plot of the dynamic rheological properties *versus* angular frequency for an EVA sample with 9.08 wt.% VA content and $\bar{M}_w$ of 228,000. The measurements were carried out under a shear stress of 200 Pa and at isothermal conditions of 200 °C.

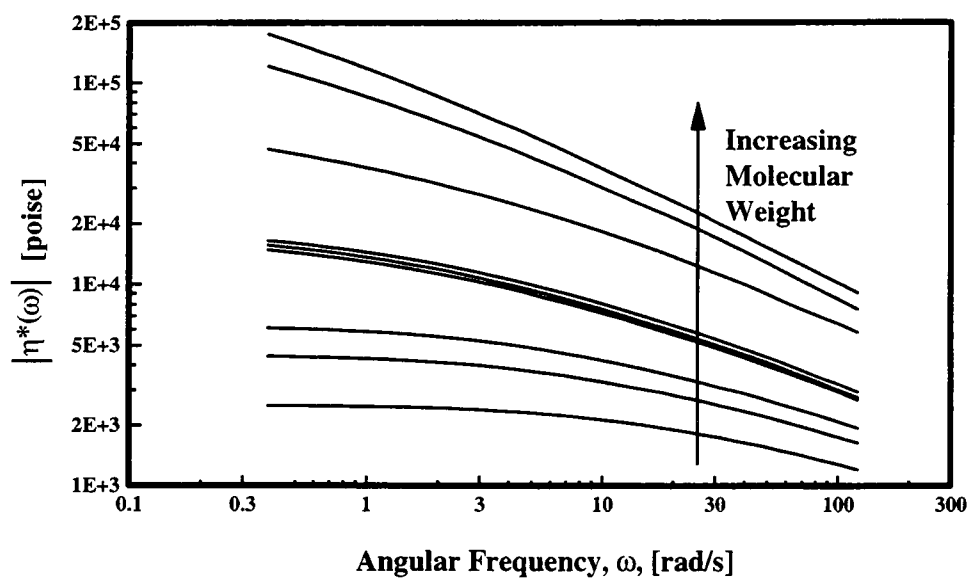


Figure 5.14 Overlaid plot of the complex viscosity response for EVA samples over an angular frequency range of 0.38 rad/s to 122 rad/s. The measurements were carried out under a shear stress of 200 Pa and at 200 °C.

representation for correlating the $|\eta^*(\omega)|$ response to NIR absorption spectra is shown in Figure 5.15. The methodology used for developing the $|\eta^*(\omega)|$ -calibration model is described in this section. There is one major difference in this analysis as compared with the MI calibration discussed before. The property being calibrated, Y ($|\eta^*(\omega)|$ response), can no longer be represented as a vector, or an $m \times 1$ matrix (calibration of MI or VA concentration). The $|\eta^*(\omega)|$ values at varying ω for the EVA samples are put in a matrix. Each column in this matrix represents the $|\eta^*(\omega)|$ values at a single ω value. Therefore, the number of columns, n , in the matrix equals the total number of frequencies at which the linear viscoelastic properties were measured. The rows in the matrix correspond to the rheological response for different samples used in the calibration. If m samples are used for calibration, then Y is of size $m \times n$. Similarly, in the X matrix ($m \times p$), the rows correspond to the absorbance values for different samples, and the columns correspond to absorbance values at different wavelengths (a total of p wavelengths).

In developing the PLS calibration model for the data sets, *principal factors* are evaluated, which give maximum reduction in the covariance, $X^T Y$, of the data. Here, X^T is the transpose of matrix X . The method for evaluating these factors involves the use of singular value decomposition (SVD). In this approach, the first singular vector and the corresponding singular value of the covariance matrix $X^T Y$ are evaluated using a decomposition procedure. This is equivalent to finding the first principal component that accounts for the largest variation in $X^T Y$. In the next step, a residual matrix is

$$\mathbf{Y}^{(m \times n)} = \mathbf{X}^{(m \times p)} \cdot \boldsymbol{\alpha}^{(p \times n)}$$

$$\begin{bmatrix} \log(\eta^*(\omega_1, \text{MI}_1)) & \log(\eta^*(\omega_2, \text{MI}_1)) & \cdots & \log(\eta^*(\omega_n, \text{MI}_1)) \\ \log(\eta^*(\omega_1, \text{MI}_2)) & \log(\eta^*(\omega_2, \text{MI}_2)) & \cdots & \log(\eta^*(\omega_n, \text{MI}_2)) \\ \vdots & \vdots & & \vdots \\ \log(\eta^*(\omega_1, \text{MI}_m)) & \log(\eta^*(\omega_2, \text{MI}_m)) & \cdots & \log(\eta^*(\omega_n, \text{MI}_m)) \end{bmatrix} = \begin{bmatrix} \text{NIR spectrum 1} \\ \text{NIR spectrum 2} \\ \vdots \\ \text{NIR spectrum m} \end{bmatrix} \begin{bmatrix} \alpha_{11} & \alpha_{12} & \cdots & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \cdots & \alpha_{2n} \\ \vdots & \vdots & & \vdots \\ \alpha_{p1} & \alpha_{p2} & \cdots & \alpha_{pn} \end{bmatrix}$$

Figure 5.15 Schematic representation for correlation of $|\eta^*(\omega)|$ with NIR absorbance spectra. The complex viscosity response in the $\mathbf{Y}$ matrix is regressed against the NIR spectral data ($\mathbf{X}$ matrix), using multivariate statistical analysis.

formed by subtracting out the contribution to $\mathbf{X}^T\mathbf{Y}$ from the first principal component. This matrix is used to extract the second principal component. This process is continued until a minimum residual error PRESS criterion is reached. This criterion results in the formation of a calibration model with optimal number of factors.

A variety of regression techniques can be used to develop calibration models for data with multiple columns of $\mathbf{Y}$. The first methodology, PLS-1, treats each column in $\mathbf{Y}$ as a single variable that would be independently regressed against the absorbance matrix [28]. Thus, n calibration models are developed (for n variables in $\mathbf{Y}$), one for the $|\boldsymbol{\eta}^*(\omega)|$ vector at each ω . In each of these n models, the principal components are evaluated by maximizing the covariance of $\mathbf{X}^T\mathbf{y}_j$, where $\mathbf{y}_j$ is the j -th column of matrix $\mathbf{Y}$. However, these calculations can be done only at the expense of valuable computational time. Also, the use of PLS-1 provides little information about the relationship between response variables in the $\mathbf{Y}$ matrix.

Another technique, entitled PLS-2 regression, treats all response variables as a single variable or block, and regression is performed on the $\mathbf{Y}$ matrix as a whole [28]. Thus, PLS-2 involves building a single calibration model for the entire $\mathbf{Y}$ matrix. An important observation is made regarding the use of PLS-2 on several response variables while evaluating the optimal number of factors. If the response variables in the $\mathbf{Y}$ matrix are independent of each other, or are not intercorrelated, then the number of factors required for building optimal models would be different for each response

variable. However, PLS-2 gives only one such value for the number of factors, and this leads to a calibration model that overfits some variables and underfits others. However, if the response variables are highly intercorrelated, PLS-2 calibration is a good choice for analysis. Again, developing a calibration model using PLS-2 requires extensive computations, as it requires evaluating the SVD of a large covariance matrix.

To circumvent these problems, a more efficient methodology based on an earlier study is used for the current work [96]. This methodology involves initial identification of the principal factors of variation, or the principal components, in the $\mathbf{Y}$ matrix alone. These principal components often relate to the actual, physical factors of variation in the data. For example, it is known that the linear viscoelastic response ($\mathbf{Y}$ matrix) of the EVA samples is governed by the $\overline{M}_w$ and MWD parameters. Therefore, the differences in $|\eta^*(\omega)|$ values, which form the $\mathbf{Y}$ matrix, can be attributed to varying $\overline{M}_w$ and MWD values in these samples. If the response variables forming the $\mathbf{Y}$ matrix are highly intercorrelated (this would happen if there were only a small number of independent physical factors affecting the data), then the matrix can be decomposed into a small number of principal components that explain most of the variance in $\mathbf{Y}$. In the above example, if the only difference in the complex viscosity response of all EVA samples were due to variation in only one physical parameter, say $\overline{M}_w$ values, then only one principal component will sufficiently explain most of the $\mathbf{Y}$ -data variance.

The linear viscoelastic behavior of these copolymers is typical of a class of polymers that are thermo-rheologically simple [89,90]. For such polymers, the

rheological behavior is oversimplified, due to the absence of factors, such as phase separation, and the viscoelastic response is influenced primarily by structural variations, which are governed by molecular weight parameters. Therefore, for such polymers, it is expected that only a few factors will sufficiently explain most of **Y**-data variance. This methodology of identifying the main factors of variation using multivariate analysis can potentially serve as a mathematical approach to separate contributions from different parameters that affect the rheological behavior.

Decomposition of the **Y** matrix into principal components can be carried out by PCA analysis. Using SVD, PCA is performed on the **Y**-data to yield the following result:

$$\mathbf{Y} = \mathbf{U}_{\text{PCA}} \mathbf{\Sigma}_{\text{PCA}} \mathbf{V}_{\text{PCA}}^T \quad \dots(5.6)$$

where the columns of $\mathbf{U}_{\text{PCA}}$ are the left singular vectors of **Y**, the columns of $\mathbf{V}_{\text{PCA}}$ are the right singular vectors of **Y**, and $\mathbf{\Sigma}_{\text{PCA}}$ is a diagonal matrix containing the singular values (square root of the eigenvalues). $\mathbf{V}_{\text{PCA}}^T$ is the transpose matrix of $\mathbf{V}_{\text{PCA}}$. The subscript **PCA** is used to identify results obtained from PCA analysis (Later on, such decomposition will be carried out for PLS as well). The first k principal components are defined as:

$$\mathbf{T}_{\text{PCA}} = [\mathbf{t}_{1,\text{PCA}}, \dots, \mathbf{t}_{k,\text{PCA}}] = [\sigma_{1,\text{PCA}} \mathbf{U}_{1,\text{PCA}}, \dots, \sigma_{k,\text{PCA}} \mathbf{U}_{k,\text{PCA}}] \quad \dots(5.7)$$

PCA decomposition is performed, such that the principal components or eigenvectors are evaluated in the order of their relative importance in explaining the data variance. Thus, the first few factors explain maximum “information” in the data, and the latter

factors contain only random noise. Using this criterion, the first k significant principal components are selected.

In the next step, the smaller matrix $\mathbf{T}_{PCA}$ ($m \times k$) is used for PLS regression against the NIR absorbance matrix, $\mathbf{X}$. The regression equation for the vectors, $\mathbf{t}_{j,PCA}$ (j -th column of $\mathbf{T}_{PCA}$), is expressed as follows:

$$\hat{\mathbf{t}}_{j,NIR} = \mathbf{X}\beta_j \quad \dots(5.8)$$

where $\hat{\mathbf{t}}_{j,NIR}$ ($m \times 1$) is the NIR predicted value of $\mathbf{t}_{j,PCA}$ ($m \times 1$) obtained from PLS regression. β_j ($n \times 1$) is a vector containing the regression coefficients. After regression of vectors $\mathbf{t}_{j,PCA}$, the original variables in the $\mathbf{Y}$ matrix are regenerated by estimating the regression coefficients, α , from the following relationship:

$$\hat{\mathbf{Y}} = \mathbf{X}\alpha \quad \dots(5.9)$$

The new set of regression coefficients, α , are related to $\mathbf{B} = [\beta_1, \dots, \beta_k]$ by the following expression:

$$\alpha = [\beta_1, \dots, \beta_k][\mathbf{V}_{1,PCA}, \dots, \mathbf{V}_{k,PCA}]^T \quad \dots(5.10)$$

An alternate and equivalent expression that relates the predictions for $\hat{\mathbf{Y}}$ with predicted $\hat{\mathbf{t}}_{j,NIR}$, $\{j = 1, \dots, k\}$ is written as follows:

$$\hat{\mathbf{Y}} = [\hat{\mathbf{t}}_{1,NIR}, \dots, \hat{\mathbf{t}}_{k,NIR}][\mathbf{V}_{1,PCA}, \dots, \mathbf{V}_{k,PCA}]^T \quad \dots(5.11)$$

For the complex viscosity calibration, data will be presented in the following section, which will support the conclusion that there is only one significant factor of

variation in $\mathbf{Y}$. Thus, from PCA analysis, it will be shown that $k=1$, and the PLS-1 regression model will be built only for the first factor.

5.5.3 Results and Discussion

This section discusses the results obtained for the prediction of $|\eta^*(\omega)|$ response from in-line NIR absorption spectra. The linear viscoelastic measurements were available for samples from both Groups I and II. Group II samples were used as an independent test set for validating the accuracy of the calibration models. The linear viscoelastic experiments were carried out on molten EVA samples in the angular frequency range of $\omega = 0.38$ rad/s to $\omega = 122$ rad/s. The $|\eta^*(\omega)|$ values were measured at a total of 31 discrete ω values in this range. In a similar manner to MI calibration, the natural logarithms of the complex viscosity response were included in the analysis. Thus, the $\mathbf{Y}$ matrix consists of $\ln(|\eta^*(\omega)|)$ values.

Ten samples, nine from Group I and one from Group II, were included in the calibration set. The Group II sample was required in the calibration because one sample in Group II had VA concentration outside the range of Group I sample concentrations. The model developed on samples in the calibration set was used to predict samples in an independent prediction set. Four samples from Group I and four samples from Group II were used in the prediction set. For the calibration, ten replicate NIR spectra were collected in-line for all the samples. One spectrum, the average of these replicate spectra for each sample, was used to construct the calibration set. As for MI calibration,

absorbance spectra in the wavelength range of 1,620-1,840 nm were used for regression. First derivatives of the absorbance spectra were utilized for calibration, in order to remove baseline offsets. The overlaid spectra for the EVA samples were illustrated earlier in Fig. 5.5.

5.5.3.1 PCA of Y Matrix: Decomposition into Principal Components

The Y matrix of $\ln(\eta^*(\omega))$ values was also standardized by mean-centering. Prior to PLS regression for obtaining the regression coefficients, PCA was performed on the Y matrix to project it into a smaller matrix, $\mathbf{T}_{\text{PCA}}$. This matrix is made up of the first few principal components that are required to quantify most of the information in $\ln(\eta^*(\omega))$ data. As shown in Table 5.4, only one principal component was sufficient to explain 99.8 % of the variance in the $\ln(\eta^*(\omega))$ data.

This result implies that, in the set of EVA samples used for this study, there is only one physical factor responsible for variation in the rheological response (which is due to change in $\overline{M}_w$). With increasing $\overline{M}_w$ values, a positive shift is observed in the complex viscosity curves. A qualitative interpretation of the first principal component is brought about from the loading ($\mathbf{V}_{1,\text{PCA}}$) and the score ($\mathbf{t}_{1,\text{PCA}}$) vector obtained from PCA decomposition. In Figure 5.16, the first loading vector is plotted against the angular frequency, ω . As expected, the first loading vector is representative of the “average” complex viscosity curve, which explains the general trend in variation of the complex viscosity response for different ω values. In such a case, the score vector is

Table 5.4 PCA on the **Y** matrix containing the complex viscosity values:
Contribution from each principal component

Principal Component Number	Variance explained by this factor (%)	Overall variance explained (%)
1	99.82	99.82
2	0.17	99.99
3	0.01	100.00

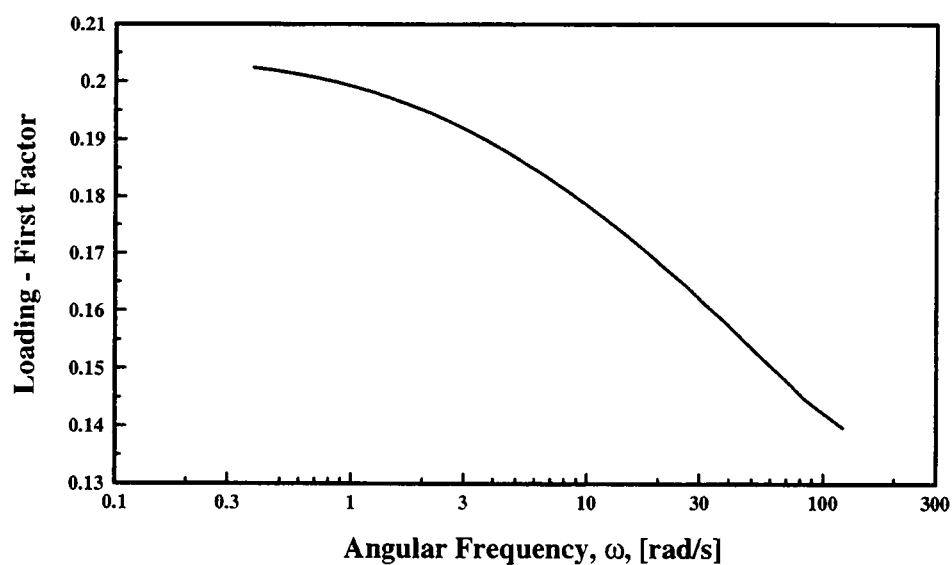


Figure 5.16 PCA analysis of Y matrix containing the complex viscosity data: Plot of loading vector for the first principal component represents the average complex viscosity curve. The magnitudes or “vertical shift factors” in the first score vector are multiplied with the loading curve to produce the original complex viscosity curves.

made of magnitudes or *vertical shift factors*, which when multiplied with the average loading spectrum, gives the individual complex viscosity curve for each sample. Similar horizontal shifting procedures are commonly used by rheologists to generate master curves to account for variations in temperature and molecular weight [90]. As an example, such shift factors are utilized to relate the specific viscosity to concentration in polymer solutions by scaling the molecular weight dependence. The above procedure can be viewed as an alternate mathematical approach to achieve similar shifting effects through eigenvector rotation, instead of commonly used superposition principles, which use curve-fitting strategies to obtain the shift factors. A comparison between the two methodologies shows that the loading vector is *analogous* to a master curve, while the score vector includes shift factors for individual curves. However, the current method using multivariate analysis, does not increase the range of ω values unlike the normal superposition procedures [90].

In the rheology data, if there were other additional effects, or factors of variation, the variance in the complex viscosity functions could not be represented by a single shift. In such cases, additional principal components would be required to account for these parametric effects. In other words, more than one principal component would be required to explain significant variance in $\mathbf{Y}$.

From the above analysis, it is seen that the $\mathbf{Y}$ matrix can be reduced into a single vector $\mathbf{t}_{1,PCA}$, which corresponds to the singular vector associated with the largest singular value. The original $\mathbf{Y}$ matrix is regenerated from the decomposed principal components using Eq. (5.9), which can be rewritten as follows:

$$\mathbf{Y}_{\text{reg}} = \mathbf{t}_{1,\text{PCA}} \mathbf{V}_{1,\text{PCA}}^T \quad \dots(5.12)$$

where $\mathbf{Y}_{\text{reg}}$ is the regenerated $\mathbf{Y}$ matrix, $\mathbf{t}_{1,\text{PCA}}$ is the first column of $\mathbf{T}_{\text{PCA}}$ and $\mathbf{V}_{1,\text{PCA}}$ is the first column of $\mathbf{V}_{\text{PCA}}$. Eq. (5.12) provides a framework for comparing the original response variables, $\ln(|\eta^*(\omega)|)$ values in the $\mathbf{Y}$ matrix, to the regenerated matrix, $\ln(|\eta^*(\omega)|)$ values in $\mathbf{Y}_{\text{reg}}$. It shows how well the information in the $\mathbf{Y}$ matrix can be obtained by using only one principal component. Figure 5.17 illustrates this feature; the complex viscosity responses, $|\eta^*(\omega)|$, from $\mathbf{Y}$ and $\mathbf{Y}_{\text{reg}}$ are plotted against ω .

5.5.3.2 PLS-1 Regression of the Reduced Matrix, $\mathbf{t}_{1,\text{PCA}}$: Regression onto $\mathbf{X}$

After PCA, a PLS-1 regression model is developed for correlating $\mathbf{t}_{1,\text{PCA}}$, of size $(m \times 1)$, onto the NIR absorbance matrix, $\mathbf{X}$. The PLS calibration is developed on the first derivatives of the absorbance spectra, using the leave-a-sample (LAS) cross-validation technique, as discussed earlier. Based on the PRESS criterion coupled with an F-statistic criterion, a four-principal component model was chosen for calibration. In Table 5.5, the contribution of each principal component is listed, in explaining the variance in the reduced matrix $\mathbf{t}_{1,\text{PCA}}$. It is observed that 99.6% of the variance in $\mathbf{t}_{1,\text{PCA}}$ can be explained by four factors. Once the optimal number of factors to be included in the calibration model is decided, a final calibration model is developed from all samples in the calibration set. This model is used to predict the desired properties of samples from an independent prediction set.

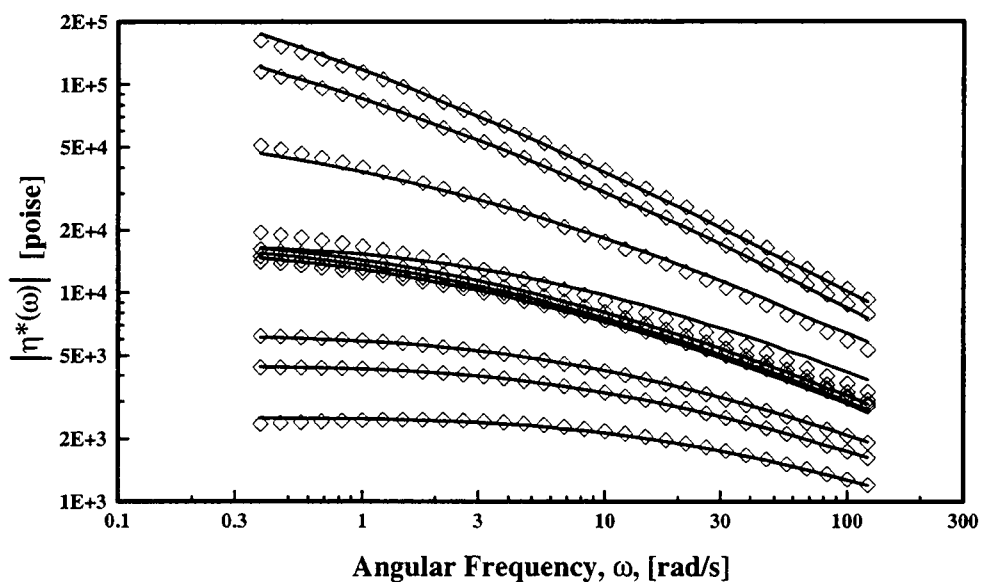


Figure 5.17 PCA analysis of $\mathbf{Y}$ matrix containing complex viscosity response: Plot comparing the original $\mathbf{Y}$ matrix (symbol - solid line) with the regenerated matrix, $\mathbf{Y}_{reg}$, (symbol - $\diamond$) which is obtained from a one principal component PCA model. The excellent fit between the two curves shows that one factor is sufficient to represent significant variance in $\mathbf{Y}$ matrix.

Table 5.5 PLS regression on the reduced matrix:
Contribution from each principal component

Principal Component Number	$t_{1,PCA}$ calibration model: Overall explained variance in $t_{1,PCA}$ (%)
1	31.5
2	94.9
3	98.2
4	99.6

Figure 5.18 shows the in-line NIR predicted $\hat{t}_{1,NIR}$ for samples in the calibration and prediction sets, with a calibration model based on four factors. The deviations of the NIR predicted $\hat{t}_{1,NIR}$ values from actual $t_{1,PCA}$ values are expressed as residual errors for both the calibration and the prediction sets. These residual errors dictate the prediction capability of the calibration model. The SEC value, or the standard residual error for calibration, was 0.38, and the SEP value, the standard residual error for samples in the prediction set, was 0.80. When the entire complex viscosity response, $\hat{Y}$, for the samples is regenerated using the predicted $\hat{t}_{1,NIR}$ values (this can be done by replacing $t_{1,PCA}$ with $\hat{t}_{1,NIR}$ in Eq. (5.12)), these residual errors translate into prediction errors for $|\eta^*(\omega)|$ values at each ω . The regenerated $|\eta^*(\omega)|$ response curves for samples in the calibration set are shown in Figure 5.19. Similarly, the predicted $|\eta^*(\omega)|$ response curves for samples in the prediction set are compared with the laboratory measured response curves in Figure 5.20. In these figures, the deviations of the in-line NIR predicted curves from the laboratory-measured response curves in the calibration and prediction sets correspond to the residual errors in the calibration model.

In a similar manner to PCA, PLS analysis also results in score and loading matrices [7,19]. A plot of the loading vector for the first principal component against NIR wavelengths, shown in Figure 5.21, typically resembles the average derivative spectrum (compare with Figure 5.5). The first principal component is expected to contain information about VA content, which is the dominant variable. For regression,

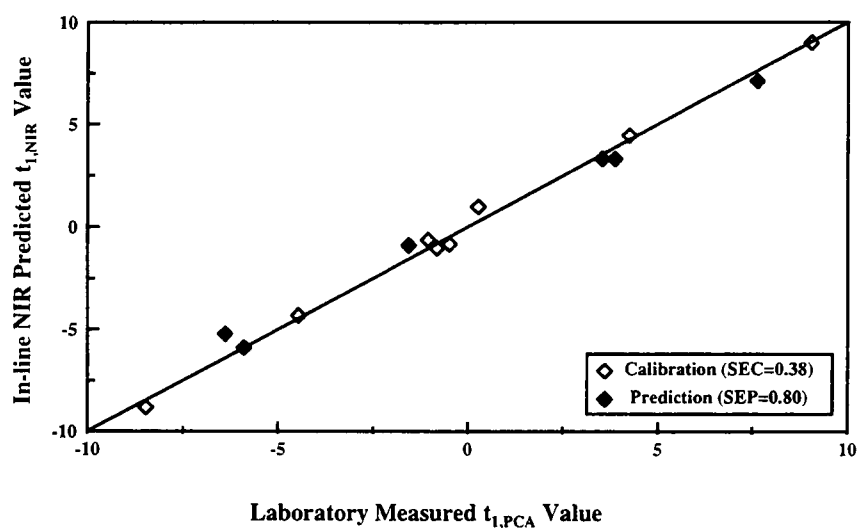


Figure 5.18 PLS calibration of $t_{1,PCA}$ with regression against NIR absorbance data: Predictions of $\hat{t}_{1,NIR}$ for samples in the calibration and prediction sets. The standard errors associated with the calibration and prediction sets are SEC = 0.38 and SEP = 0.80, respectively.

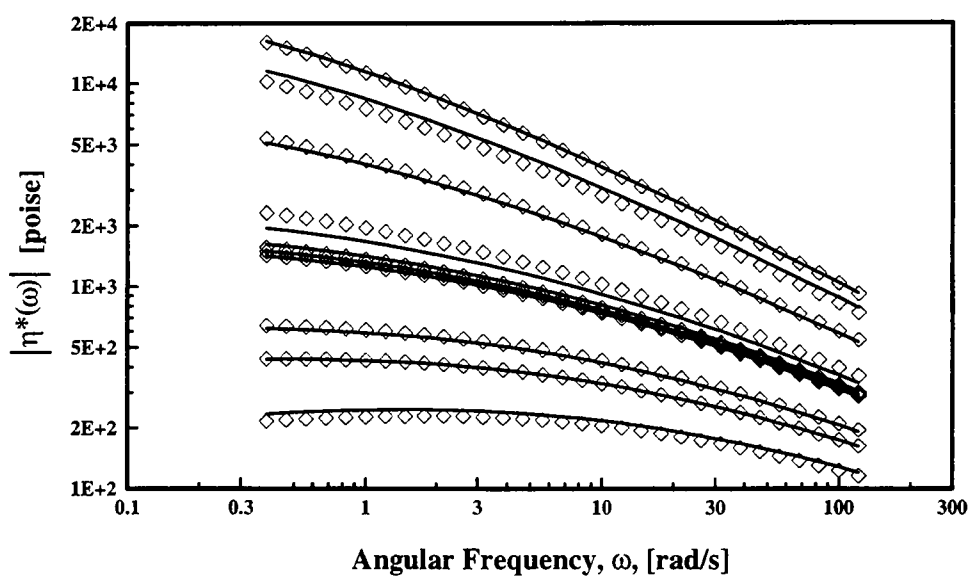


Figure 5.19 **Calibration Set:** Predictions for rheological response - $|\eta^*(\omega)|$ versus ω - for EVA samples. The complex viscosity curves are regenerated from the PLS-predicted $\hat{t}_{1,NIR}$ values using Equation (5.12). The standard error associated with the calibration set is $SEC = 0.38$. The solid curve represents the original curve, and the symbol $\diamond$ represents the PLS-predicted curve.

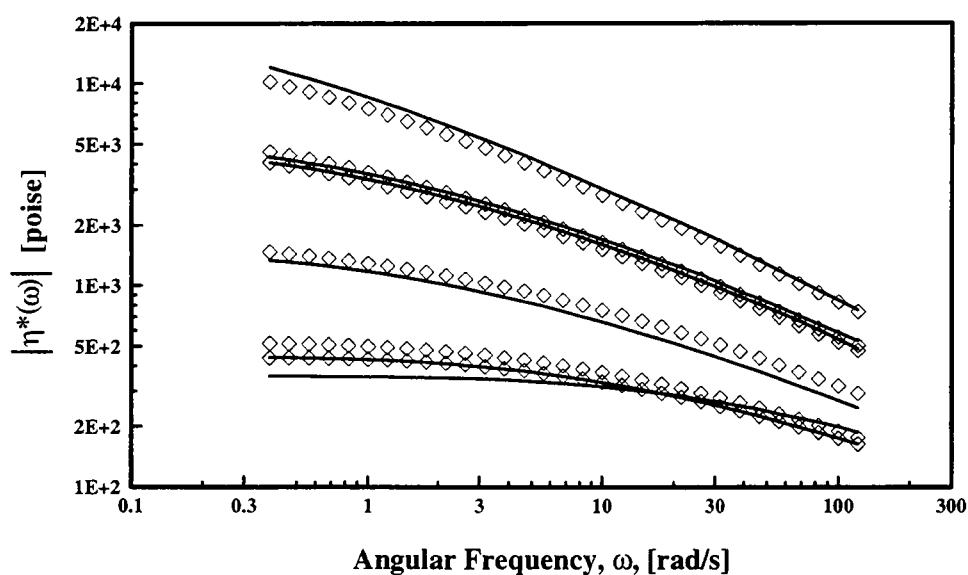


Figure 5.20 **Prediction Set:** Predictions for rheological response - $|\eta^*(\omega)|$ versus ω - for EVA samples. The complex viscosity curves are regenerated from the PLS-predicted $\hat{t}_{1,NIR}$ values using Equation (5.12). The standard error associated with the prediction set is $SEP = 0.80$. The solid curve represents the original curve, and the symbol $\diamond$ represents the PLS-predicted curve.

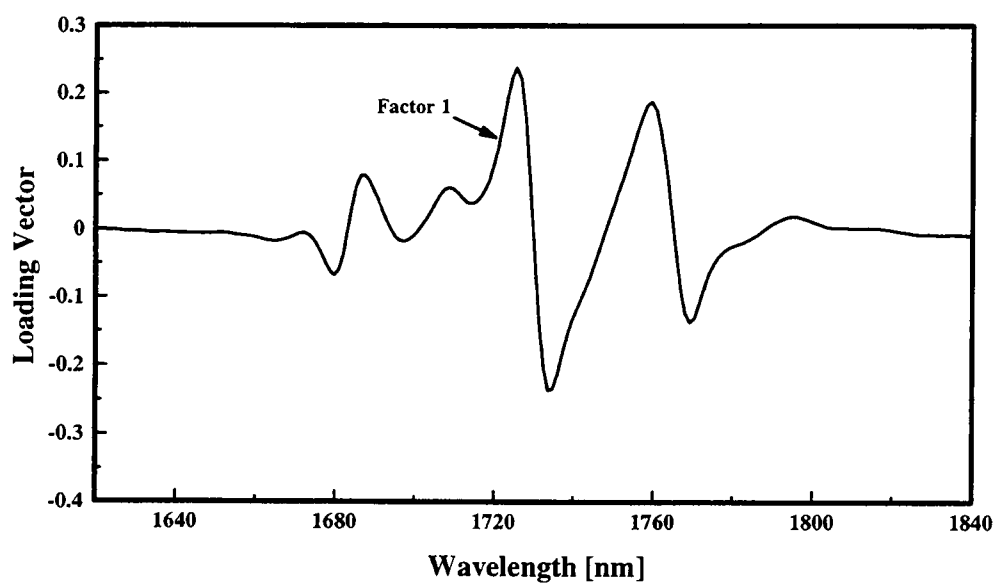


Figure 5.21 PLS calibration of $t_{1,PCA}$: Loadings plot for the first factor. The loading vector for the first principal component contains information about VA content (primary variation) in the EVA copolymers. The loading weights are higher in the wavelength region corresponding to the C—H stretch peaks.

wavelengths with larger loading values are relatively more important (in explaining variance in the response variables) than wavelengths with lower loading values. From the first loading plot, it is observed that information for VA content lies in the wavelength range of 1,720-1,780 nm that contains the polyethylene doublet peaks in the original absorbance spectra. The score vector for the first principal component is plotted against the VA concentration, as shown in Figure 5.22, which shows a linear trend as expected. Therefore, the first factor has most of the information about VA content variation, but little information about the rheological response.

The “secondary” effects on NIR spectra, due to rheological flow, are expected to dominate in the higher factors. As observed in Table 5.5, the second principal component contains maximum information about the rheological response because this principal component explains maximum variance in *Y* data (an additional 63.4% variance is explained by the second factor). The loading and score vectors for the second principal component should explain this feature. Figure 5.23 shows a plot of the second loading versus the NIR wavelength. It is observed that higher loading weights are associated with absorbances in the wavelength region of 1,680-1,720 nm. This region corresponds to the shoulder of the methylene stretch. (Note the presence of the shoulder in the overlaid absorbance plot in Fig. 5.4). Changes in the slope of the shoulder are observed about an inflection point at around 1,715 nm, which lies in a trough in the first derivative plot. A similar observation is made in the wavelength regions of 1,730-1,745 nm and in 1,745-1,760 nm, which form shoulders of the doublet peaks.

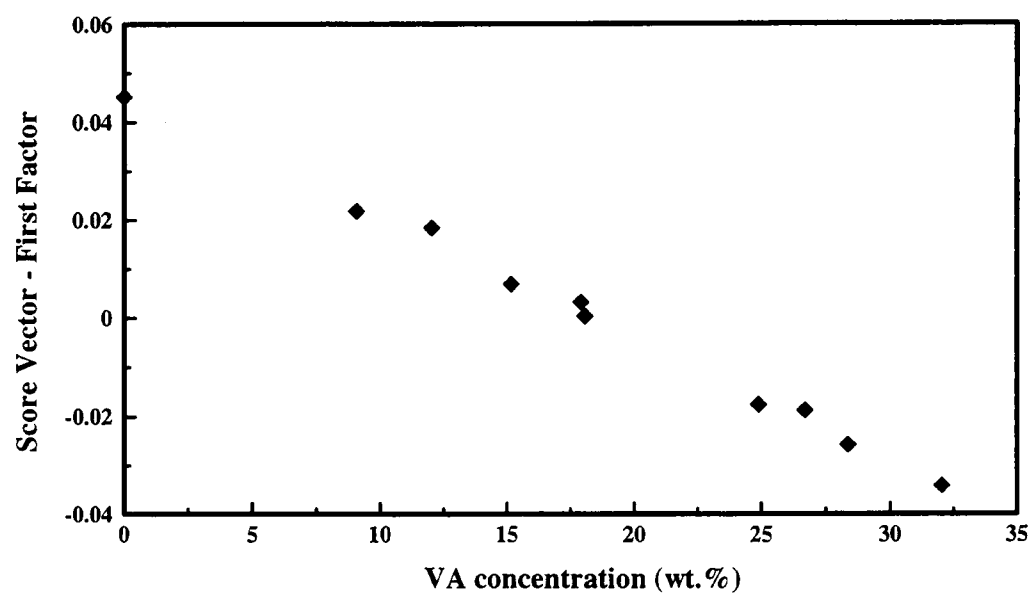


Figure 5.22 PLS calibration of $t_{1,PCA}$: Scores plot for the first factor. The score vector for the first principal component shows a linear trend with varying VA concentration.

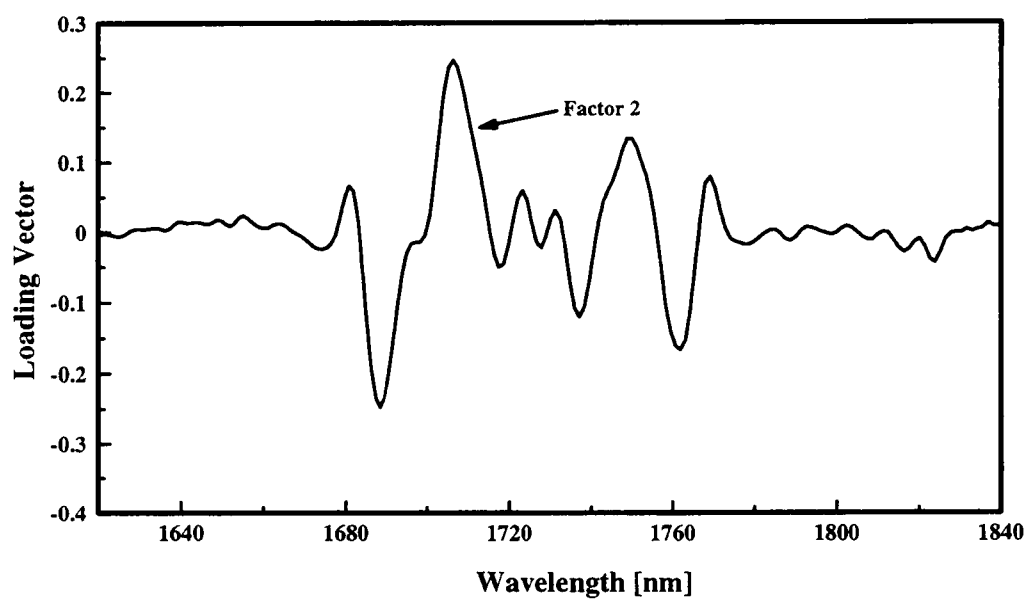


Figure 5.23 PLS calibration of $t_{1,PCA}$: Loadings plot for the second factor. The loading vector for the second principal component contains information about rheological response (secondary variation) in EVA copolymers. The loading weights are higher in the wavelength regions corresponding to shoulders of the C—H stretch peaks.

By looking at the loadings in the first derivative domain, it is possible to determine which wavelengths have heavier loadings in the original absorbance spectrum. This observation is presented in a schematic form in Figure 5.24. For example, it is seen in Fig. 5.24 that the wavelength region of 1,700 nm to 1,710 nm has higher loading weights for the second principal component. Combining this information with that obtained from Table 5.5, it is concluded that the variance in absorbance values in this wavelength region explains information pertaining to the rheological response. Similarly, other wavelength regions are identified that contain information about the $|\eta^*(\omega)|$ response. Based on the qualitative analysis using loadings plots, Figure 5.25 illustrates the wavelength regions in the original absorbance plot that are identified with information relating to VA content and rheological response.

5.5.3.3 Origin of Spectral Information Relating to Rheological Response

It is tempting to assume that these wavelength regions, which correlate with the rheological properties, contain information about end-group concentrations. It is common knowledge that polymer chain end-group concentrations are inversely proportional to average molecular weight, and monitoring these concentrations has led to direct correlations with molecular weight parameters in earlier NIR studies [5]. However, such work has been done only with polyol oligomers or very low molecular weight macromolecules, especially with hydroxyl end groups, which have strong spectral signatures in NIR. In the present study, for the high molecular weight EVA copolymers, a rough estimate of the typical end group concentration, from the polymer

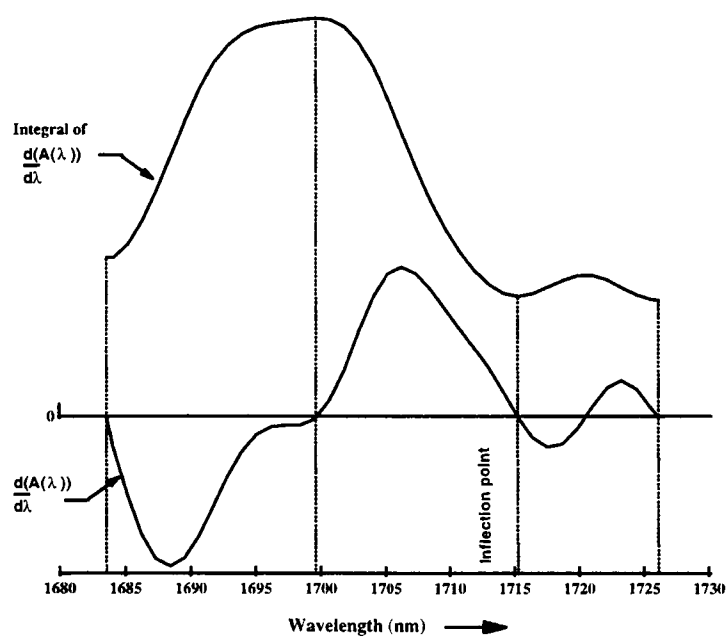


Figure 5.24 Schematic illustrating a methodology to identify the wavelength regions in the original absorbance spectrum with heavy loading weights for a given factor, for example factor 2 in Fig. 5.23.

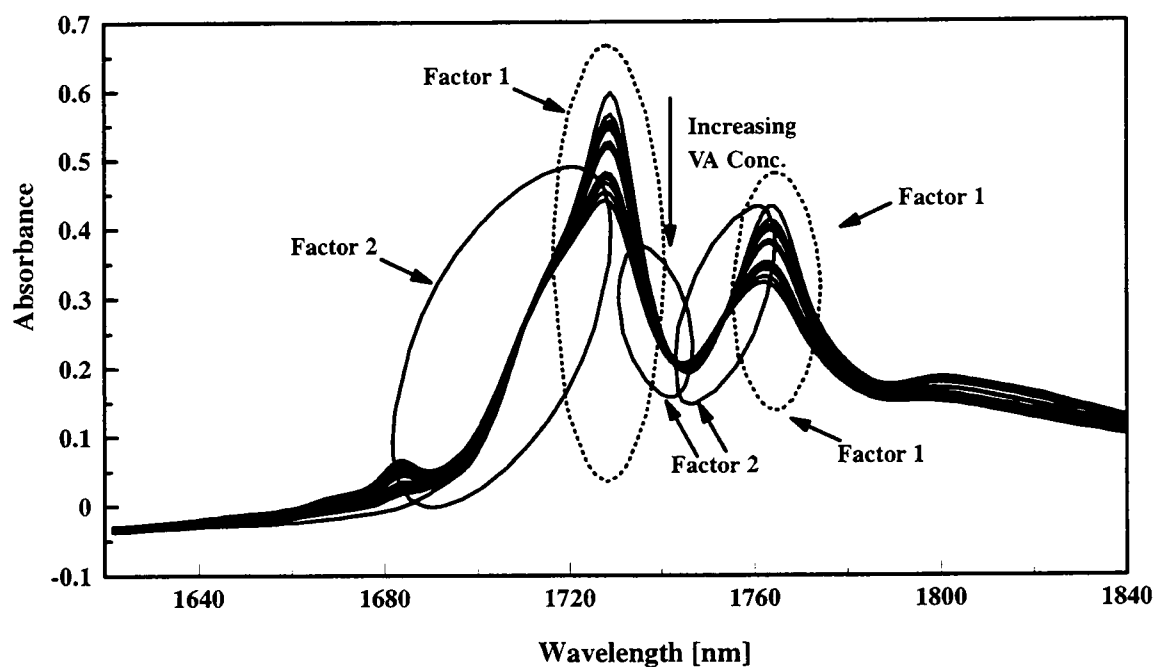


Figure 5.25 Overlaid plot of NIR absorbance spectra of EVA copolymers in the C—H stretch, first overtone region (1,620-1,840 nm). The wavelength regions associated with the primary variation, VA content (Factor 1); and the wavelength regions correlating with secondary variation, rheological properties (Factor 2) are identified from PLS analysis.

number-averaged molecular weight and monomer molecular weights, gave a value of around 0.2%. Such concentrations are very low compared to the strong backbone signature due to C—H stretches. Hence, for the current system, it seems unlikely that the end group measurements would have any direct correlation with rheological properties.

One the other hand, as mentioned in the beginning of this dissertation, during flow of molten polymers in a polymeric process such as extrusion, rheological effects on NIR spectra become significant. For the current experimental setup, the flow cross-section of these molten polymers changes from 9.5 mm × 25.0 mm at the exit port of the gear pump to a restricted flow cross-section of 2.5 mm × 25.0 mm in the optical measurement volume of the flow cell. Figure 5.26 shows a schematic of the contraction in flow that leads to orientation of the flowing polymer chains. Under constant nominal shear rates ($\sim 25 \text{ s}^{-1}$), these polymers would exhibit orientation effects that would vary with differences in molecular weight parameters. Subsequently, these factors would affect the NIR absorption spectra, though to a lower-order magnitude as compared to the strong variations due to chemical composition. It is assumed that these effects are also non-linear; and hence, using natural logarithms of the material functions during regression, amounted to extracting a first-order relationship from the rheology-absorbance correlation.

Thus, this methodology was used to separate two features — varying VA content and varying rheological behavior — from the NIR absorbance spectra. The score vector for the second factor was plotted against the response variable vector $\mathbf{t}_{1,\text{PCA}}$, as shown in

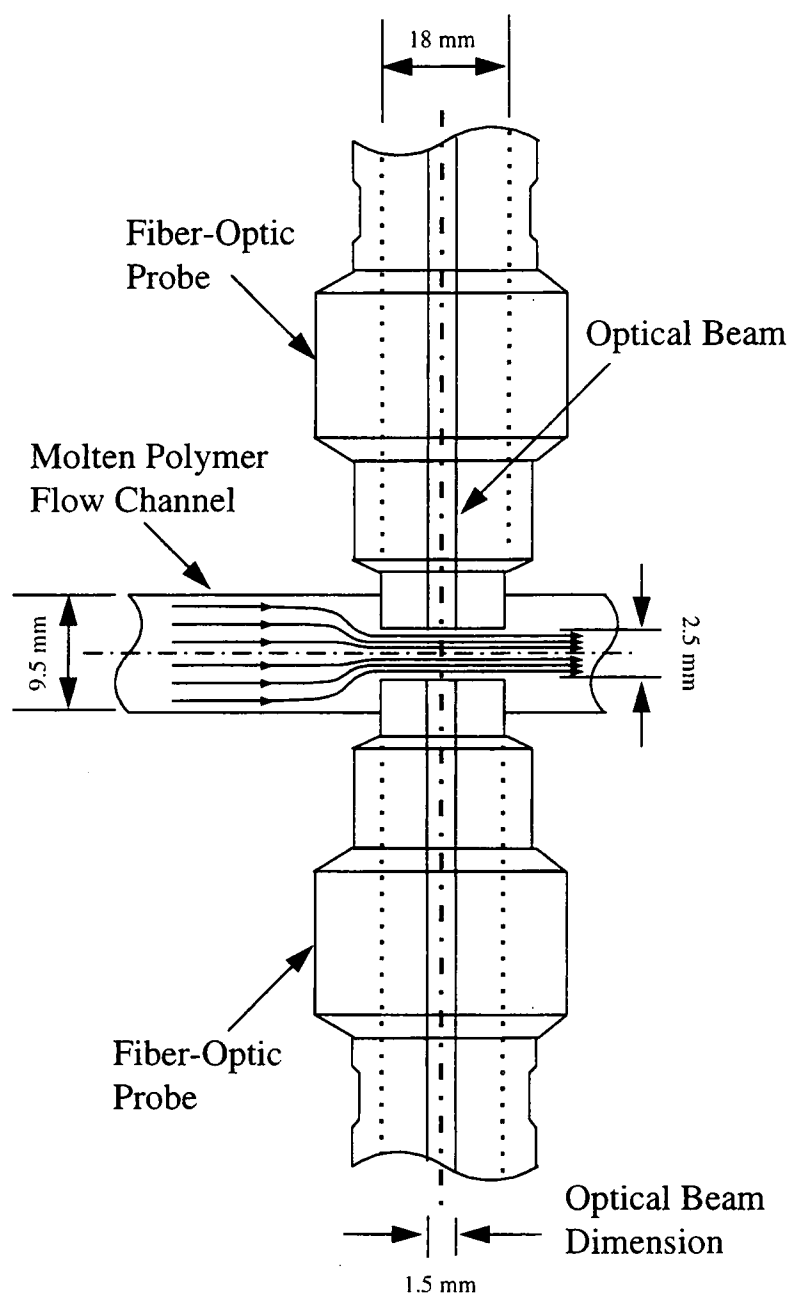


Figure 5.26 Schematic representation of contraction flow through the flow cell

Figure 5.27. If the rheological behavior were completely identified in the second factor alone, then the score vector for the second factor would be expected to show a strictly linear relationship with $t_{1,PCA}$. Because the second factor alone is not sufficient for predicting rheological response, only a general trend of linearity is observed in the second score plot of Fig. 5.27. One reason for the deviation from linearity is the lack of samples available for calibration with uniform distribution of rheological properties. (Note the “holes” in calibration data in the higher end of calibration set, which is evident from the values of $t_{1,PCA}$ in Fig. 5.27.)

5.5.3.4 Real-time Predictions in an In-line Extrusion Process

Finally, the stability of the predictions using the calibration model was tested in a real-time in-line extrusion process. Four Group I samples, followed by four Group II samples, which were not included in the calibration set, were continuously fed into the extruder, and test scans taken. Two samples with very low $|\eta^*(\omega)|$ values ($MI = 143.0$ g/10 min and $MI = 370.0$ g/10 min) were excluded from the analysis, as they gave larger residual errors. As explained in the previous section, these large errors are attributed to lack of a uniform distribution of sample space. Each absorbance scan was preprocessed and used for predictions of the rheological response. The calibration model built on the reduced response matrix, $t_{1,PCA}$, was used to predict the $\hat{t}_{1,NIR}$ value for each test scan. Therefore, for every test scan, a value for $\hat{t}_{1,NIR}$ is predicted. The $\hat{t}_{1,NIR}$ values are plotted against the extruder run time in Figure 5.28. The detection limits for predictions

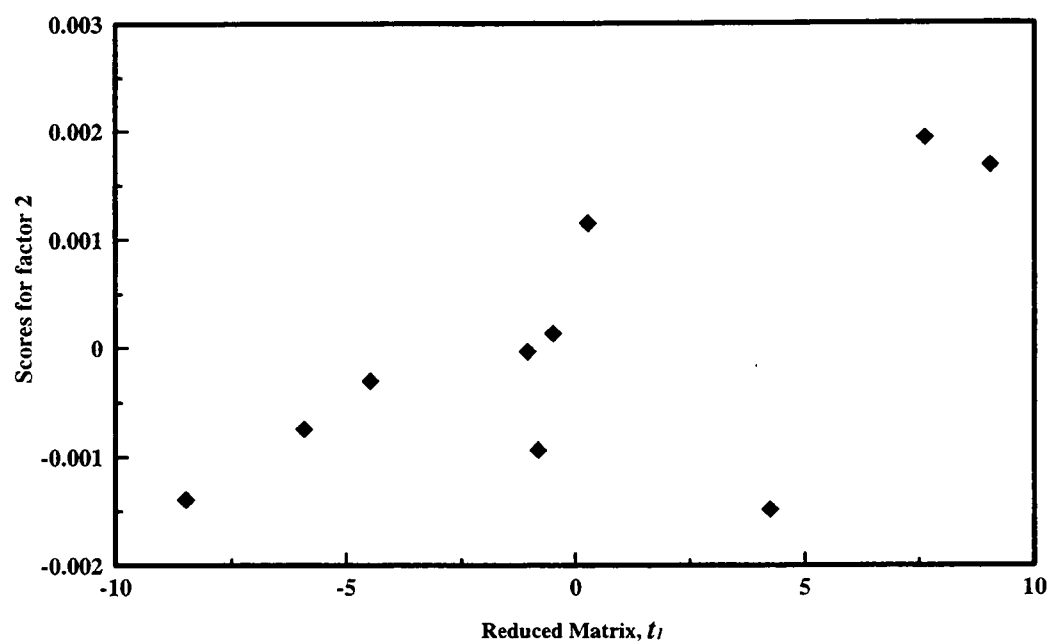


Figure 5.27 PLS calibration of $t_{1,PCA}$: Scores plot for the second factor. If the second factor had complete information about the rheological response, a strictly linear trend would be expected. Because additional factors are required, only a general trend in linearity is observed. Also, this score vector reflects the lack of uniform distribution of sample properties for the calibration model.

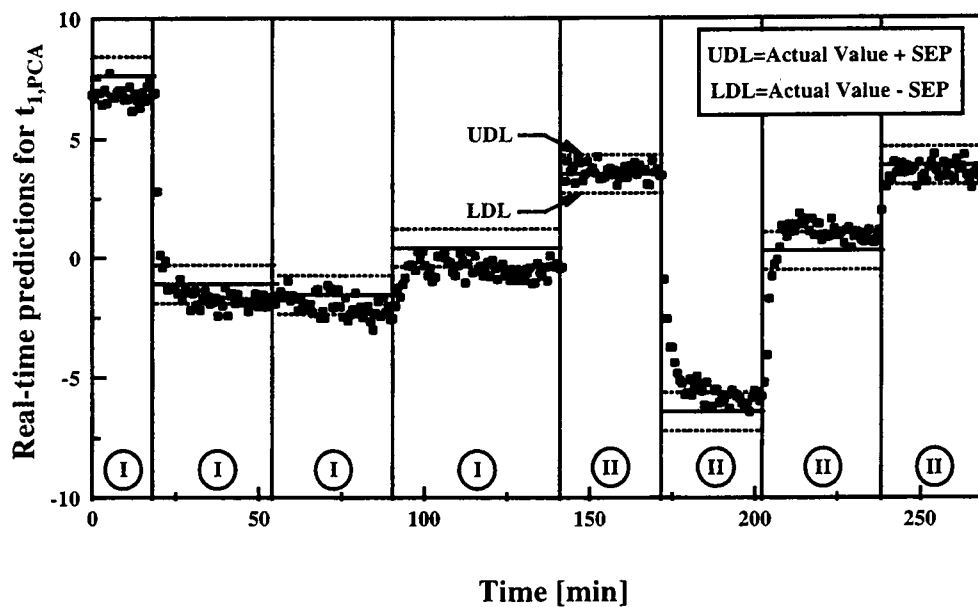


Figure 5.28 In-line real-time predictions of $\hat{t}_{1,NIR}$ in Group I and Group II samples: Four Group I samples followed by four Group II samples were fed into the extruder in an extrusion process and test scans collected: the predictions lie within the SEP limits associated with the calibration models. (SEP = 0.80; UDL = upper detection limit; LDL = lower detection limit)

are decided by the SEP values obtained from the calibration model. It is observed that most predictions lie within the limits defined by the SEP.

Once the predicted $\hat{t}_{I,NIR}$ values are obtained by PLS, the entire complex viscosity response is regenerated using Eq. (5.12), as explained in the previous section. Therefore, for every test scan, one linear viscoelastic curve was estimated. Several such curves, which were obtained over the entire extruder run-time, are shown in Figure 5.29 as a 3-dimensional plot. This plot shows the complex viscosity response versus ω with polymer extrusion time. As observed during the predictions of MI in near real-time, the transition of $|\eta^*(\omega)|$ response is smooth from one sample to another. The transition region also indicates the average residence time of the sample in the polymer monitoring system.

5.6 EXPERIMENTAL LIMITATIONS

In the experimental set of EVA samples chosen, the rheological data showed only one factor of variation. This conclusion is drawn from the results obtained from PCA analysis, which showed that the first principal component captured about 99.82% variation. This meant variation in only one physical factor, probably differences in polymer average molecular weight among various EVA samples. (Assumedly, the polymerization process and termination conditions were similar for these random copolymers from both Groups I & II.) Such variation in molecular weight values resulted in a vertical shift in various complex viscosity responses. With additional

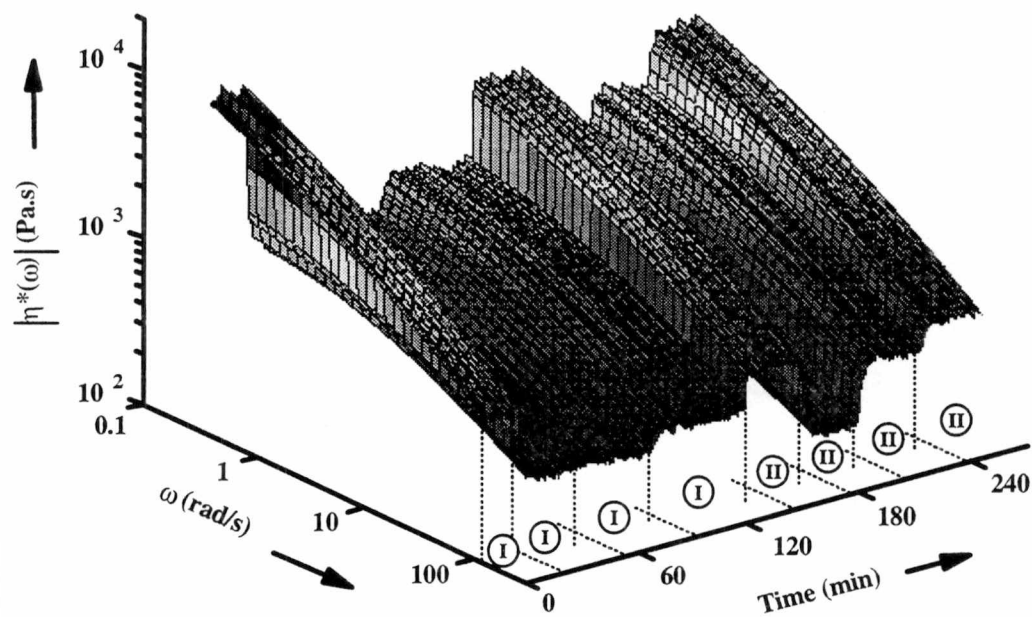


Figure 5.29 Three-dimensional plot showing the real-time predictions for the rheological response of Group I and Group II samples (these samples were not included during calibration): The complex viscosity curves are regenerated from the PLS- predicted $\hat{t}_{I,NIR}$ values (shown in Fig. 5.28) using Equation (5.12). The rheological data used for correlation with NIR spectra had only physical factor of variation.

physical parameters, such as branching parameters and *MWD* affecting rheological behavior, the resulting rheology data will be more complex. In such cases, PCA analysis will highlight the need for larger number of principal components to explain significant variance in the *Y* data. However, this experimental limitation does not imply a deficiency in the calibration methodology. With additional factors required for PCA, the procedure for PLS regression will remain essentially the same. Only, additional calibration models need to be developed for predictions of several principal components, $t_{j,PCA}$, $\{j = 1, \dots, k\}$. The entire rheological response can still be regenerated from Eq. (5.11). Because these additional physical parameters are also expected to affect the rheological flow behavior during extrusion, and subsequently, the NIR absorption spectra, the methodology described in the previous sections should hold for complicated rheological behavior as well.

Temperature is an important variable, which would have a large effect on rheological properties, but only a subtle peak-shifting effect in the NIR data. The current study has focused only on isothermal studies, and temperature was not included as an independent variable during calibration. During extrusion, factors such as viscous heating will lead to temperature changes; although for this study, a precise quantitative measurement was not available for estimating such temperature increase. However, the operating conditions for the linear viscoelastic experiments, and for extrusion, were held within nominal fluctuations about the temperature set point. In addition, it should be noted that the strong effect of temperature on rheological properties is suppressed to a great extent by using natural logarithms of the rheological functions during calibration.

The calibration model built here is by no means universal in its applicability to all EVA polymers using any near-infrared instrument. However, a methodology has been proposed, and feasibility of its use has been successfully demonstrated. Typically, a very large set of samples is required to build a robust calibration model. It is crucial for such a large sample set to include samples with uniform and wide variation in the rheological parameters. Also, the distribution of the $\overline{M}_w$ parameters and VA content in these samples should be random. At the same time, it is important that the entire ranges of VA and rheological variations (the primary and secondary factors of variation, respectively) be represented in the calibration set.

5.7 CONCLUSIONS

The “primary” or the dominant factor of variation in the NIR absorption spectra is the VA content in the copolymer, and appears as the first principal component. The “secondary” factors that affect the absorption spectra are attributed to the anisotropic rheological flow behavior of molten polymers during extrusion. Under nominal shear rates, the level of molecular orientation will be different for flowing polymer melts associated with varying molecular weight parameters. This anisotropic nature of flow will result in lower-order magnitude effects on absorption spectra. These subtle variations in NIR spectra appear in higher factors or loadings; and correlate with polymer rheological properties, such as linear viscoelastic material functions.

This study has demonstrated the feasibility of predicting rheological properties of molten polymers during an extrusion process in near real-time. In conjunction with

predictions of MI, it has been shown that dynamic mechanical properties of the molten polymers can be estimated using in-line fiber-optic NIR spectroscopy [97,98]. The calibration models are robust in that predictions are stable in a real-time process, and lie within SEP limits set by the models. Temperature effects on the spectra are also important, although in this study, the temperatures of the molten polymer in the flow cell remained constant with a minimal variance of about 1-3 °C. However, the calibration models can be further improved by including temperature as an independent variable alongside the absorbance spectra, in the **X** matrix. The methodology presented here for $|\eta^*(\omega)|$ would be equally applicable to $\eta(\dot{\gamma})$ versus $\dot{\gamma}$, the shear rate data.

CHAPTER 6

ESTIMATION OF ADDITIVE CONTENT IN POLYMER MELTS

INTRODUCTION

Ever since the beginning of the plastics industry, it was realized that useful products could be produced only if certain additives were incorporated into polymers. Additives are chemicals that are physically dispersed in a polymer matrix, usually in small concentration levels, to modify crucial properties of polymers. Such properties relate to thermal, oxidative, hydrolytic, and biological degradation, mechanical properties, flammability, cost, and processability. Some commonly used additives for enhancing these properties are antioxidants, ultraviolet (UV) stabilizers, plasticizers, fillers, reinforcing agents, modifiers, colorants, antistatic agents, flame retardants, slip or release agents, *et cetera* [87,99]. Often, one or more additives are added in varying concentration levels to obtain desired properties. Because small concentrations of additives significantly alter polymer properties, quality control is a serious issue. Current off-line techniques involve time-consuming HPLC methods for measuring these trace level concentrations. Therefore, an alternative methodology using fiber-optic spectrometric techniques is desired, which would offer capabilities for in-line measurements. The current research will utilize the techniques of NIR and UV spectrometries for additive quantification.

In the previous chapter, NIR spectroscopy was introduced as a powerful analytical method for in-line analysis of polymeric processes. For additive systems, absorbances are very low in the NIR region owing to typically small additive concentrations, (usually in *ppm* or very low percent levels), in the base polymer resin. To some extent, this limitation can be overcome by using larger optical pathlengths for spectral data collection. From Beer's law, (which establishes a direct, linear relationship between absorbance and optical pathlength), it follows that larger pathlengths lead to higher absorbances. However, the effectiveness of this approach is greatly dependent on the particular chemical systems under study, their concentrations, and the absorptivities of specific chemical moieties. Thus, in order to use NIR spectroscopy for in-line additive monitoring, improved instrumentation is required, which can provide better signal-to-noise ratio scans. Also, powerful mathematical techniques are needed for handling such noise-sensitive data. Furthermore, with the availability of these tools, there is need to set quantitative limits of detection (in terms of smallest identifiable concentration levels) for additive systems of interest.

An alternate technique for in-line estimation of additive concentrations utilizes UV spectrometry. Many commonly used additives have strong spectral signatures in the UV region even at very low concentrations [99]. This feature makes the UV region a viable substitute for treating additive systems. In the past, UV spectrometry had problems associated with lack of robust instrumentation in terms of detectors and fiber-optics. In addition, the UV region is ridden with broad bands and overlapping peaks (most additives have similar structures for absorption in UV), much like the NIR region,

only more so. Thus, considerable mathematical analysis is required, in order to deconvolute such overlapping peaks and identify specific chemical interactions.

In the past, very little effort has been made in this direction addressing the aforementioned issues, and there is not much information available in the literature. Fidler [100] previously reported analysis of erucamide in high density polyethylene, using FT-IR spectroscopy, on a slip stream from an extruder. Khettry [7] conducted feasibility studies on trace levels of erucamide, using NIR spectrometric measurements directly on flowing polymer melts.

The primary objectives of the current research were to provide experimental schemes for two additive systems, in order to test feasibility for in-line monitoring using NIR or UV spectrometry, improve monitoring schemes by providing quantitative analysis using multivariate techniques, and to conduct qualitative studies on these systems, which would lead to a better understanding of the available information in the NIR and UV regions. The specific objectives and the systems are detailed as follows:

(1) To conduct experimental studies on a secondary hindered amine additive system in polypropylene (PP). Results will be presented from quantitative analysis using NIR and UV spectrometries. A new approach using correlation of NIR—UV spectroscopy will be detailed, which offers great potential in solving problems, such as identifying interactions between additives, resolving overlapping absorbance peaks, *et cetera*. This work leads to a hitherto unexplored subject of simultaneous application of NIR-UV spectrometric techniques for in-line monitoring.

(2) To establish measurement limits in the NIR region on a sample set of erucamides in EVA copolymers, using an FT-NIR spectrometer. This study focuses on setting measurement limits for these additives using NIR spectroscopy, which are present in EVA copolymers in *ppm*-levels. Results from qualitative and quantitative analyses will be presented in the following sections.

6.1 HINDERED AMINE ADDITIVES IN POLYPROPYLENE

6.1.1 Introduction

The physical properties of polypropylene's (PP) structure determine its processability and its performance characteristics. PP exhibits excellent chemical resistance, exhibits the lowest density of any commercial polymer, and processes well in injection molding and extrusion. However, it is extremely susceptible to degradation by ultraviolet (UV) light, and has limited high-temperature resistance. As compared to polyethylene (PE), PP has poorer stability in the presence of UV radiation. This instability in PP is attributed to easier abstraction of the hydrogen atom from the tertiary carbon atom (i.e. an attack on the pendant methyl group in the PP polymer chain) [87]. Therefore, in the absence of additives, PP degrades under prolonged exposure to UV radiation.

Hindered amines are chemicals that belong to a class of additives that prevent the oxidation of UV-exposed PP and provide long-term stabilization. These chemicals also provide thermal stabilization and are used as antioxidants. The common chemical name of such secondary amines is tetramethyl piperidines. These amines exhibit

important physical properties, such as excellent thermal stability, very little tendency toward discoloration, and no restrictions for food contact applications. Such advantages have led to wide spread usage of these chemicals as light stabilizers, hence the term *hindered amine light stabilizers* (HALS) is used to define them.

The sterically hindered amine stabilizers are multifunctional with regard to their action. Through a variety of cyclic reactions, the parent form, N—H or N—R, and the principle oxidized species, NO· NOR, and NOH, serve as hydroperoxide decomposers and peroxy radical scavengers. The hindered amines stabilize *via* regenerative cycles that reform the active species many times. Details of the reaction mechanism can be found elsewhere [99,101]. In general, these light stabilizers are added in concentrations between 0.05 wt.% and 2 wt.%. The concentrations to be used are a function of several factors, such as the inherent light stability of the PP resin to be stabilized, the specific application under consideration, and other additives used in the formulation, e.g. antioxidants, pigments, and fillers.

In the current application, the secondary HALS additive is incorporated into PP resin in the concentration range of 0.3 wt.% to 2 wt.%. For proprietary reasons, the chemical structure of this additive cannot be provided. The resin into which this additive was compounded contains approximately 1000 ppm of a HALS additive, namely octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propanoate which is a phenolic primary antioxidant, and approximately 500 ppm calcium stearate. This additive shows strong spectral signature in the UV region due to electronic transitions [87], and absorption in the NIR region due to N—H stretch vibrational modes [22].

In the following section, a brief description is provided for the experimental procedure, which is followed by discussion of results obtained by NIR spectroscopy.

6.1.2 Experimental

In this application, nine PP resin samples were available, which differed from one another in their additive concentrations. The sample concentrations to be assayed are tabulated in Table 6.1. The table lists target values and the primary laboratory analysis for the HALS additive concentrations. The primary analysis was performed using HPLC technique at the laboratory facility of the company that provided the samples. The standard deviations for the composition measurements from HPLC are also tabulated, which gave an estimate for the SEP value. [During regression, errors associated with the primary analysis carry over to predictions using any secondary methodology. It can be shown that the variance of the predicted concentration values is directly proportional to the variance associated with the primary method [94].]

The nominal processing temperatures for extrusion of PP are around 230 °C [1]. In the experimental setup, the final extruder temperature was set at 230 °C, with a stepwise gradient in temperature in three different zones. Dry nitrogen supply to the setup was not necessary for this particular set of experiments as the polymeric system under study is not hygroscopic. The operating conditions for extrusion involved maintenance of a nominal mass flow rate of about 1.0 lb/hr and gear pump pressures in the range of 600-700 psi.

Table 6.1: Concentration of primary HALS additive in PP resins

Note the discrepancy in the primary analysis of sample # 3. In the NIR region, this sample showed no signature in the N—H stretch overtone region, and the sample concentration was taken as 0.0 wt.% during multivariate analysis.

Sample Code	Target Concentration (wt.%)	Primary Analysis using HPLC method (wt.%)	Standard Deviation (wt. %)
1	1.12	1.13	0.05
2	1.375	1.39	0.03
3	0.0	-0.37	0.003
4	1.50	1.61	0.04
5	1.00	1.00	0.04
6	0.75	0.34	0.03
7	1.25	1.25	0.03
8	0.75	0.77	0.07
9	1.75	1.97	0.14

Replicate spectra were collected for each additive sample, and these spectra were utilized for analysis in both UV and NIR regions. Because the absorbances in the NIR region are lower in intensity as compared to the strong electronic transitions in UV region, different optical pathlengths in the flow cell were used for experiments in NIR and UV regions. In the current experimental setup, the largest available optical pathlength of 9.5 mm was utilized for measurements in the NIR region. A nominal pathlength of 2 mm was used for analysis in UV region, which kept the average absorbance to less than 1.0. The operating conditions of temperature, pressure, and flow rate were maintained more or less identical during both studies. This reduced variability during spectral collection in the two regions, and enabled simultaneous correlations of spectra in both regions. Details of this analysis will be presented in later sections.

6.1.3 NIR spectroscopy — Results and Discussion

The analyzer used for measurements in the NIR region was an Analect[®] FT-NIR spectrometer. This spectrometer provides excellent long-term wavelength reproducibility and better frequency accuracy than conventional dispersive instruments [102]. At an optical pathlength of 9.5 mm, NIR absorbance spectra were collected of molten, flowing PP resins with varying secondary HALS levels. The background spectrum was taken with air in the optical beam path, and this reference was averaged over 256 scans. Such large number of scans were necessary in order to improve signal-to-noise ratio of the spectrum. Ten replicate spectra were taken for each sample; each spectrum was averaged over 128 scans and ratioed with the background spectrum.

Figure 6.1 shows an overlaid absorbance plot of sample spectra in the NIR region. One distinct region was observed in the NIR spectrum, which showed absorbance peak variation with changing additive concentration. The first absorbance band is tentatively assigned to N—H stretch, first overtone vibrational mode for a secondary amine [22]. This band is observed in a wavelength region of 6,600-6,400 nm (1,515-1,565 nm), with an absorbance peak around 6,500 nm (1,540 nm). Another important observation is that there are significant baseline shifts in the spectra. These shifts are attributed to scattering effects due to the presence of calcium stearate additive in the PP resin. The baseline effects are removed by taking first derivatives of the absorbance spectra, which are shown in Figure 6.2. The first derivatives show a clearer trend in absorbance variation with increasing HALS composition. From Figure 6.3, a rough estimate of the overall absorbance peak variation is evaluated for the sample with the largest HALS composition, and this value is shown to be only about 0.025 units. Such low absorbances highlight concerns of signal-to-noise ratio and wavelength reproducibility in the spectra. This justified the use of larger pathlengths and more data averaging to improve signal-to-noise ratio.

Multivariate analysis was performed for additive content using PLS regression methods. The calibration model results for this additive system are discussed here. One representative spectrum from each sample was chosen for PLS calibration. The LAS cross-validation method (as discussed in previous analyses in Chapter 5) was used to determine the number of principal components required for optimal calibration. Using the PRESS criterion, a one principal component model was found to be optimal for

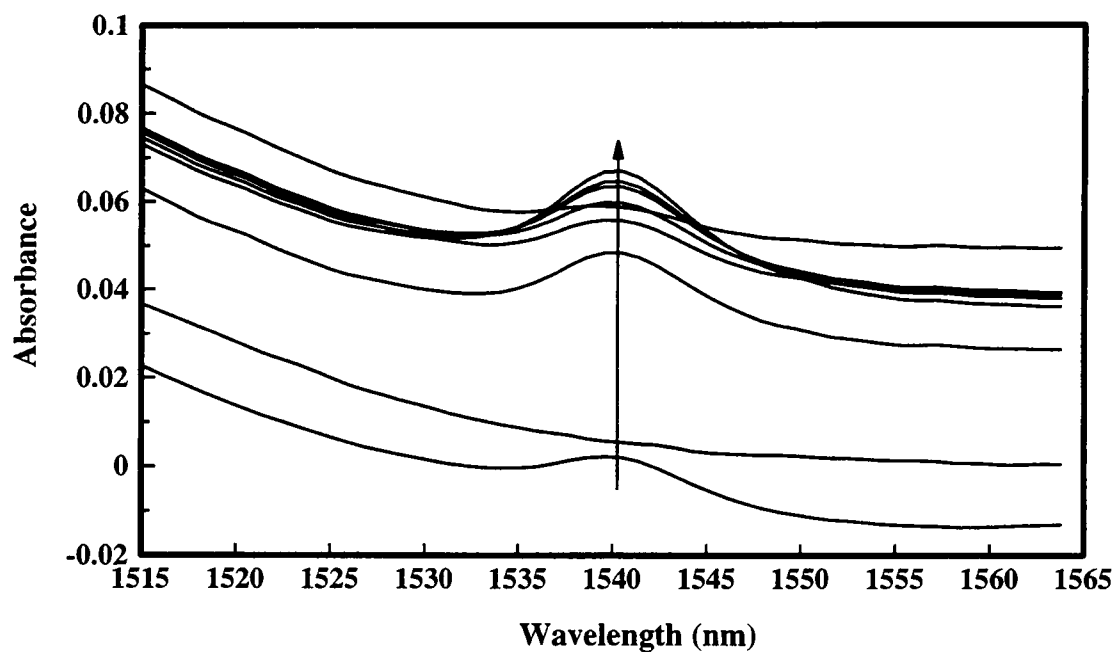


Figure 6.1 Overlaid absorbance plot of PP resins with varying secondary HALS additive content showing spectra in the NIR wavelength region of 1,515-1,565 nm. The absorbance peak at 1,540 nm is attributed to N—H stretch, first overtone vibrational mode for a secondary amine.

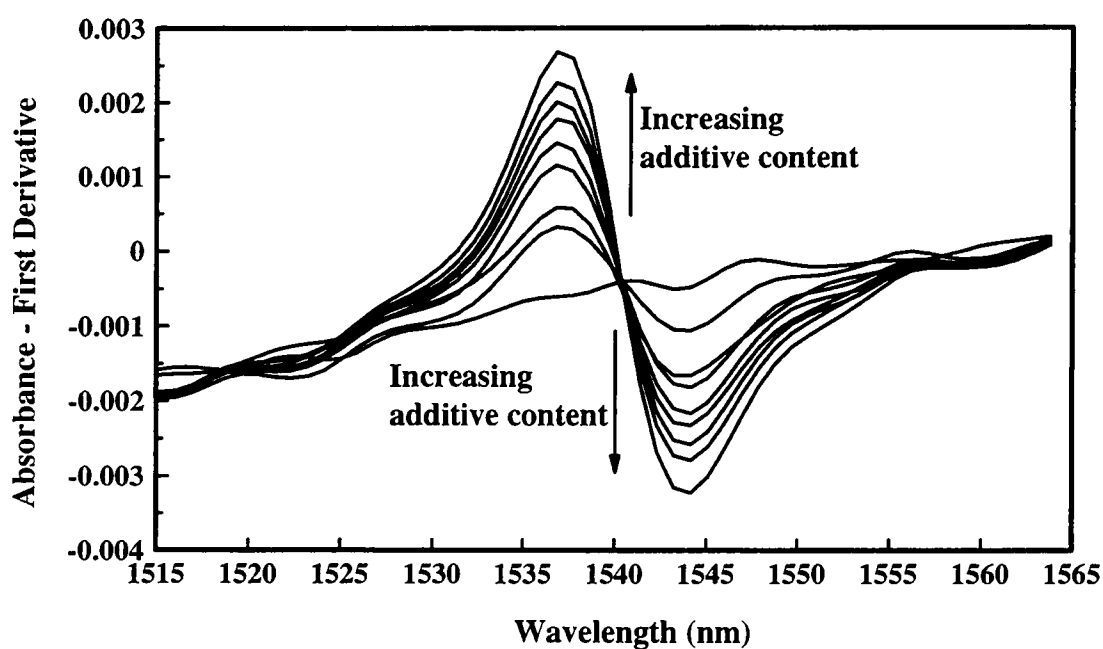


Figure 6.2 Overlaid plot of absorbance-first derivative for PP resins with varying secondary HALS additive content. The plot shows spectra in the NIR wavelength region of 1,515-1,565 nm. The absorbance peak at 1,540 nm is attributed to N—H stretch, first overtone vibrational mode for a secondary amine.

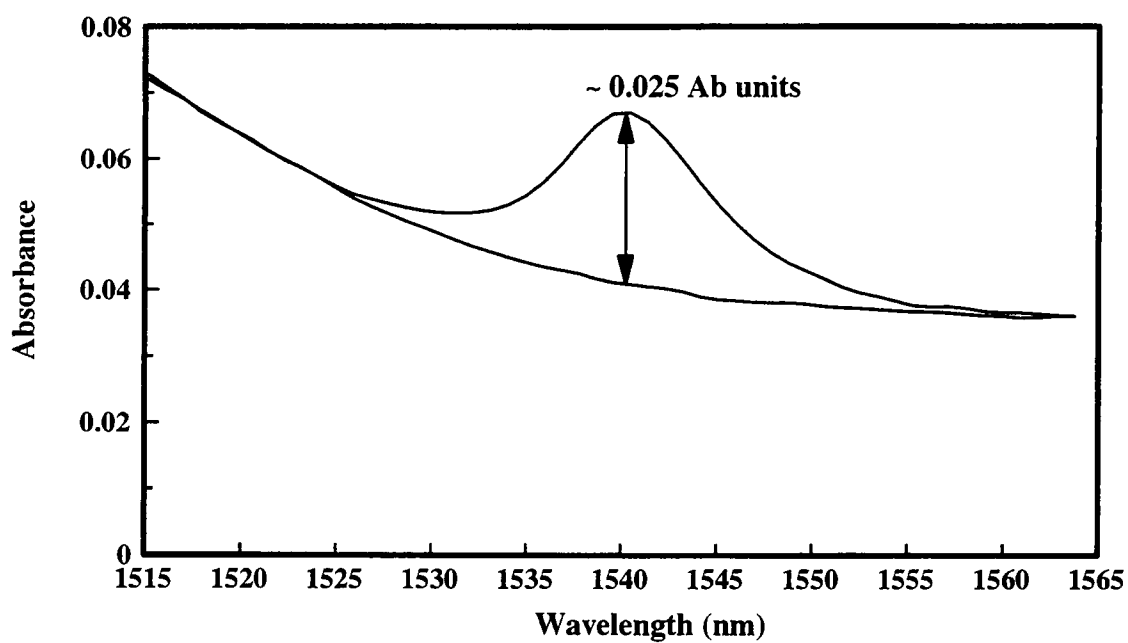


Figure 6.3 Plot showing maximum variation in absorbance peak height for sample with 1.97 wt.% secondary HALS concentration. Such low absorbances highlight concerns of signal-to-noise ratio and wavelength reproducibility in the spectra.

predictions. The prediction set consisted of five spectra from each sample. These spectra were obtained from an external spectral data set that had not been included during calibration. Figure 6.4 shows the standard errors (SEC/SEP) plot for the different principal component models. As expected, the SEC shows a decreasing trend with additional principal components, while the SEP reaches a minimum and then increases. Beyond one factor, random experimental noise is built into the calibration model, and hence, the residual errors associated with predictions for higher principal component models increase. The SEC value for one principal component model was 0.065 wt.%, and the SEP value was 0.075 wt.%.

Because there is only one physical factor of variation in the NIR absorbance spectra due to differing additive levels, a one PC model is justified. Figures 6.5.a and 6.5.b show the first loading vector and the corresponding regression coefficient vector obtained from PLS regression, plotted against NIR wavelengths. In these figures, it is observed that both vectors mimic the average derivative spectrum with higher intensities at wavelengths which correspond to larger variances. Figure 6.6 shows a plot of the first score vector plotted against the sample concentration. The first score vector is a representation of the “magnitudes” which are multiplied by the corresponding loading vectors. A linear relationship implies validation of Beer-Lambert’s law as seen in Eq. (2.9), and a linear relationship between the sample responses. However, for systems with such low concentration levels, the calibration models are often susceptible to small changes in actual numerical entries in the data. Therefore, it was essential to validate the results with an alternate regression technique, which was not based solely on choice of

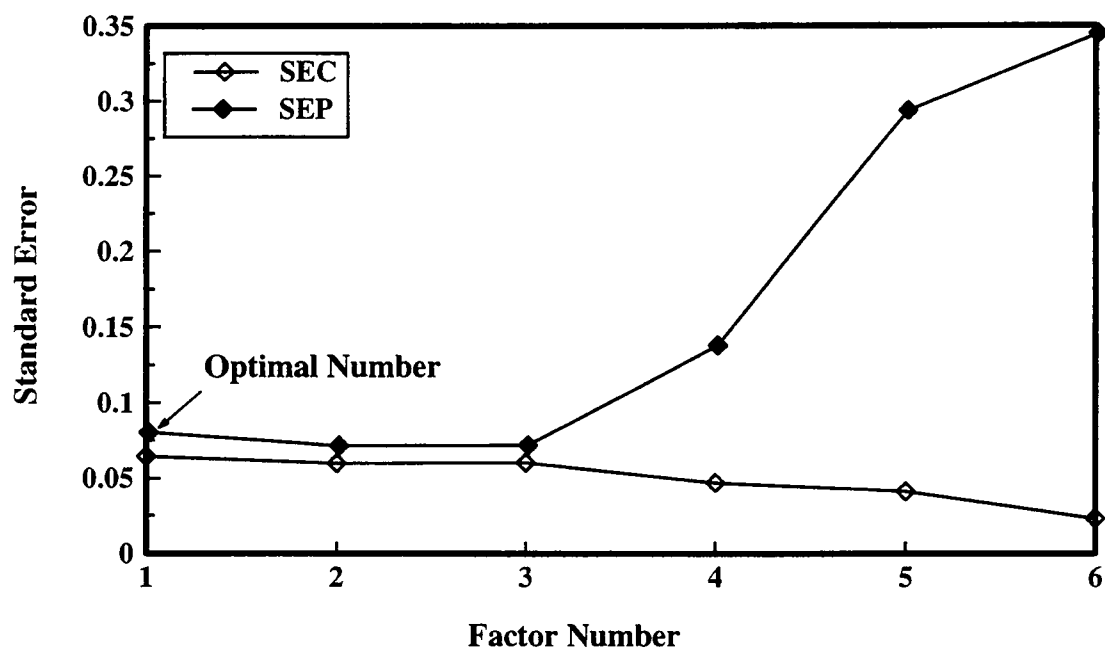


Figure 6.4 Standard Errors plot for PLS models with different principal components. As expected, the SEC decreases with increasing number of factors. The optimal number of factors is decided by the minimum PRESS value.

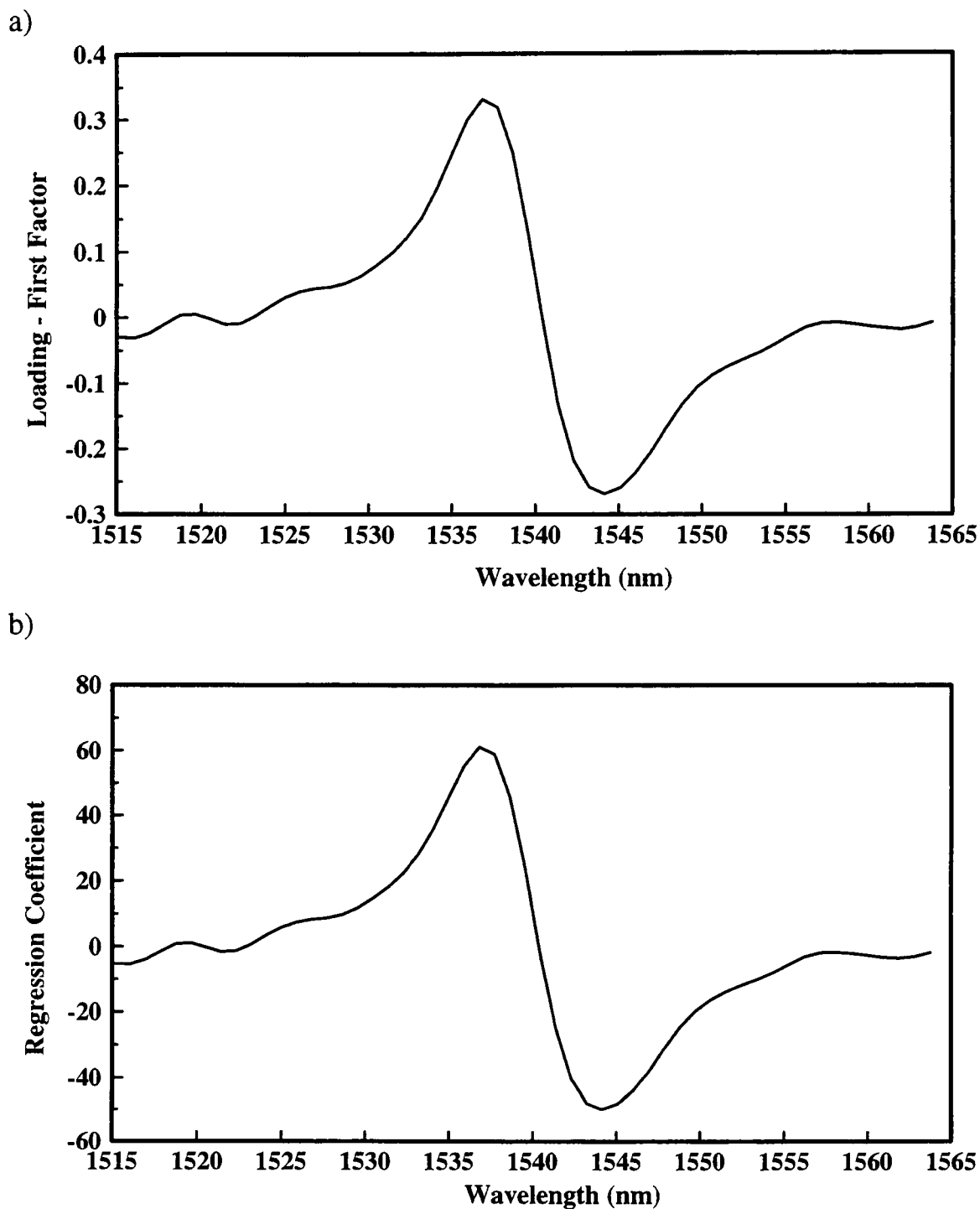


Figure 6.5 Plots illustrating a) loading vector for the first principal component and b) regression coefficient vector for a one-factor PLS model. It is observed that both vectors follow the trend of the average first-derivative absorbance spectrum.

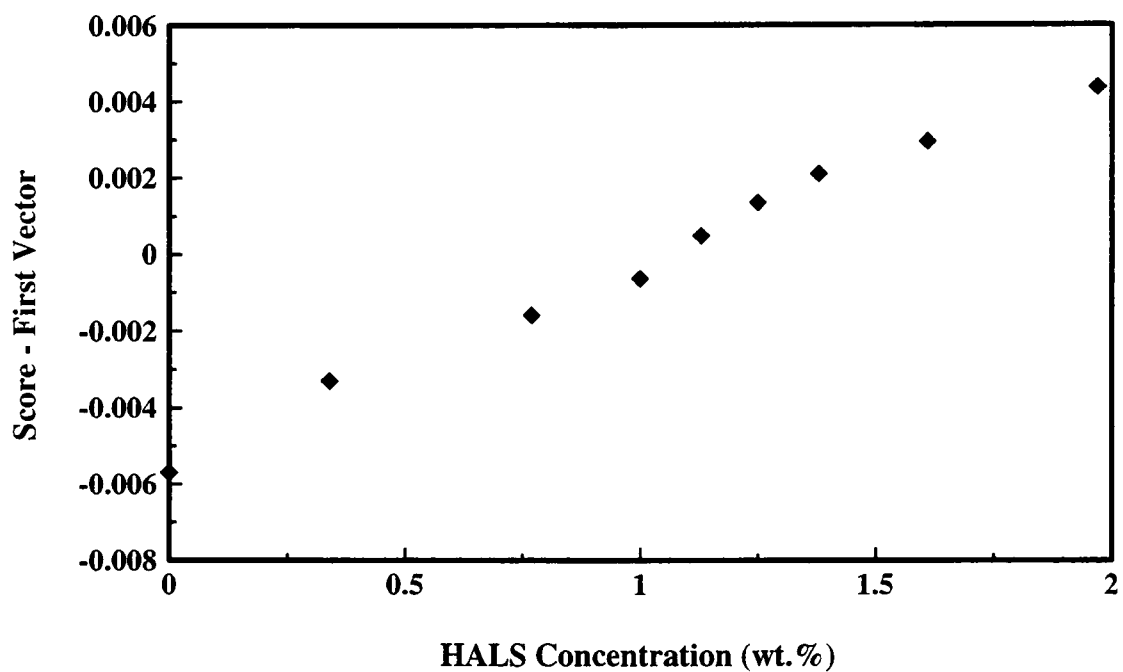


Figure 6.6 Plot of the first score vector *versus* additive concentration. A linear correlation between the score vector and the additive levels implies a linear relationship between the sample responses and satisfaction of Beer-Lambert's law.

number of principal component. With this objective, ridge regression (RR) is introduced here as a validation method for PLS regression. Like PLS regression, RR is also based on biased estimation procedure with one difference [103]. In RR, the ill-conditioned, or rank deficient, matrix is stabilized before inversion by adding a small positive bias during regression. This is in contrast to PCR and PLS techniques, where a pseudo-inverse is taken of the ill-conditioned matrix. During ridge regression, the regression coefficient is defined in terms of a *ridge estimate* parameter, α , which is optimally chosen, such that it makes the matrix invertible and simultaneously minimizes the residual errors:

$$\hat{\beta}^{RR}(\alpha) = (\mathbf{X}^T \mathbf{X} + \alpha \mathbf{I})^{-1} \mathbf{X}^T \mathbf{y} ; \quad \alpha \geq 0 \quad \dots(6.1)$$

where $\hat{\beta}^{RR}(\alpha)$ represents the set of biased regression coefficients; and $\mathbf{I}$ is the identity matrix. Eq. (6.1) is derived from the minimization of an objective function:

$$\chi^2 = (\mathbf{y} - \mathbf{X}\beta)^T (\mathbf{y} - \mathbf{X}\beta) + \alpha(\beta^T \beta - L^2) \quad \dots(6.2)$$

where β is the actual unbiased estimate for the regression coefficients; α is a “damping factor”, which softens the large error bounds in β due to singularities in $\mathbf{X}$; the scalar L^2 represents an energy parameter which incorporates large instabilities in β variation from small random experimental errors [103,104]. Standard minimization techniques involving partial derivatives are used to solve Eq. (6.2), which return the optimized solution as a function of α .

It is immediately observed that a criterion is required for optimum choice of α . The PRESS criterion using LAS cross-validation introduced earlier is used for this method as well. A range of α values are chosen, and the PRESS value is evaluated by summing the residual error terms of predictions from the LAS routine. The optimal α value is given by the minimum PRESS criterion. The PRESS term is expressed in the form of an equation as follows:

$$\text{PRESS}(\alpha) = \sum_{i=1}^{NV} (y_i - \hat{y}_{i,\alpha})^2 \quad \dots(6.3)$$

where y_i is the true composition value obtained from primary analysis; $\hat{y}_{i,\alpha}$ is the predicted composition for a given α value; and NV is the number of samples used in cross-validation. It should be noted that as α approaches zero, the residuals increase due to increased ill-conditioning in the matrix. At very large α values, the solution for the regression coefficient lacks a good fit leading to large errors. Thus, the optimum value for the ridge estimate, α , is a compromise solution between the stability of the solution and the goodness of fit.

For this analysis, a value of α of 10^{-6} was used for optimal predictions, using the PRESS criterion. The cumulative PRESS plot is shown in Figure 6.7. Ridge regression lacks in the wealth of qualitative information that PLS and PCR techniques provide in the form of scores and loadings. However, it is a robust regression method and serves as a good, secondary validation technique for comparative studies. Figure 6.8 shows the regression coefficient vector obtained from RR, which is compared with the PLS

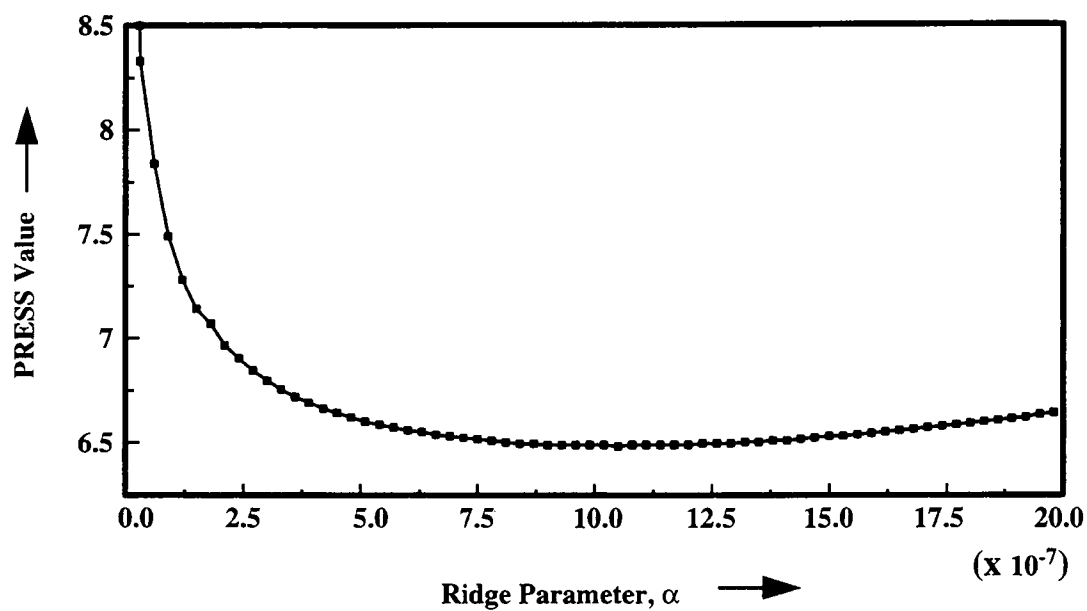


Figure 6.7 PRESS plot for ridge regression analysis. The PRESS criterion shows an optimal calibration model at a value of $\alpha = 1 \times 10^{-6}$.

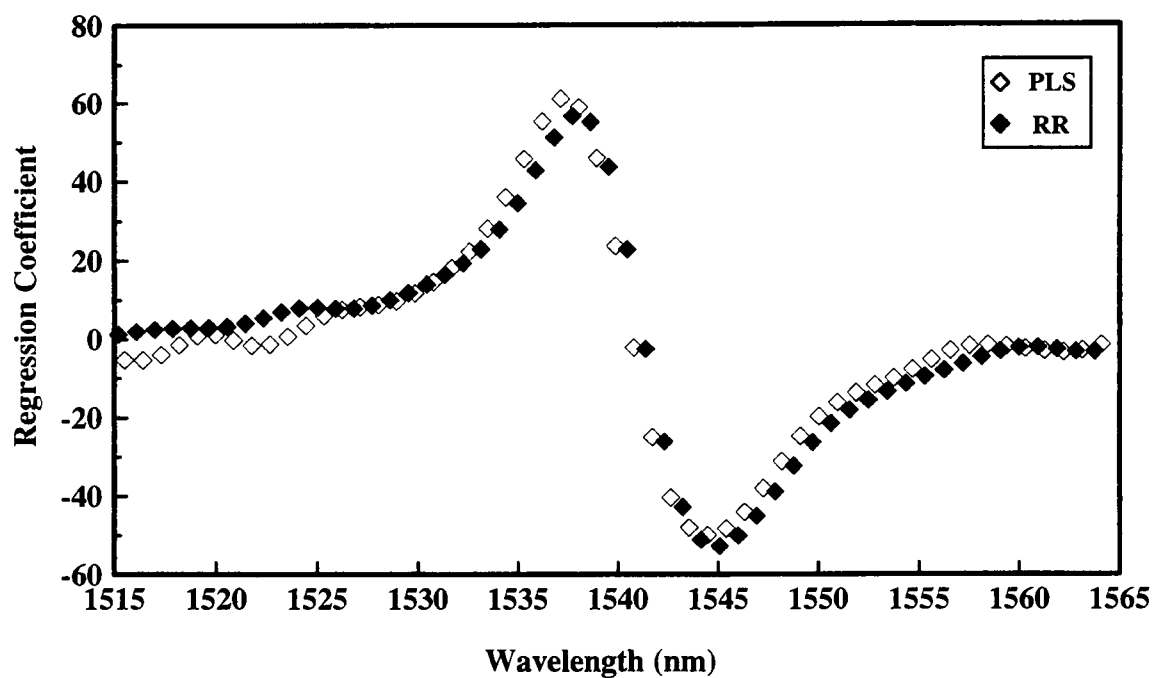


Figure 6.8 Comparative plot for the results obtained from ridge regression (RR) and a one-factor PLS method. Based on the excellent agreement, it is conjectured that a one-factor PLS method is justified.

regression coefficient for a one-factor model. From comparison of the results, it is conjectured that the choice of one principal component for the PLS model was justified. Figures 6.9.a and 6.9.b show the model predictions for samples in the calibration and the prediction set.

It is observed that sample # 3, which seemed to have anomalous primary analysis, could be modeled in the NIR region with an “assumed” concentration value of 0.0 wt.%. The presence of the phenolic primary antioxidant additive in the base resin did not pose any problem in the NIR data analysis. This additive lacks N—H moieties in its chemical structure and therefore, does not show any spectral signature in the wavelength region used for quantification.

In the following section, a brief introduction will be given on the origin of spectra in the UV region. Results from multivariate analysis on UV spectral data will be detailed in the subsequent sections.

6.1.4 UV spectroscopy

The spectra in the UV (and visible) region of the electromagnetic spectrum arise from transitions between electronic states and are associated with simultaneous changes in the vibrational and rotational states. These changes lead to large energy differences, and consequently, absorption occurs at large frequencies (or relatively short wavelengths). Therefore, in the electromagnetic spectrum, UV and visible regions occur at shorter wavelengths as compared to the infrared region [105,106].

The relations between the various energy levels and corresponding spectra are

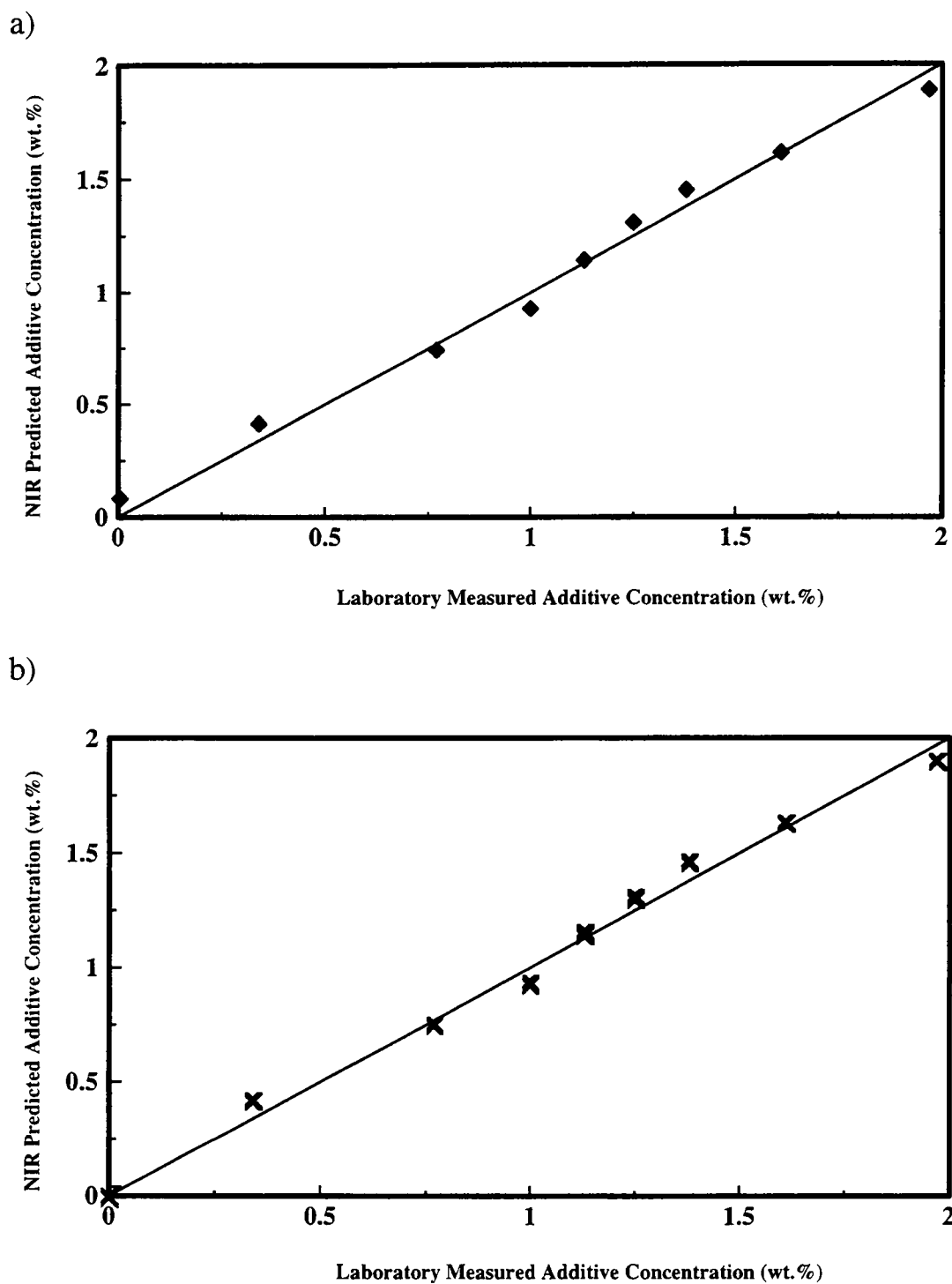


Figure 6.9 Plots illustrating the NIR predictions of additive content for samples in a) calibration set and b) prediction set. The SEC value for the one-factor PLS model was 0.065 wt.% and the SEP value for the prediction set was 0.075 wt.%.

illustrated in Figure 6.10, which shows the energy states in a diatomic molecule. In this figure, the vertical line *AB* corresponds to a transition in pure rotation as the electronic and vibrational levels do not change for this transition. The line *CD* corresponds to a transition in the vibration-rotation spectrum, and being longer than *AB*, represents a larger change in energy, and therefore, absorption of light at shorter wavelengths. The line *EF* corresponds to the largest energy change due to an electronic transition, and represents absorption at still shorter wavelengths.

Each electronic state is associated with a large number of vibrational and rotational states. Therefore, a transition between two electronic states does not correspond to a single change in energy and does not result in a single spectral line. A large number of lines result from the transition, and these are not widely separated from each other, especially in case of liquid and solid samples. In absorption spectra, it is not possible to separate rotational lines associated with a single vibrational transition, and these superpose to produce a single vibration band. This explains the presence of broad bands in the UV region.

The compounds which exhibit strong UV signature have typically free π -electrons in their molecular structure; some examples are resonance stabilized aromatics and other compounds with ring structures [105,106].

6.1.5 UV spectroscopy — Results and Discussion

The UV region was used for this additive system as a preliminary feasibility study for in-line monitoring. As was mentioned earlier, lack of previous experimental

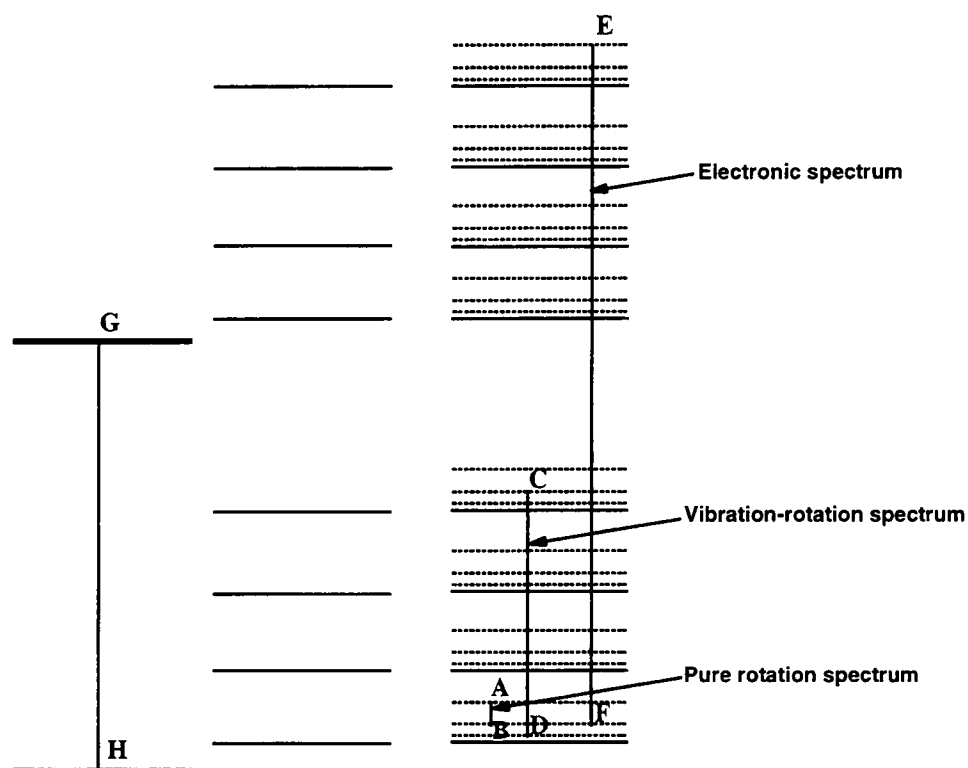


Figure 6.10 Absorption in the ultraviolet region of the electromagnetic spectrum from the energy states of a diatomic molecule. Line *AB* represents a transition between energy levels leading to a pure rotational spectrum; Line *CD* represents an energy transition leading to a combined vibration-rotation spectrum; Line *EF* represents an electronic transition and represents absorption at relatively shorter wavelengths. *H* represents the ground state and *G* represents an excited state.

[Source: G. H. Schenk, *Absorption of Light and Ultraviolet Radiation* (Allyn and Bacon, Inc. Boston, 1973).]

work for in-line UV monitoring is attributed to the unavailability of robust instrumentation in terms of detectors and fiber-optics. Long-term stability for work using fiber-optics in the UV region is a challenge because of solarization of the fibers. Also, spectrometers which use photomultiplier tubes (PMT) as UV detectors are unreliable in wavelengths below 250 nm. Unfortunately, there is a wealth of information in the lower wavelength range of 190-250 nm. For example, some common polymers, such as PP and PE, show spectral signature at lower wavelengths (attributed to the backbone structure in these polymers). Hence, the inaccessibility of lower wavelength region led to neglect of the UV region. However, this scenario is fast changing with development of fiber-optics with long-term stability and linear-array based detectors [107,108].

To illustrate the effect of instrumentation and fiber-optics, the extrusion melt of the current additive system was monitored using a Guided-Wave Model 260 dispersive spectrometer. This spectrometer is equipped with a PMT detector, a deuterium lamp source, and a diffraction grating. The grating is grooved at 1,200 lines/mm of the surface. A slit width of 0.25 mm was used for collecting dispersive absorption spectra, data were scanned at 0.1 nm wavelength step. Figure 6.11 shows an overlaid plot of raw spectra for the PP samples with varying additive levels. The first observation is low signal-to-noise ratio in the absorbance spectra. Another observation is the absence of any spectral signature below 250 nm (Note: pure PP signature is absent in the spectra). This is attributed to limits of detection of the PMT detector, which in combination with the fiber-optics, has a cut-off below 250 nm. This feature is observed in a background/

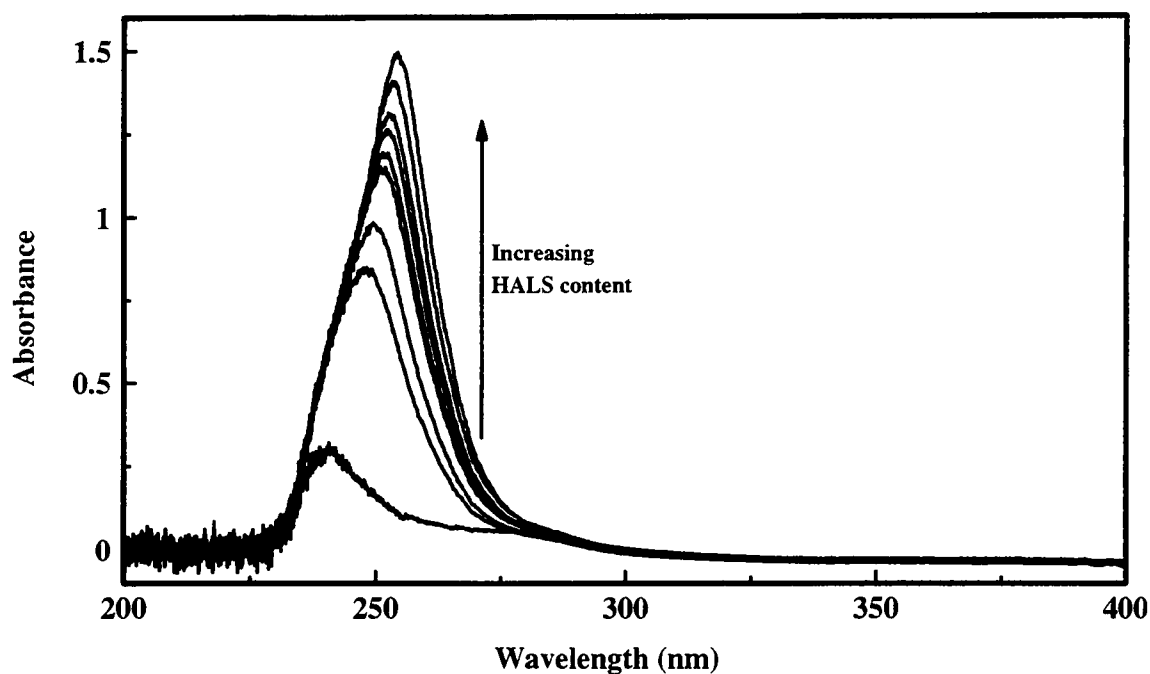


Figure 6.11 Overlaid absorbance plot of PP resins with varying secondary HALS additive content showing spectra in the ultraviolet (UV) wavelength region of 200-400 nm. These measurements were carried out with a spectrometer based on a PMT detector, which had a cut-off below 250 nm.

reference plot, shown in Figure 6.12, which shows a decrease in signal intensity below 250 nm.

The final set of experiments was performed using a linear-array based detector, which has good detection limits up to 230 nm. Because the additive shows signature at wavelengths above 250 nm, these data were satisfactory for quantification. Figure 6.13 shows a plot of overlaid spectra for the PP samples with varying HALS concentrations. In comparison with Fig. 6.11, spectra obtained have higher signal-to-noise ratio. The spectra are also better resolved as compared to data from the dispersive instrument.

In Fig. 6.13, it is observed that sample # 3 (which is tentatively assigned 0 wt.% concentration) has some absorbance in the wavelength region where the secondary HALS additive shows spectral signature. These additional peaks are attributed to the presence of the primary phenolic antioxidant additive (tentatively at 280 nm) in the PP base resin. This leads to an overlap of absorbance peaks, (an expected result as both chemicals have similar structures for UV absorption), and this feature is resolved better in the first derivative plot, as shown in Figure 6.14. In this figure, in addition to an increase in the absorbance peak heights, shifts are observed in the region of 270-280 nm. These features are observed as a movement of the derivative “trough” (inflection point in the original absorbance plot) along the wavelength axis with changing additive levels. It is conjectured that this shift is due to overlapping peaks of the second additive.

The PRESS plot from a LAS cross-validation PLS method is illustrated in Figure 6.15. Based on the PRESS criterion, a one factor model is chosen for final calibration. However, from the figure, it is observed that PRESS values at higher factors

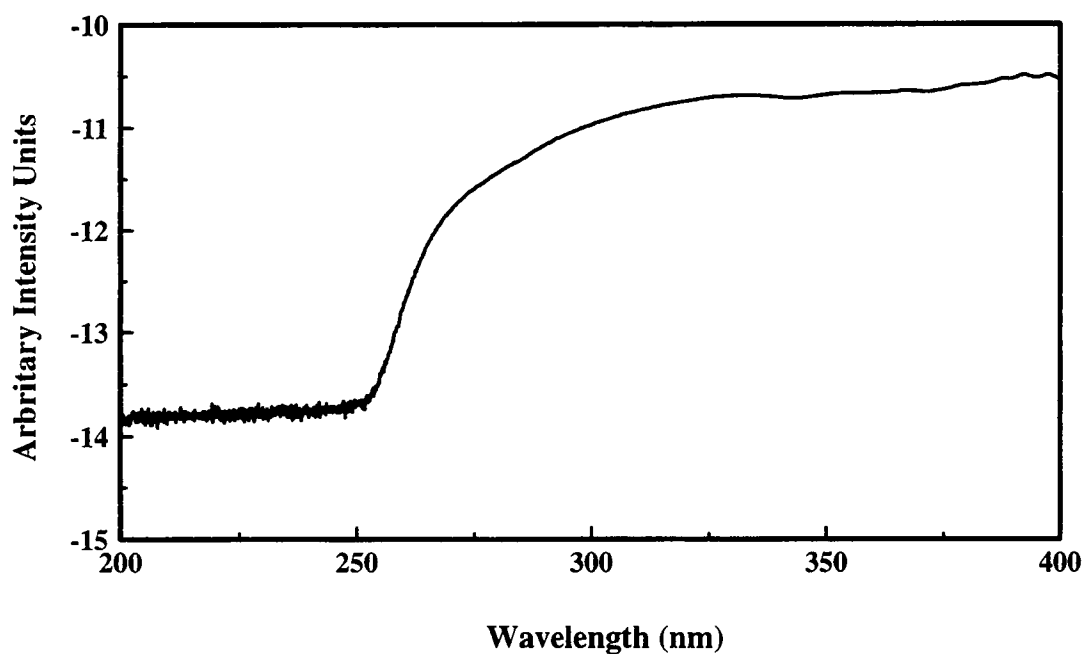


Figure 6.12 Background intensity response in the UV region for the dispersive spectrometer, which shows a cut-off below 250 nm. Lower intensities below 250 nm imply very low signal-to-noise ratio and possible loss of spectral signatures. Such spectra cannot be used for quantitative analysis.

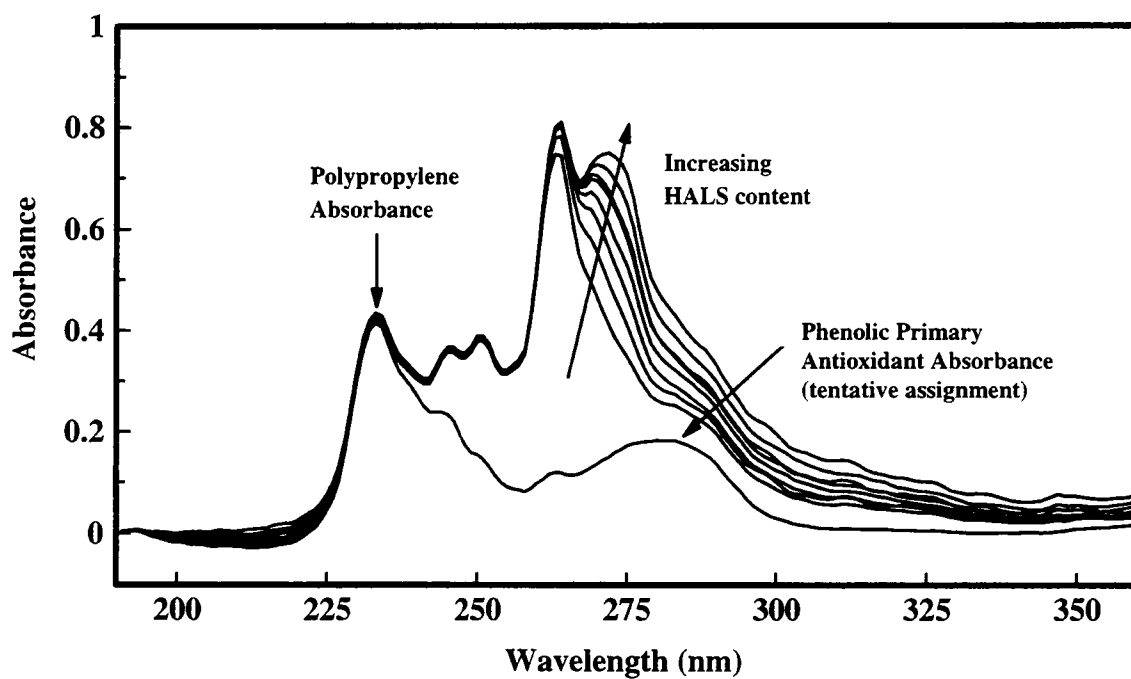


Figure 6.13 Overlaid absorbance plot of PP resins with varying secondary HALS additive content showing spectra in the ultraviolet (UV) wavelength region of 190-360 nm. These measurements were carried out using a linear array based spectrometer.

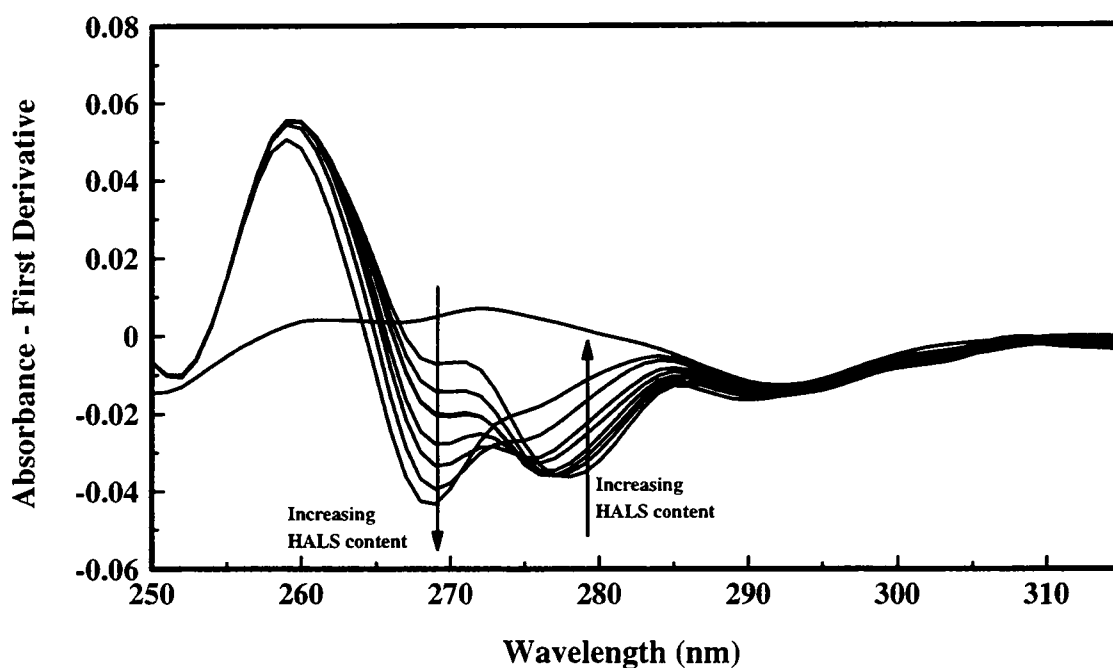


Figure 6.14 Overlaid plot of absorbance-first derivative for PP resins with varying secondary HALS additive content. In this figure, in addition to an increase in the absorbance peak heights, shifts are observed in the region of 270-280 nm. These features are observed as a movement of the derivative “trough” (inflection point in the original absorbance plot) along the wavelength axis with changing additive levels. It is conjectured that this shift is due to overlapping peaks of the second additive.

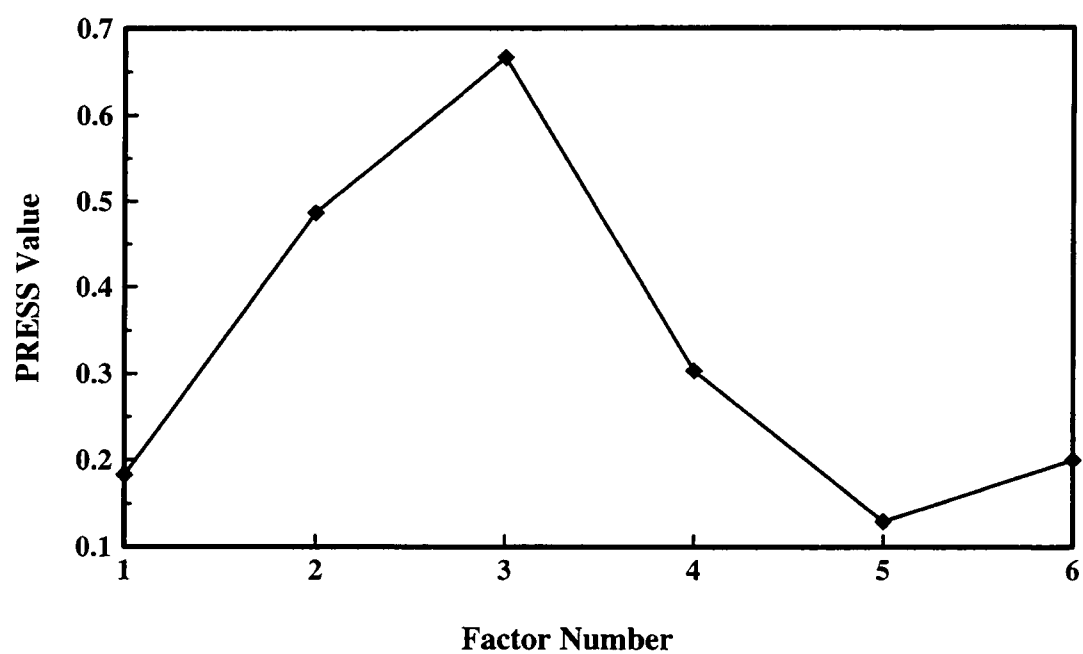


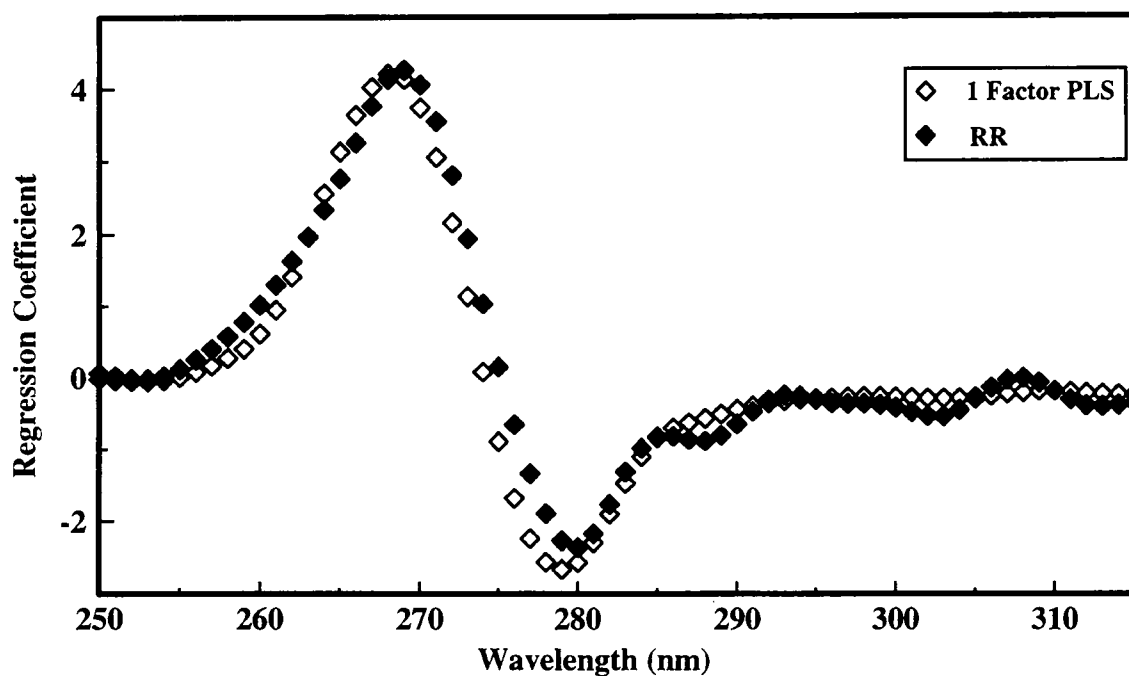
Figure 6.15 PRESS plot for various factors in a PLS model.

(>3) are of similar magnitude to that obtained from a one factor model. Therefore, it was necessary to validate the PLS model with results from an alternate regression technique. RR was introduced earlier as another robust regression methodology, and this method is used here for comparative studies. In Figures 6.16.a and 6.16.b, the regression coefficients for a one and a four factor PLS model are compared with the results obtained from RR analysis. Such analysis validates the one-factor PLS model. This result is also in agreement with the parsimony model introduced by Seasholtz and Kowalski [109]. According to this approach, while comparing any two calibration models that give similar predictions (or similar SEP values), the calibration model with lower number of factors is always chosen for future predictions. In other words, larger number of principal components imply greater susceptibility to random, experimental noise. In Fig. 6.16, it is observed that the regression coefficient vector obtained from a four factor model is more oscillatory as compared to the one factor model.

6.1.6 NIR—UV Correlation spectroscopy

In the preceding sections, it was demonstrated that multivariate calibration models can be developed for providing quantitative measurements of additive levels. Despite low absorbances in the NIR region, NIR spectroscopy, coupled with powerful multivariate statistical analysis tools, provides an elegant solution for the prediction of additive levels. Feasibility studies established that the UV region is amenable for additive measurements in wavelength regions of 250-360 nm. Also, it was determined from multivariate analysis that there is only one physical factor of variation in the NIR

a)



b)

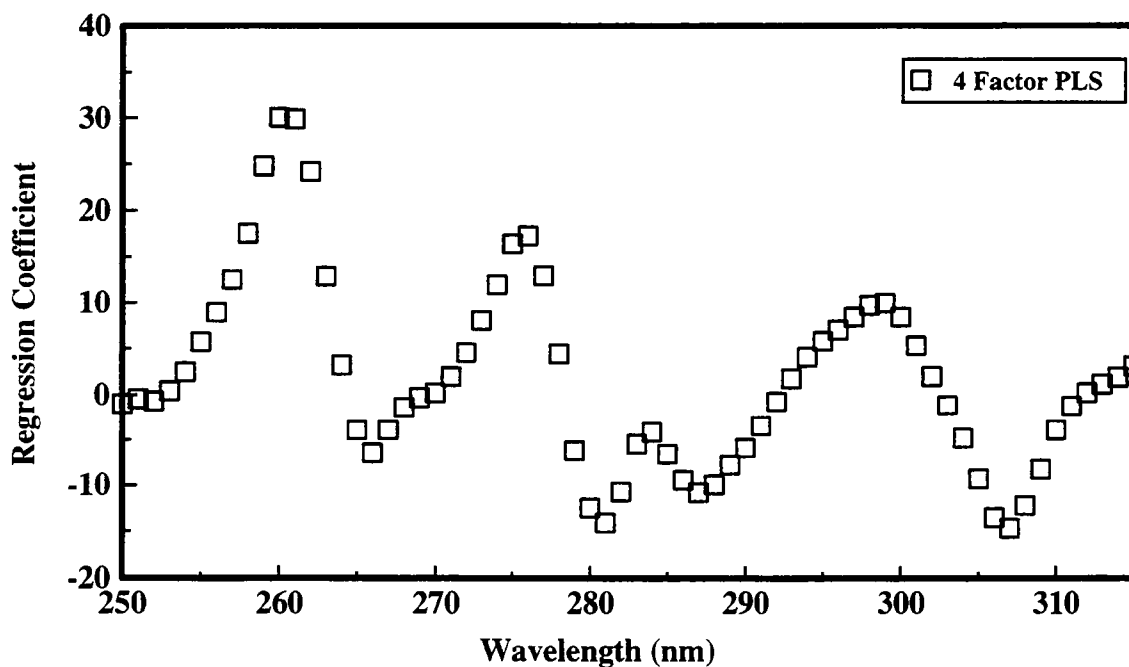


Figure 6.16 Plot of the ridge regression (RR) results compared with (a) a one-factor PLS method and (b) a four-factor PLS method. It is conjectured that a one-factor PLS method is justified.

and UV absorbance spectra. This variation is attributed to varying HALS additive levels in the PP resin.

In this section, a methodology to correlate NIR and UV spectroscopy is introduced, which aims for better qualitative and quantitative interpretation in both regions. One potential application of this technique is in interpretation and assignation of unknown spectral peaks to specific chemical moieties, given known spectral signature in a different wavelength region of the electromagnetic spectrum. Another application of this technique is as an analytical tool in deconvolution of overlapping peaks by correlating against known, individual spectral bands at other wavelengths.

This methodology is derived from an earlier attempt by Lew and Balke [110] who applied multivariate analysis for obtaining mid-infrared (MIR) spectra from NIR spectra. The motivation for the earlier work was to correlate broad, overlapping bands in NIR spectra to sharp, narrow fundamental bands in MIR spectra. Because spectra in the NIR region are overtones and combinations of MIR fundamentals, such correlations could be used to identify and assign NIR peaks in terms of well known MIR vibrational modes.

The interaction between NIR and UV spectra is more complex in nature. Unlike the NIR—MIR relationship, the spectra in NIR and UV regions have different physical origins. While NIR spectral bands correspond to overtone and combination vibrations of molecular bonds, UV spectra occur as a result of electronic transitions. In addition to differences in the physics of their origin, some chemical structures are more amenable

for absorbance in UV (such as aromatics), while others such as aliphatics show little or no response in UV. On the other hand, as an example, the methylene (C—H) stretch overtone bands for aliphatics and aromatics are separated only by a few wavelengths in NIR.

In general, correlation between NIR and UV spectra is not as definitive as the MIR—NIR relationship. However, it is possible to utilize multivariate techniques to correlate small wavelength regions of each spectrum, in order to obtain better physical interpretation of the absorbance signatures in both regions.

For example, for the polymeric system under study, one region each was identified in both NIR and UV spectra, which is attributed to the secondary HALS additive. It was observed that the NIR region of N—H overtone bands showed no interference from the second additive, while such interferences were seen in the UV region in the form of overlapping peaks. In the previous section on UV spectroscopy, the effect of such overlapping peaks was emphasized in the first-derivative plot of Fig. 6.14.

Despite this difference in absorbance data of the two regions, it should be noted that multivariate techniques correlate only *data variances* and therefore, can be used to correlate absorbance peak variations in two separate regions of the electromagnetic spectrum which have different physical origins. In other words, although the presence of absorbance peaks in NIR region have no bearing on the presence of absorbance peaks in UV and *vice versa*, the variance in absorbance peaks in NIR region due to varying concentrations of a given chemical moiety should correlate with peak variance for that

species in UV region. This assumption is valid only because Beer-Lambert's law holds universally. [In theory, for the present system, if the second additive were also varying in concentration independent of the primary additive, the spectra in the NIR region of 1,515-1,560 nm, (which is attributed to the primary additive alone), could still be used to deconvolute the overlapped peaks of the primary and secondary additives in the UV region of 250-300 nm.]

6.1.6.1 Results and Discussion

Figure 6.17 shows a schematic for NIR—UV correlation spectroscopy. In spirit, mathematical analysis for this study is analogous to correlation of complex viscosity response to NIR absorbance spectra, as discussed in Chapter 5. In PLS notation, the absorbances in the two regions are written as below:

$$\left. \begin{aligned} \mathbf{A}_{\text{NIR}} &= \mathbf{T}_{\text{NIR}} \mathbf{P}_{\text{NIR}} + \mathbf{E}_{\text{NIR},\text{NIR}} \\ \mathbf{A}_{\text{UV}} &= \mathbf{T}_{\text{UV}} \mathbf{P}_{\text{UV}} + \mathbf{E}_{\text{UV},\text{UV}} \end{aligned} \right\} \quad \dots(6.4)$$

where

$\mathbf{A}_{\text{NIR}} = (m \times p)$ matrix corresponding to NIR absorbance spectra

$\mathbf{A}_{\text{UV}} = (m \times k)$ matrix corresponding to UV absorbance spectra

$\mathbf{T}_{\text{NIR}} = (m \times f)$ reduced matrix corresponding to scores for f factors for NIR data

$\mathbf{T}_{\text{UV}} = (m \times h)$ reduced matrix corresponding to scores for h factors for UV data

$\mathbf{P}_{\text{NIR}} = (f \times p)$ reduced matrix corresponding to loadings for f factors for NIR data

$\mathbf{P}_{\text{UV}} = (h \times k)$ reduced matrix corresponding to loadings for h factors for UV data

$$\mathbf{Y}^{(m \times n)} = \mathbf{X}^{(m \times p)} \cdot \boldsymbol{\alpha}^{(p \times n)}$$

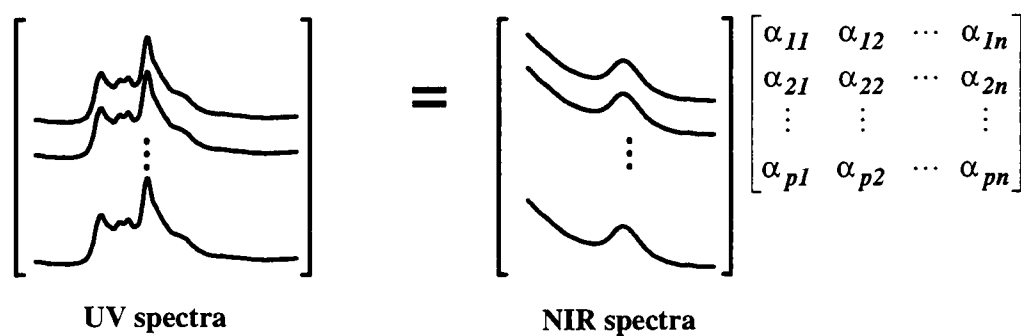


Figure 6.17 Schematic representation for NIR—UV correlation spectroscopy. The spectral data obtained in the UV region are regressed against the NIR spectral data, using multivariate statistical analysis.

$E_{\text{NIR}} = (m \times p)$ residuals matrix for NIR spectra

$E_{\text{UV}} = (m \times k)$ residuals matrix for UV spectra.

While performing multivariate analysis, the choice of the independent and dependent variables depends on the desired information. For the current study, the NIR data is chosen to represent the $\mathbf{X}$ matrix because the deconvolution of spectral peaks in the UV region is desired. The UV spectral data is chosen as the $\mathbf{Y}$ matrix.

A detailed mathematical description for regression of multiple y -variables was provided in Chapter 5. As in the previous case study for correlating rheological properties, PLS-2 regression is avoided for developing the calibration model. Instead, PCA is initially performed on the UV data matrix. After choosing the appropriate number of principal components, scores vectors are evaluated for PCA analysis. PLS calibration is carried out on the reduced scores matrix, $\mathbf{T}$, one score vector being predicted at a time. The predicted scores matrix, $\hat{\mathbf{T}}$, when multiplied with the loadings matrix, $\mathbf{P}$, gives an estimate for $\hat{\mathbf{Y}}$. Because developing a calibration model using PLS-2 is computationally more intensive, the PCA/PLS-1 methodology is used for correlating NIR and UV spectra.

PCA of Y-Matrix : Decomposition into Principal Components

One representative UV spectrum in the wavelength region of 250-300 nm for each sample was used to form the $\mathbf{Y}$ matrix. The UV absorbance-first derivative data in the $\mathbf{Y}$ matrix were standardized by mean-centering. Prior to PLS regression, PCA was

performed on $\mathbf{Y}$ in order to decompose it into smaller matrix, $\mathbf{T}$. As shown in Table 6.2, one principal component explained 92.5% of overall variance in $\mathbf{Y}$, and the second principal component explained an additional 7.09%. The first principal component is expected to have information, which correlates with the HALS additive concentration. The second principal component is expected to contain some unexplained contribution in the overall variance, which is attributed to the presence of the overlapping peaks of the phenolic antioxidant. Figure 6.18 shows a plot of the first and second score vectors, $\mathbf{t}_1$ and $\mathbf{t}_2$, against additive concentrations. As expected, the first score vector shows a linear relationship, while the second score vector does not show any correlation. The first and second loading vector plots are illustrated in Figure 6.19. The first loading vector represents the average absorbance-first derivative spectrum in UV region. Figure 6.20 shows the spectra regenerated from PCA analysis, after including only one principal component. In comparison with the absorbance-first derivative plot in Fig. 6.14, it is seen that the unexplained information comes about due to the presence of overlapping peaks.

PLS-1 Regression of $\hat{\mathbf{t}}_1$: Regression onto $\mathbf{X}$ matrix (NIR Data)

After PCA, a regression model is developed for $\mathbf{t}_1$ using PLS-1 regression. In the $\mathbf{X}$ matrix, one representative NIR spectrum for each sample was used in the wavelength region of 1,515-1,560 nm. Standard cross-validation PLS algorithms were used for determining the number of factors required for optimal calibration of $\mathbf{t}_1$ onto

Table 6.2: Contribution of individual principal components in explaining the overall data variance

Factor Number	% variance explained by this principal component	Overall % variance explained
1	92.54	92.54
2	7.09	99.62
3	0.28	99.90
4	0.07	99.97

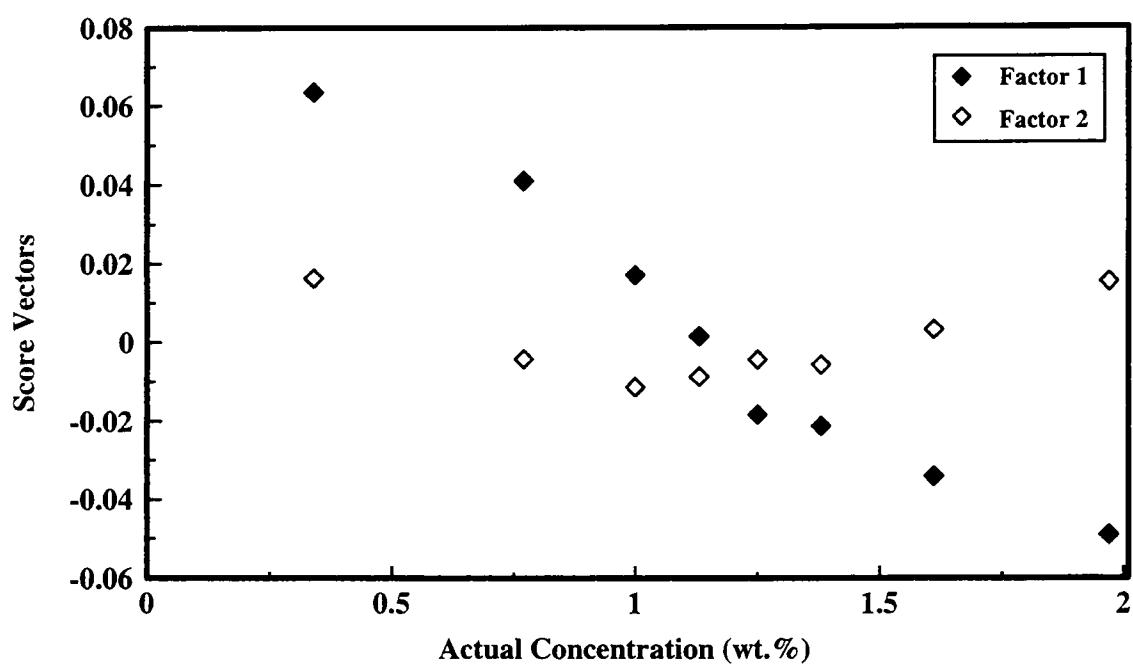


Figure 6.18 Score vectors for the first two principal components plotted against HALS additive concentration. As expected, the first score vector shows a linear relationship, while the second score vector does not show any correlation.

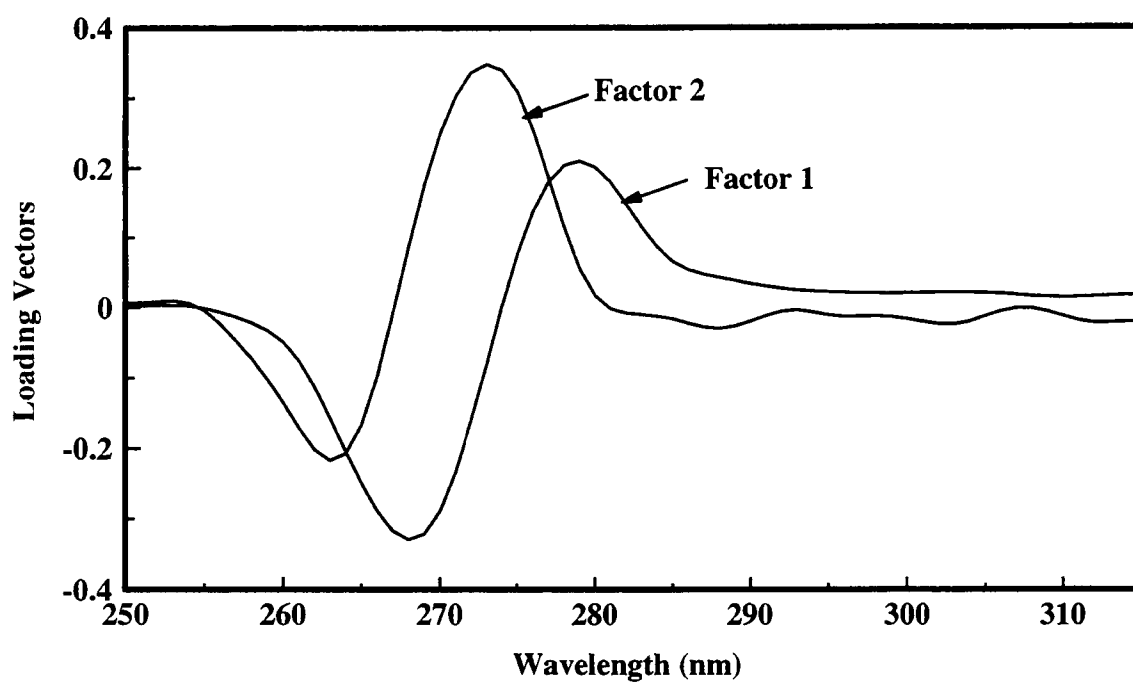


Figure 6.19 Loading vectors for the first two principal components. The first loading vector represents the average absorbance-first derivative spectrum in UV region. The second loading vector contains contribution of the overlapping peaks of the second additive in the PP resin.

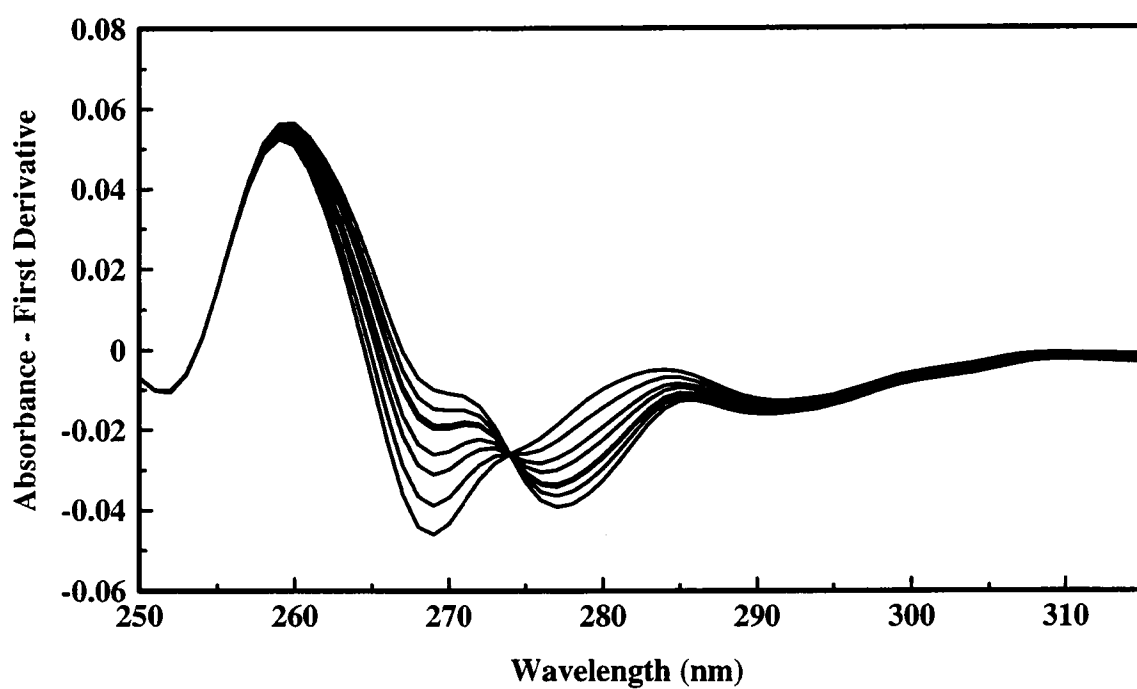


Figure 6.20 UV spectra regenerated from PCA analysis, after retaining only one principal component. In comparison with the absorbance-first derivative plot in Figure 6.14, it is seen that the unexplained information comes about due to the presence of overlapping peaks.

the NIR data matrix, $\mathbf{X}$. A one-factor model was found optimal for the calibration model. As illustrated in Figure 6.21, the NIR-predicted $\hat{\mathbf{t}}_1$ values show excellent agreement with the first PCA score vector, $\mathbf{t}_1$. This reiterates that the variation due to additive content in the UV spectra can be correlated to NIR spectra. From the predicted values of $\hat{\mathbf{t}}_1$, $\hat{\mathbf{Y}}$ is obtained by premultiplying $\hat{\mathbf{t}}_1$ to the first loading vector, $\mathbf{p}_1$. The predicted $\hat{\mathbf{Y}}$ values, which contain regenerated spectra obtained from NIR predictions, are compared with original $\mathbf{Y}$ values (from Fig. 6.14), as shown in Figure 6.22. The differences in the NIR-predicted UV spectra from the original spectra denote the effects of overlapping peaks. On the other hand, an excellent agreement is observed between the NIR-predicted UV spectra and the PCA-regenerated data (Fig. 6.20).

6.1.7 Conclusions

The experimental study on the hindered amine system has demonstrated that quantitative analysis of additives in both NIR and UV regions can be performed successfully in an in-line extrusion process. The weak absorptions in the NIR region for low levels of additives were magnified to some extent by increasing the pathlengths. Robust calibration models were developed using multivariate techniques, such as partial least squares. The results were validated by another biased regression methodology, namely ridge regression.

The strong electronic transitions of these additives make them amenable for measurements in the UV region, even at lower optical pathlengths. The availability of

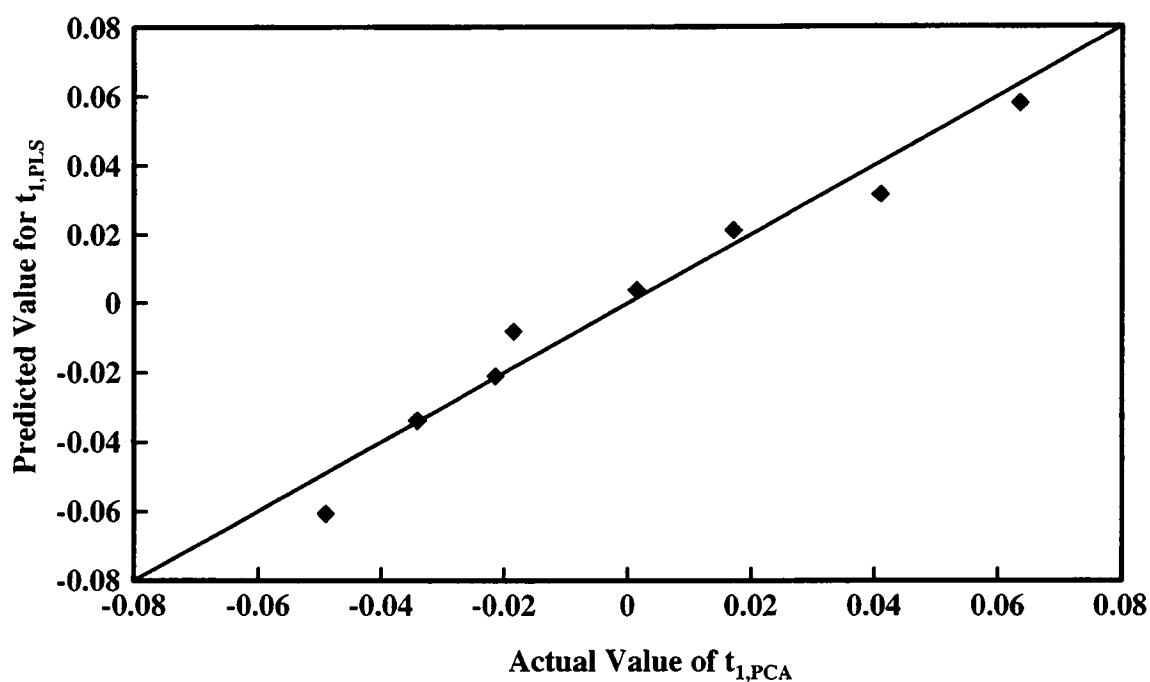


Figure 6.21 PLS Calibration of $\hat{t}_1$: NIR-predicted $\hat{t}_1$ values show excellent agreement with the first PCA score vector, t_1 . This reiterates the fact that the variation due to additive content in the UV spectra can be correlated to the NIR spectra.

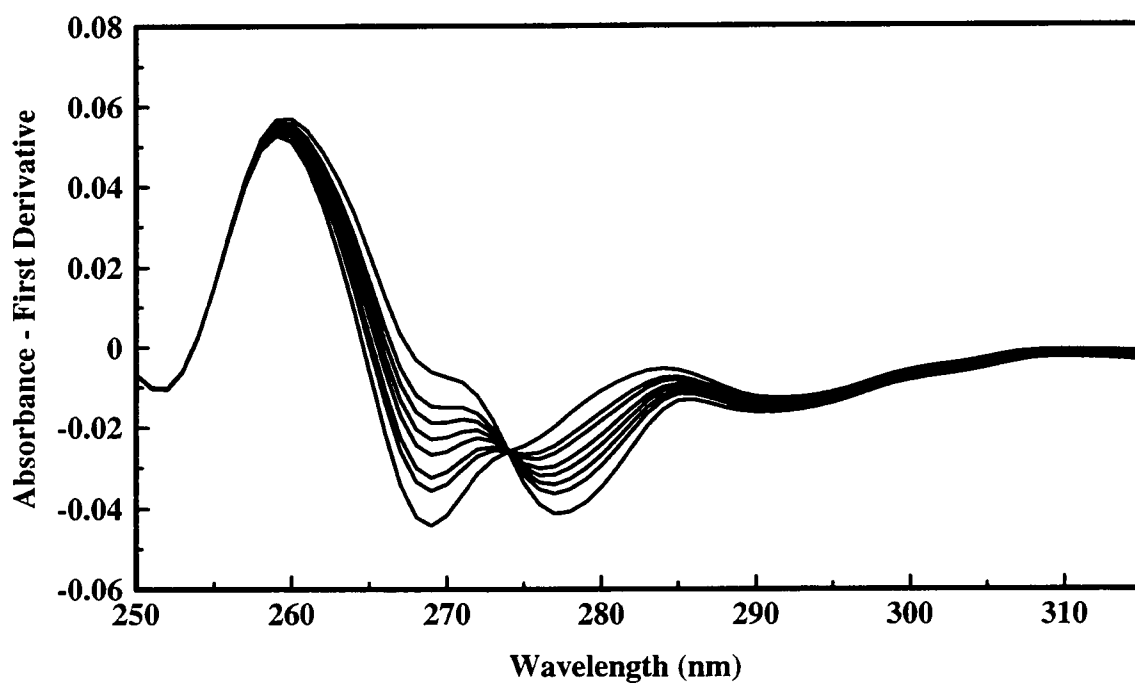


Figure 6.22 PLS analysis of $\hat{t}_1$: The original spectra are regenerated after retaining only one principal component in the PLS model. In comparison with the PCA-regenerated UV spectra in Figure 6.20, an excellent fit is obtained by regression against the NIR spectra.

instrumentation that provides high signal-to-noise ratioed data and robust fiber-optics have made possible such measurements in the UV region. The multivariate methods of PLS provided qualitative and quantitative information about spectral signatures of individual chemical species and resolved overlapping peaks in the UV region. Thus, this study has demonstrated feasibility of in-line predictions of additives using UV spectroscopy; and has shown the UV region to be a viable alternative for trace level additive monitoring.

The concept of correlation spectroscopy has been introduced by multivariate regression of NIR and UV spectra and successfully used to interpret overlapped spectral features in the UV region. The absorbance peak pertaining to the electronic transitions of the HALS additive in the UV region could be correlated directly, using one PLS factor, to the N—H stretch wavelength region in the NIR region. The residual information, which was unexplained after regression against the NIR spectra, was attributed to the presence of constant levels of a second additive in the PP resin. This approach has potential application in interpretation and assignment of unknown spectral peaks to specific chemical moieties. Thus, knowledge of spectral information in one region of the electromagnetic spectrum can be used to provide qualitative feedback about another wavelength region. Another potential application is in instrument standardization during optical multiplexing, which involves process monitoring with several analyzers that provide simultaneous spectral information from different regions of the electromagnetic spectrum.

6.2 ERUCAMIDES IN EVA COPOLYMERS

6.2.1 Introduction

Thermoplastic processing of polymeric materials is carried out at temperatures above their melting point. In case of EVA copolymers, typical processing temperatures are about 200 °C. As was discussed in earlier chapters, these copolymers have a wide range of melt viscosities, depending on their macromolecular structures. For high viscosity EVA copolymers, melt processing is usually carried out under pressure. The resulting shear leads to dissipation of mechanical energy. In particular, at points of high flow resistance, such as the die head of an extruder, such heat generated due to viscous dissipation can accelerate degradation reactions. Additives, which function as lubricants, are incorporated into EVA polymers with intent to decrease the melt viscosity conditions and to increase the ease of operation.

The most common additive in EVA copolymers is a slip agent or lubricant, called erucamide, which assists in processing operations for EVA melts, such as extrusion. Erucamide is a primary amide of erucic acid, a fatty acid. The chemical structure of the additive is shown in Figure 6.23. This additive is used to lower the melt viscosity of EVA copolymers, and also to prevent molten polymer from adhering to metal surfaces in processing equipment. They are included in EVA resins in very low concentrations, usually in the ppm range. Owing to such low concentrations, their quantification in the NIR region is a challenging task

The objective of this study is to establish feasibility criteria for simultaneous monitoring of erucamide concentration and comonomer content (wt.% VA in EVA

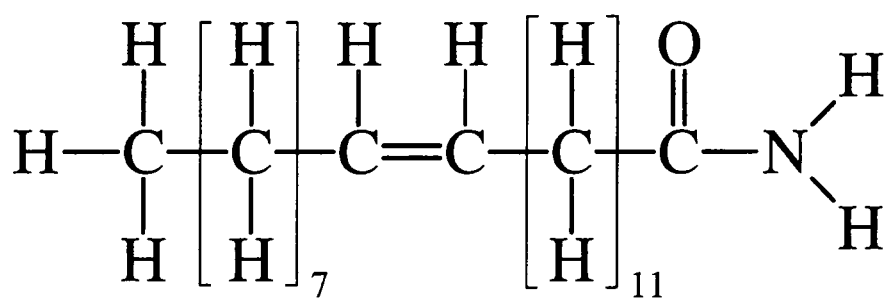


Figure 6.23 Chemical Structure of Erucamide

copolymers) using NIR spectroscopy. One approach taken for this study will use qualitative tools, such as exploratory data analysis tools (HCA and PCA), which are robust wavelength selection methods. These methods are also used for identifying clusters with similar properties in the data. For quantitative analysis, standard multivariate techniques, such as PLS will be used for setting quantitative limits of identification for these samples.

6.2.2 NIR Spectroscopy

Unlike the previous additive system, erucamides are aliphatic compounds that do not have chemical structures amenable for absorption in UV, and strong absorbances due to electronic transitions are absent. Thus, these additives have to be monitored in the NIR region, and problems have to be addressed relating to low absorbances in the NIR region.

As in the previous case studies, the Analect® FT-NIR analyzer was used for measurements in the NIR region. Because of such low concentrations, the entire pathlength of the flow cell of 9.5 mm was utilized for these experiments. The background spectrum was averaged over 256 scans to improve signal-to-noise ratio. Five replicate spectra were taken of the EVA resins with varying erucamide concentrations; each spectrum was averaged over 128 scans.

Table 6.3 shows the sample sets available for quantitative analysis. There are two groups of samples, which are described below:

Table 6.3: Concentration of erucamides in sample sets of EVA resin

The primary analysis for erucamide content was available only for samples in Set 1.

Sample Code	VA Content (wt.% VA)	Erucamide Content (ppm)
Set11	12.04	0
Set12	12.04	182
Set13	12.04	363
Set14	12.04	557
Set15	12.04	729
Set16	12.04	922
Set17	12.04	1114
Set18	12.04	1705
Set19	12.04	2295
Set21	18.06	0
Set22	18.06	250
Set23	18.06	500
Set24	18.06	1000
Set25	18.06	2000

(1) Set 1 consists of EVA samples with 12.04 wt.% VA in the base resin. Erucamides in the concentration range of 0 ppm to 2295 ppm were incorporated into the EVA copolymer. Of the nine samples in Set 1, only five samples (I.D. # 1, 3, 5, 7, 9) were originally made available by the manufacturer. The remaining samples were physically blended from the original samples. While blending, there were concerns with regard to homogenization during the actual blend process of solid pellets, and also, during melt formation in the extruder. The EVA samples did not differ much in their pellet sizes, thus, homogenization was not a problem during physical blending. Also, because the base EVA resins have more or less similar properties of melting temperatures and diffusion, a physical blend of two or more EVA copolymers with varying erucamide concentrations would melt homogeneously inside the extruder.

(2) Set 2 consists of EVA samples with 18.06 wt.% VA in the base resin. Five samples of erucamides were available in the concentration range of 0 ppm to 2500 ppm. These values were only target concentrations, and the samples were not used for quantitative analysis. However, these samples served as an excellent, secondary set of samples for qualitative, cluster analysis.

In addition to these samples, a concentrate sample with 7.25 wt.% erucamide was utilized for diagnostic purposes. This sample enabled identification of absorbance peaks associated with the presence of erucamide in the copolymer.

6.2.3 Results and Discussion

Figure 6.24 shows an overlaid plot of NIR absorbance spectra for two samples of

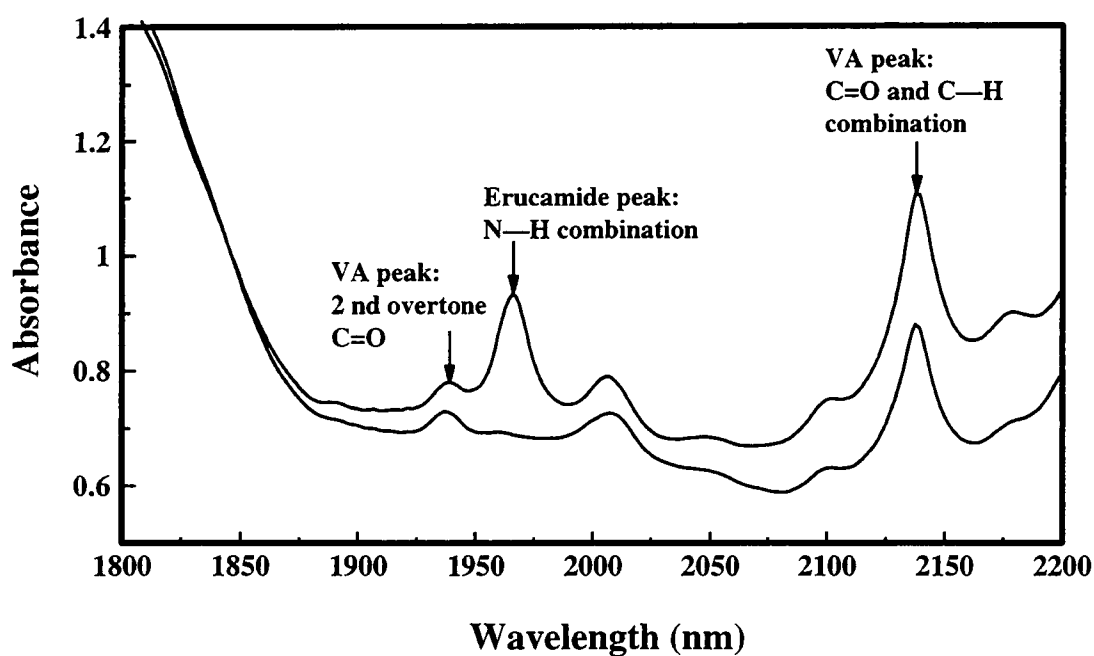


Figure 6.24 Overlaid absorbance plot of EVA samples with varying erucamide concentrations. The figure illustrates absorption spectra in the NIR wavelength region of 1,800-2,200 nm. The absorbance peak at 1,965 nm is attributed to N—H combination vibrational mode in erucamide; the absorbance band around 1,935 nm is tentatively assigned to the 2nd overtone vibrations of carbonyl group in VA; and an absorbance between 2,040-2,160 nm is attributed to a combination band of C=O and C—H stretches in VA.

EVA. One sample was pure EVA with 12 wt.% VA and no erucamide; and the second sample was the concentrate with 12 wt.% VA and 7.25 wt.% erucamide. A strong absorbance band is identified at 1,965 nm for erucamide, which is tentatively assigned to a combination of the fundamental asymmetric N—H stretching vibration at 2,820 nm and the N—H deformation band at 6,400 nm [22]. Because of a large optical pathlength, the C—H stretch first overtone doublet in 1,680-1,760 nm shows very high absorbances (> 3), and cannot be used to quantify VA. The combination band of VA in the wavelength region of 2,020-2,160 nm is an obvious choice for VA quantification. However, there is a third wavelength region of interest at around 1,935 nm, immediately to the left of the erucamide peak. The absorbance peak in this wavelength region is tentatively assigned to a weak, second overtone of carbonyl (C=O) band from VA.

Figure 6.25 shows an overlaid plot of the first derivative absorbance spectra of EVA samples with varying erucamide concentrations. The proximity of two peaks, due to absorbance of erucamide and VA, leads to overlapping effects. Such effects are amplified in the first derivative plot, where the left shoulder of the erucamide peak shows different slope due to the presence of VA in a neighboring region. Thus, depending on the relative concentration of VA and erucamide, one or both peaks can show variations in the presence of the other.

This problem necessitated some form of robust analysis technique, preferably classification methods for identifying these individual moieties. Such preliminary classification methods help identify clusters in data, which can then be used for developing quantitative calibration models. The exploratory data analysis methods

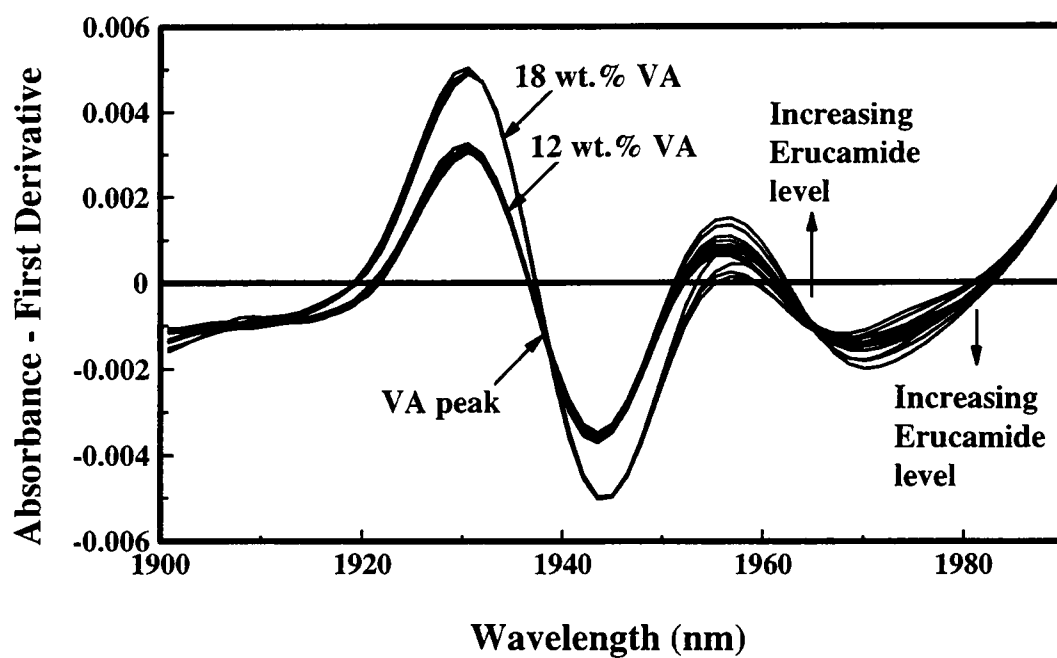


Figure 6.25 Overlaid plot of absorbance-first derivative for EVA samples with varying erucamide content. The proximity of the two peaks of VA (carbonyl second overtone band) at 1,935 nm and erucamide (N—H combination band) at 1,965 nm leads to peak overlap. In this plot, the left shoulder of the erucamide peak exhibits a change in slope due to the neighboring VA peak.

detailed in Chapter 2, such as HCA and PCA will be used in the following section for qualitative analysis.

6.2.3.1 HCA Analysis

Cluster analysis [38,39,111] is performed using HCA on mean-centered data. Five replicate spectra of each sample from the two groups, (as shown in Table 6.3), are used for analysis. Sample categorization is done using the nearest neighbor clustering technique. Computations, involving formation of links and branch lengths, were carried out on MATLAB environment using the Chemometrics PLS Toolbox, ver. 1.5.1 [112] and the commercial software of Pirouette [41].

Figure 6.26 shows a pictorial representation of sample clusters in the EVA samples in the form of a dendrogram. It is observed that the tree splits the EVA sample sets into two dominant clusters, which are based on VA content. As was mentioned in Chapter 2, the branch lengths are relative determinants of the similarity values between the samples. Therefore, the longest branches show that samples, which split according to VA content, i.e. differ most from each other. Within each sample cluster, there are sub-clusters which further classify samples based on their erucamide concentrations. In the figure, the sample codes correspond to the sample identities tabulated in Table 6.3. For sample set 1, it is observed that these sub-clusters identify samples with concentrations < 500 ppm, between 500-1200 ppm, and > 1200 ppm. Formation of such sub-clusters is dependent on the actual concentration distribution of erucamide samples. In the far left region of the dendrogram, the tree splits into leaves, which are the shortest

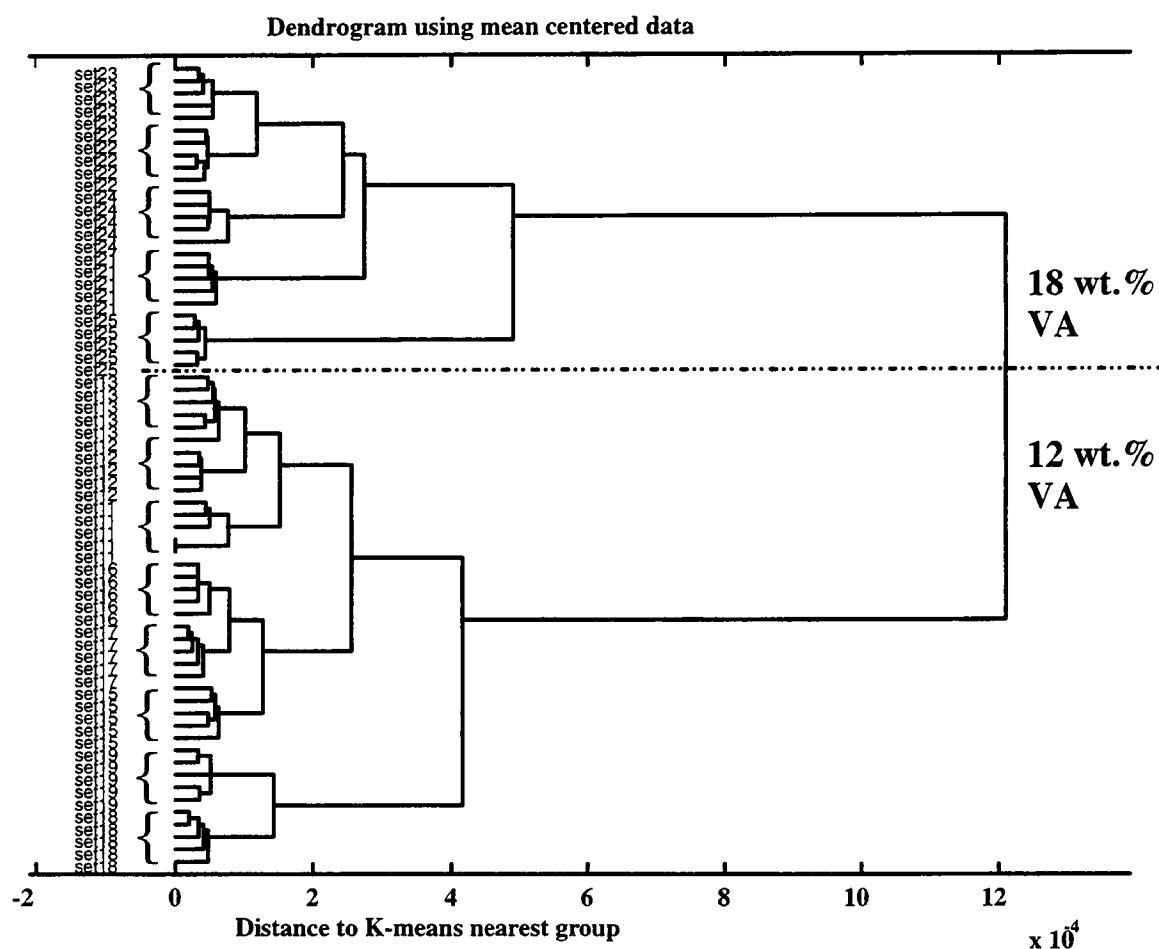


Figure 6.26 Dendrogram for erucamide sample sets. This figure is a pictorial representation of the inherent sample clusters in the spectral data. These clusters are formed on the basis of similarity values, or a relative measure of the Euclidean distances, between the samples. According to this figure, two distinct clusters pertaining to varying VA concentration are formed. The sample codes correspond to the sample identities tabulated in Table 6.3.

branches and represent spectra for the same sample. If the spectra were perfectly identical, the leaf length would be zero, but that is rarely the case because of random experimental noise in the spectra. (Set11 has two more or less identical spectra which show a leaf length close to zero.)

Based on HCA analysis and the information obtained from the dendrogram, quantitative models using multivariate analysis can be developed for (a) samples *within* a single cluster, and for (b) samples from different clusters. In the latter case, a unified model can be developed only if a uniform distribution of samples from all clusters is available for calibration. In the current example, calibration models can be developed for erucamide content by using samples *within* any single cluster (which have same VA content). However, such models cannot be universally applied for samples with a different VA concentration (within a different cluster), unless samples from other clusters have equivalent representation during calibration. Thus, HCA analysis provides a qualitative framework for choice of calibration samples. In addition, this technique can be used for identifying outlier spectra for a given sample, and also outlier samples.

Another exploratory analysis which provides valuable qualitative information is PCA. A PCA analysis provides extensive information about inherent sample clusters in the data in the form of loadings and scores plots. Figure 6.27 shows the loadings plot from a PCA analysis. For this analysis, two principal components were required to explain about 97.5% variance in the absorbance data. From a comparison of the loadings plot with the first derivative plot, as shown in Fig. 6.25, it is noted that the first

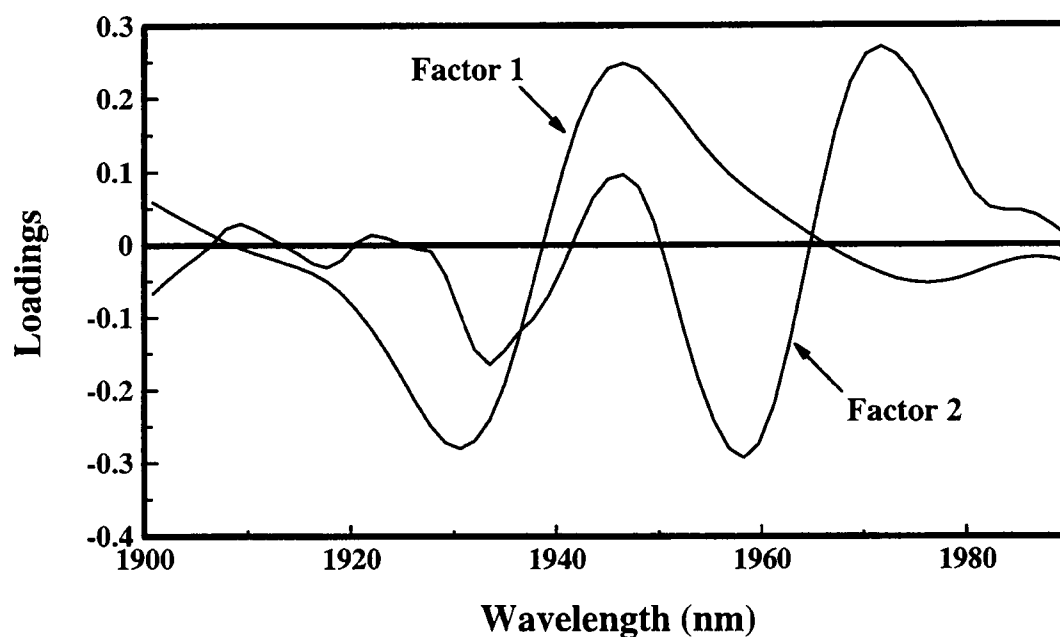


Figure 6.27 Loadings plot for two principal components from a PCA analysis. In comparison with the first-derivative plot of Fig. 6.25, it is observed that the first loading explains information about VA content. The second principal component explains maximum information pertaining to erucamide content.

principal component explains variance related to VA content, while the second principal component principally contains information about erucamide content.

The score vectors for the first few principal components reflect the sample clusters inherent in the data. Figures 6.28 illustrates a 3-dimensional plot of the first three score vectors. An analogy can be drawn with HCA analysis in the interpretation of the results obtained from scores analysis. Two distinct clusters are seen in the scores plot, which identify samples with varying VA content. Figure 6.29 presents the same information in a different azimuthal orientation. Within each cluster, samples with *similar* erucamide content form smaller clusters, which can be used to identify spectral outliers, if any.

In the following section, a classification methodology, namely KNN analysis will be used to classify EVA samples with varying erucamide contents into different groups.

6.2.3.2 Classification using KNN Analysis

Classification techniques aim to categorize a large set of samples into different groups based on their similarity values. These techniques are based on a calibration-prediction type of approach; the objective of such an approach is to assign an unknown sample to a specified class variable. This assignation is achieved quantitatively by comparing their Euclidean distances to other samples. To elucidate this technique, the two sets of erucamide-VA samples were chosen for a KNN analysis.

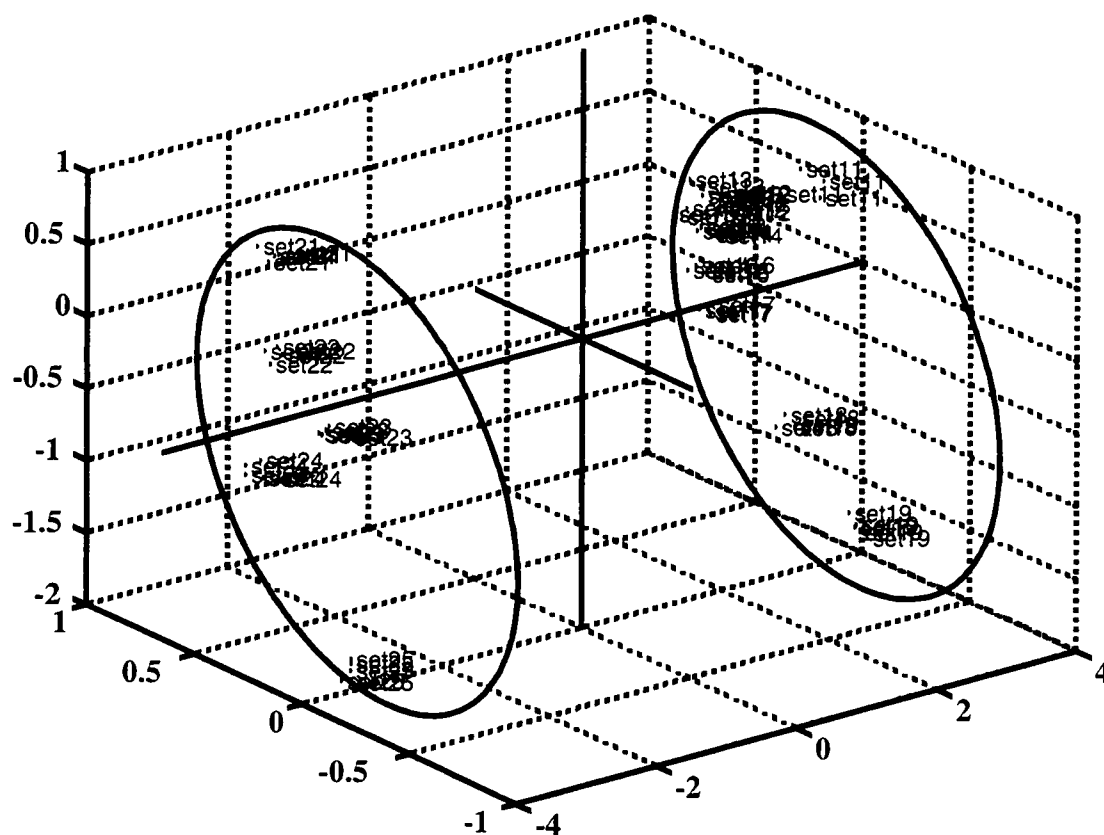


Figure 6.28 Plot illustrating the scores plots for the first three principal components. This figure helps in the identification of sample clusters among the erucamide samples. In an analogous manner to HCA, the primary clusters are formed based on VA content. In addition, sub-clusters are formed within each primary cluster based on erucamide content.

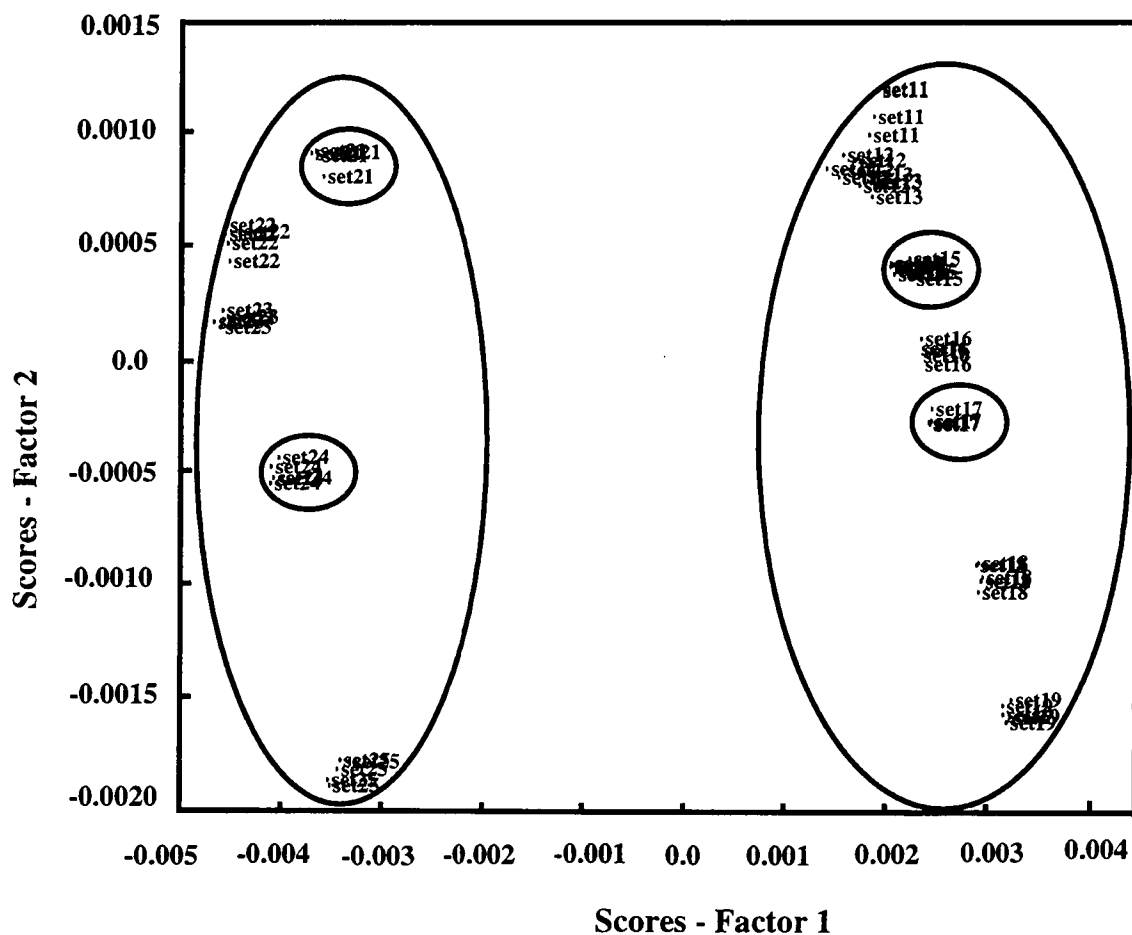


Figure 6.29 Plot illustrating the scores plots for the first two principal components. This figure helps in the identification of sample clusters among the erucamide samples. In an analogous manner to HCA, the primary clusters are formed based on VA content. In addition, sub-clusters are formed within each primary cluster based on erucamide content.

The data matrix has inherently two distinct class variables — (1) erucamide levels and (2) VA content. (A class variable is similar to a dependent variable, with a difference that the values in the class variable vector are only used for identification purposes, and are not used as regressed variables). The choice of the individual groups that would represent a single class variable is often problem-specific. For example, one specific application could be to separate erucamide samples into three classes, say, into samples with additive levels < 500 ppm, between 500-1000 ppm, and > 1000 ppm. In such a case, spectra for all samples with additive levels < 500 ppm (Set11, Set12, and Set13) are placed in the first category, and so on. Once the KNN validation is developed using the training set, any new sample is assigned to one of the three designated groups, after comparing its Euclidean distances from each group.

The KNN modeling is described in this section, with classification for both VA content and erucamide concentrations. In the first case, the erucamide concentration is chosen as a class variable. For this system, it is assumed that each sample is an individual class variable, and that the classification is to be carried out into one of these class values. (For example, an unknown sample with an actual additive value of 800 ppm, say, would be assigned a class value of either 729 ppm or 922 ppm, depending on its proximity to one of the two classes based on relative similarities). Also, for convenience, the actual concentration values are used to represent the individual samples in each of these class variables. It is important to reiterate that the concentration values are never used for actual computations; hence, KNN classification is only a exploratory method and does not involve regression. Three replicate spectra are chosen

for each sample; and all samples are included in the representative training set. Two external spectra for each sample were placed in a matrix to form an independent prediction set.

The LAS methodology for KNN modeling was discussed earlier in Chapter 5, and this method will be used for this study. The maximum number of nearest neighbors was chosen at a K value of 5. In the LAS strategy, all values of K from 1 to 5 are chosen, and a votes matrix is generated for each K level, which contains the estimated class values for each sample. Figure 6.30.a shows a bar graph representation of the estimated class values for each sample in the training set for $K = 1$. The class values are matched with the actual values in the training set, as shown in Table 6.3. Of all samples in the training set, only one sample is wrongly identified, and the associated spectrum is considered as an outlier. This outlier spectrum is attributed to some inhomogeneity during physical blending of the samples. Figure 6.30.b is an alternate representation of the results. The optimum K value is chosen after plotting the misses vector, which contains the erroneous classifications, as shown in Figure 6.31. The K value with a minimum misses value ($K = 1$) is chosen as the optimum. This criterion is analogous to the PRESS criterion used during PLS regression. Because the classes are well separated, a value of K of 1 is obtained from Fig. 6.31.

Another important result from KNN analysis is in the form of the misclassification matrix. This matrix is presented for KNN validation in Table 6.4, and it summarizes the results as a function of classes in the training set. In this matrix, a tabulation is made of how many samples known to be in one class were predicted in

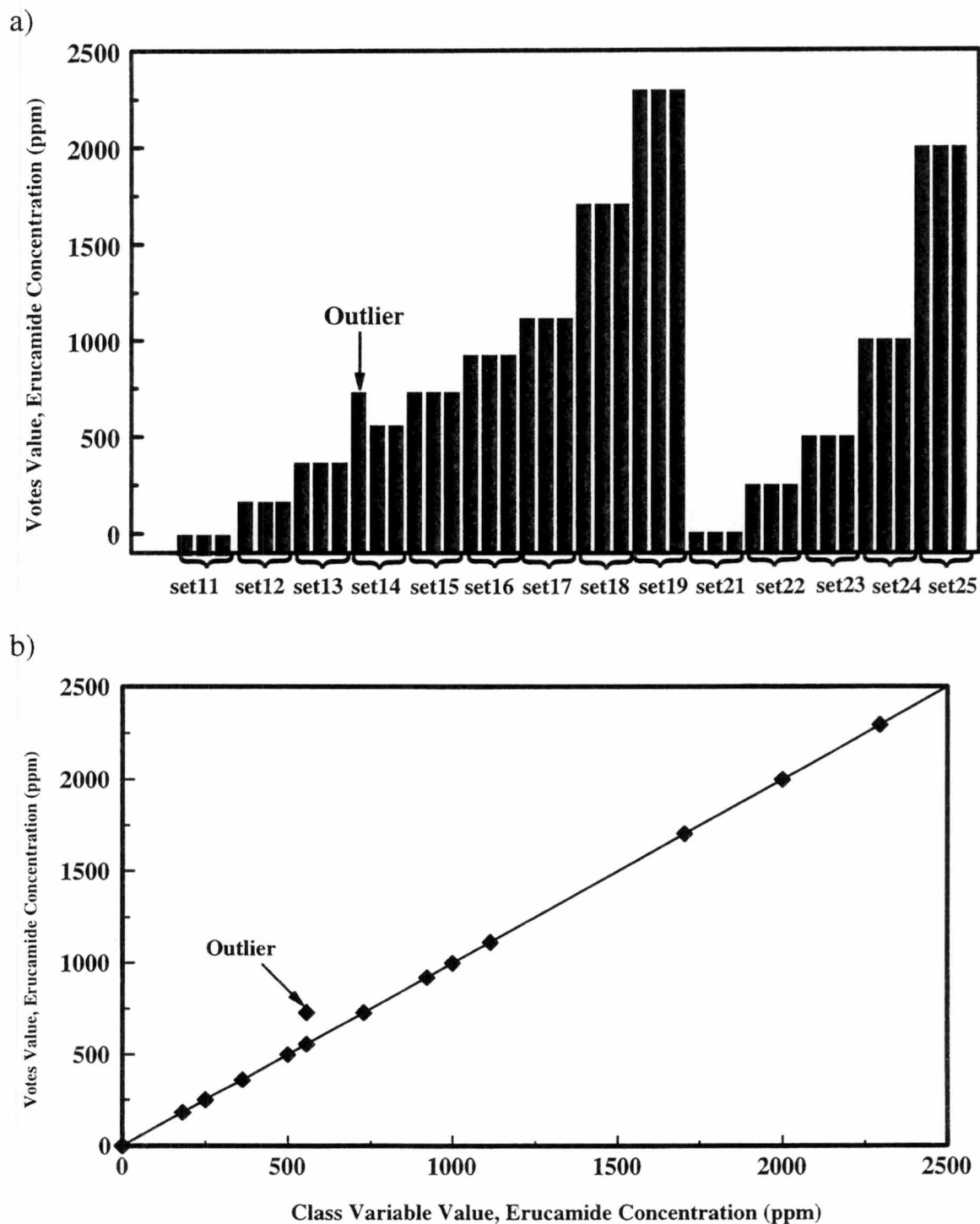


Figure 6.30 Plot showing a) bar representation of the votes matrix and b) equivalent representation of the votes matrix using a scatter plot. The votes matrix contains the estimated class values for each sample. The outlier sample is attributed to inhomogeneity during mixing.

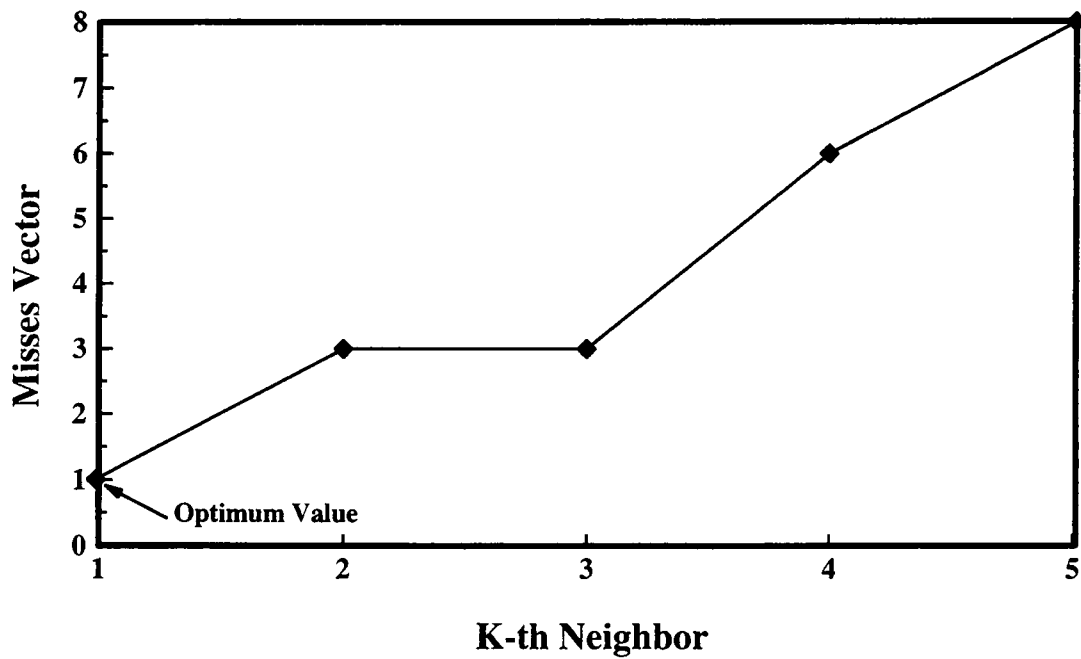


Figure 6.31 Plot of the misses vector against the K -th neighbor. The misses vector contains the erroneous classifications. In the LAS method for KNN modeling, the optimum number of nearest neighbors, or optimum K value, is decided by the minimum value for the misses vector.

Table 6.4: The misclassification matrix for KNN validation

	Predicted Class Value												
	0	182	250	363	500	557	729	922	1000	1114	1705	2000	2295
Measured Class Value	0	6	0	0	0	0	0	0	0	0	0	0	0
	182	0	3	0	0	0	0	0	0	0	0	0	0
	250	0	0	3	0	0	0	0	0	0	0	0	0
	363	0	0	0	3	0	0	0	0	0	0	0	0
	500	0	0	0	0	3	0	0	0	0	0	0	0
	557	0	0	0	0	0	4	1	0	0	0	0	0
	729	0	0	0	0	0	0	2	0	0	0	0	0
	922	0	0	0	0	0	0	0	3	0	0	0	0
	1000	0	0	0	0	0	0	0	0	3	0	0	0
	1114	0	0	0	0	0	0	0	0	0	3	0	0
	1705	0	0	0	0	0	0	0	0	0	0	3	0
	2000	0	0	0	0	0	0	0	0	0	0	0	3
	2295	0	0	0	0	0	0	0	0	0	0	0	3

each of the tested classes. The labels along the rows are the measured class values in the training set, and the labels along the columns are the corresponding predicted classes. The values located along the matrix diagonal indicate samples that were correctly classified; the off-diagonal values represent the number of samples misclassified by the KNN validation procedure. In the training set, three spectra from each sample were included (Because both set 1 and set 2 had a sample with 0 ppm erucamide, there were six spectra with a class value of 0. For all other classes, there were 3 spectra.). From the diagonal values in the table, it is observed that most samples were accurately classified, except one spectrum from the 729 ppm class. This spectrum was falsely classified into the 557 ppm class. Thus, the numerical entries in the classification matrix show a value of 2 ($3 - 1$) for the 729 ppm column, and a value of 4 ($3 + 1$) for the 557 ppm column. Thus, the misclassification matrix can be used to identify outlier spectra.

Once the KNN model is developed, two external spectra from each sample were used to form an independent prediction set with “unknown” classes. The KNN model is used to categorize these samples. Figure 6.32 shows the classifications; most samples are identified correctly to their respective classes. This figure also shows an outlier, where a 729 ppm class sample was falsely identified into a 557 ppm class variable. This spectrum is attributed to inhomogeneity during physical blending of the intermediate samples. Outlier sample spectra are usually removed from quantitative analysis, such as PLS calibration models.

In a similar manner to erucamide classification, VA content is chosen next as a class variable. Again, because of distinct clusters, a $K = 1$ model is sufficient for a KNN

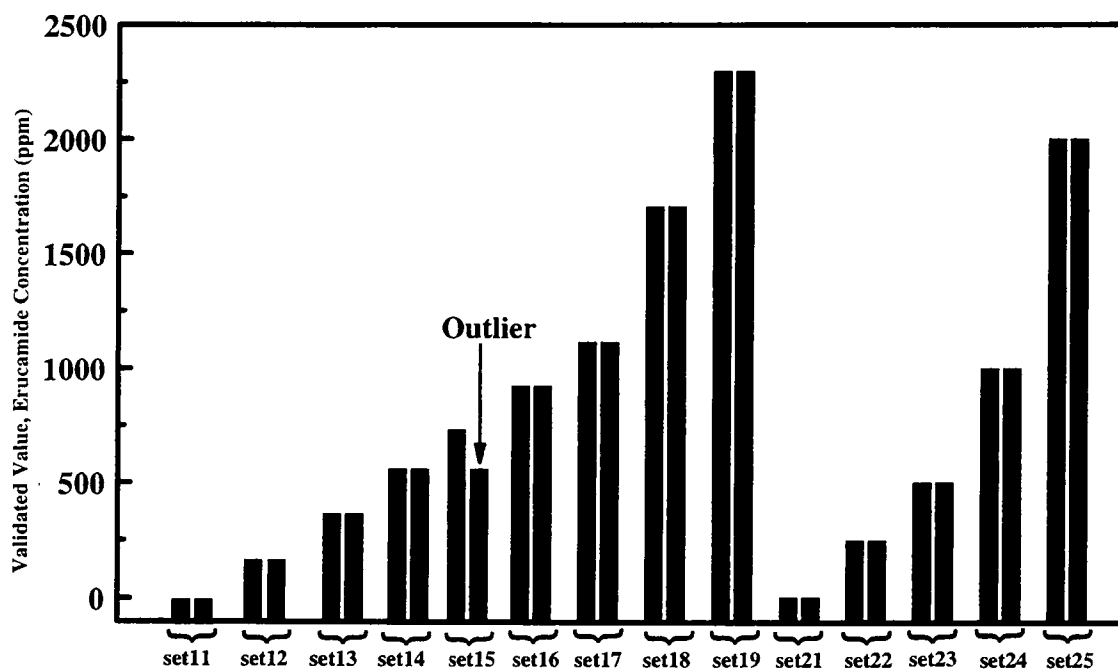


Figure 6.32 Bar representation of the votes values for erucamide samples in the prediction set. The KNN validation model with $K = 1$ was used to categorize these “unknown” samples. All samples, with the exception of one sample, were categorized correctly.

model. Figures 6.33 and 6.34 show the KNN validation and prediction results with VA content as the class variable. The separation for VA content is better than that for erucamide content. Thus, KNN modeling is an elegant algorithm for classification based on sample similarities. There are other classification techniques, such as soft independent modeling for class analogy (SIMCA) which can be used to categorize variables [111]. For the additive system at hand, the KNN method provided excellent results.

6.2.3.3 PLS and RR Analysis

In conjunction with results obtained from qualitative analysis, a calibration model is developed on this additive system with intent to address two issues: (1) quantify erucamides within each sample cluster, specifically for Set 1 EVA samples with 12.04 wt.% VA and (2) to assess feasibility of simultaneous monitoring of VA and erucamide in the copolymer. PLS regression was used to provide definitive quantitative analysis.

The calibration model for erucamide quantification alone (12.04 wt. % VA) was developed on first-derivative spectra in the extended wavelength region of 1,900 nm to 1,990 nm. This wavelength region included the VA peak in addition to the erucamide. Figure 6.35 shows a plot for the predictions for samples in both calibration and prediction sets. The standard error associated with the model are an SEC of 43 ppm for the calibration set, and SEP of 57 ppm for the prediction set. Figure 6.36 shows the regression results from a one-factor model. The first factor accounted for more than

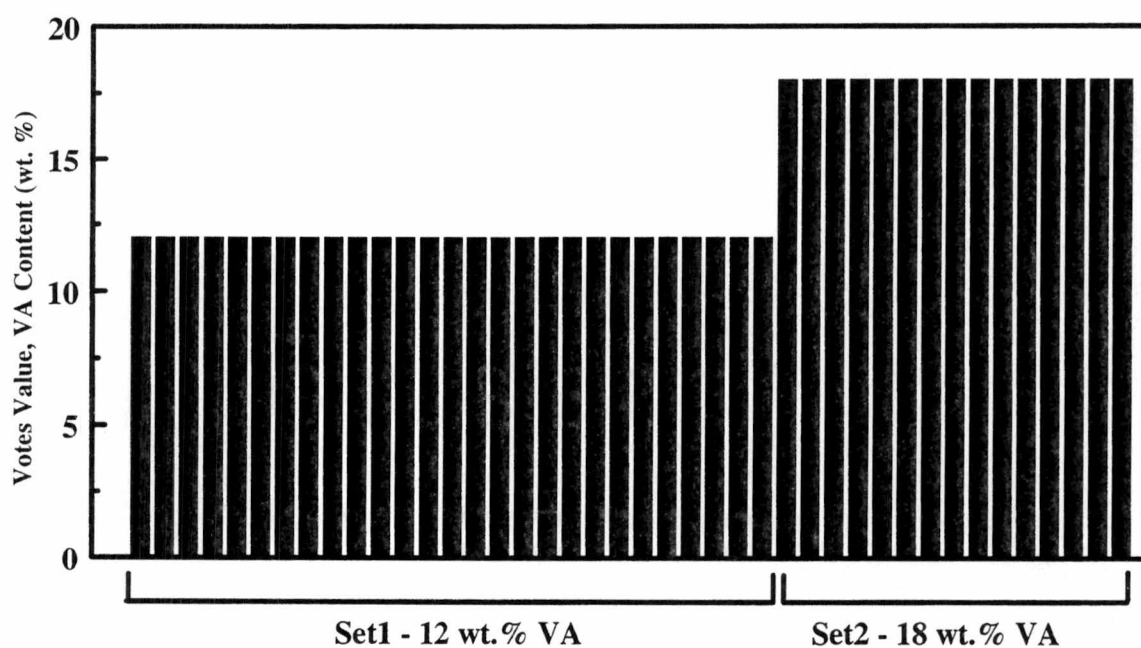


Figure 6.33 Plot showing a bar representation of the votes matrix for the classification of VA content. The votes matrix contains the estimated class values for each sample.

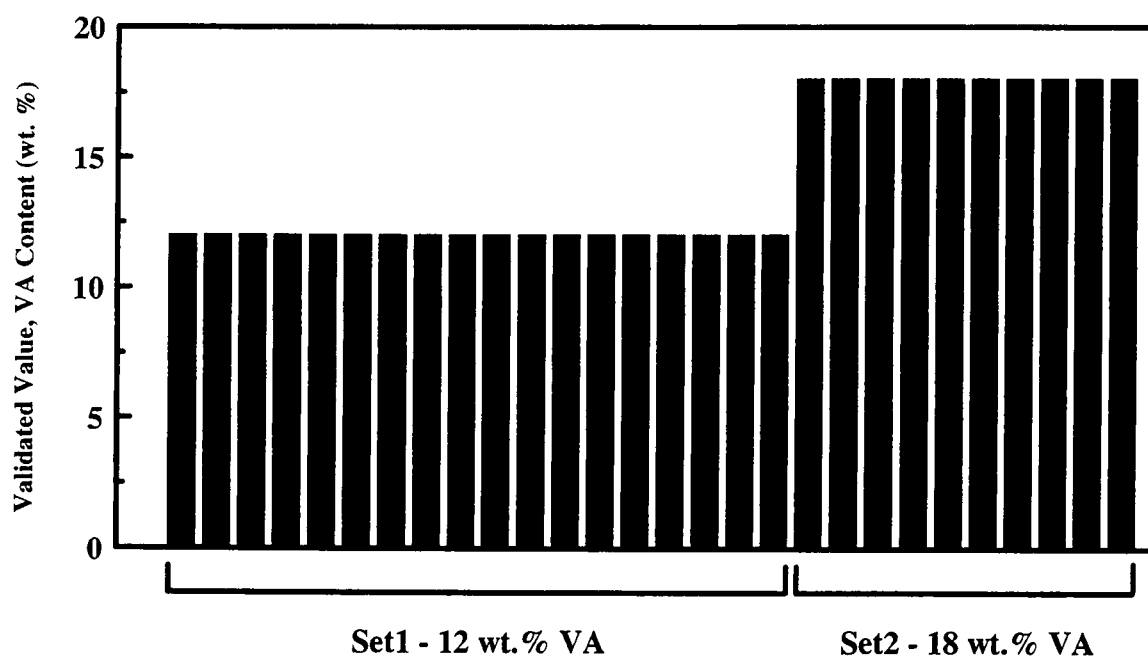


Figure 6.34 Bar representation of the votes values for VA samples in the prediction set. The KNN validation model with $K = 1$ was used to categorize these “unknown” samples. All samples were categorized correctly.

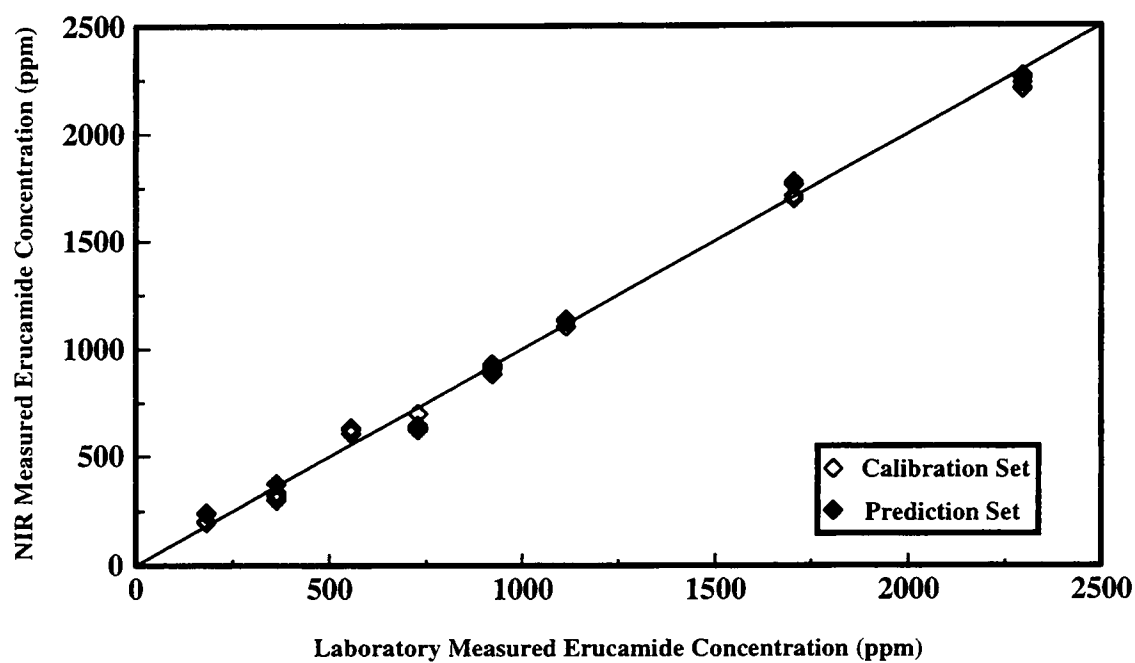


Figure 6.35 PLS regression results for a one-factor model. The SEC value for the calibration model was 43 ppm, and the SEP value was 57 ppm.

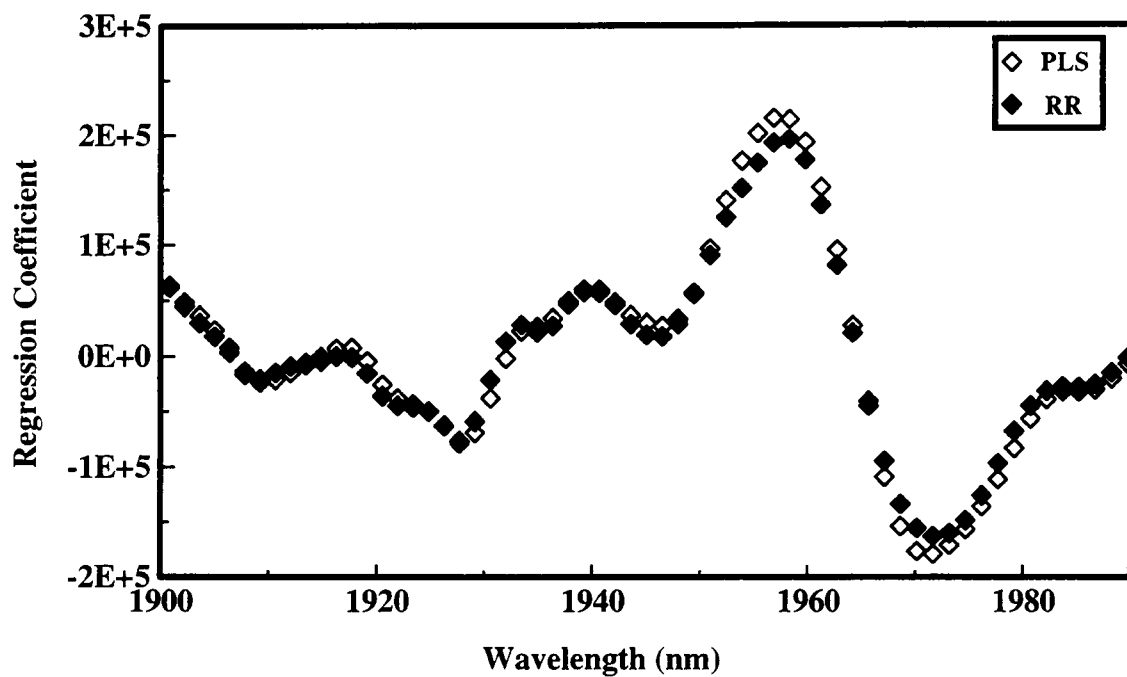


Figure 6.36 Comparative plot for the results obtained from ridge regression (RR) and a one-factor PLS method. Based on the excellent agreement, it is conjectured that a one-factor PLS method is justified.

98% variance in the data. The regression coefficients show most of the information originating in the N—H region of 1,940-1,990 nm. These results were compared with regression coefficients obtained from RR with a ridge estimate parameter of 10^{-6} . These quantitative measurements are a definite improvement over the results obtained by Khettry using a dispersive instrument [7]. Therefore, the above study provided sufficient evidence for successful quantification of additives in the ppm-range, using NIR spectroscopy.

The second issue of simultaneous VA and erucamide monitoring is addressed by developing a calibration model in the wavelength region of 1,900-1,990 nm. Because there are only two different VA concentrations for calibration, only a proof-of-concept study will be presented using qualitative analysis from loadings plots. Again, for erucamide samples of Set 2, only target concentrations were made available; and hence, this study will be considered only as a feasibility study for monitoring erucamides with varying VA content. The actual SEP value will have no true significance in the absence of primary analysis for all samples. The objective of this technique is to also test the ability of PLS calibration to deconvolute overlapping peaks.

During LAS calibration, samples from both clusters were included in the data analysis. The dependent variable during the analysis is erucamide concentration. The PRESS plot for erucamide calibration shows requirement of a two principal component model. It is observed that the first principal component explains about 26.2% variance, while the second principal component explains 73% variance in erucamide content. Figure 6.37 illustrates the loadings plot from PLS calibration, which highlights the first

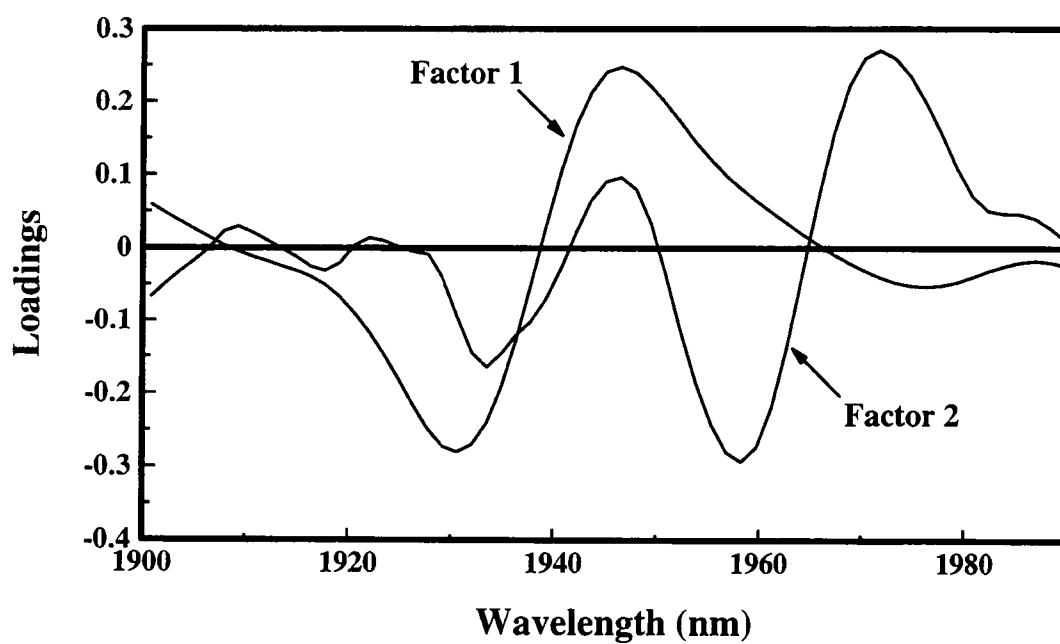


Figure 6.37 Loadings plot for two principal components. The first loading explains information about VA content, while second principal component explains maximum information pertaining to erucamide content. Thus, PLS regression can deconvolute spectral features pertaining to individual chemical moieties.

component as having information about VA content and only some erucamide information. The second principal component contains maximum information about the presence of erucamide. Therefore, PLS regression can separate spectral features pertaining to individual chemical species. In this case, the first factor does contribute some information about erucamide levels but the major part of the information is obtained from the second factor. A similar calibration model can be developed for VA content, provided there are several available clusters with varying VA concentrations. Because the first loading contains most of the information about VA, it is expected that a calibration model developed to estimate VA concentration would require only one principal component for optimal predictions.

Feasibility criteria for simultaneous VA and erucamide monitoring primarily involve a wide and uniform representation of samples from several clusters during calibration. Calibration models using samples from a single cluster are not universally applicable for predictions of samples belonging to other clusters. The above study has demonstrated that simultaneous quantitative predictions can be carried out for VA and erucamide content in EVA copolymers using NIR spectroscopy.

6.2.4 Conclusions

The experimental study described in the previous sections suggests that the NIR region can provide reasonable quantitative estimation for trace-level additives in polymers. The study established a quantitative prediction error limit of 57 ppm for a set of erucamide additives in EVA random copolymers, which was a significant

improvement over earlier results [7]. This improvement is attributed to better instrumentation, with higher signal-to-noise averaging capabilities. In addition, a careful analysis was carried out to identify inherent features in the spectral data in the form of clusters. Such detailed qualitative analysis, which involves identifying clusters and removing outliers, is a prerequisite for developing dependable calibration models. PLS regression models can be developed that can independently estimate VA content and erucamides in EVA copolymers. These aliphatic additives do not show any spectral signature in the UV region of 230-360 nm, and hence, advantage cannot be taken of strong electronic transitions.

The second additive system of hindered amine additives in PP resin was studied in both UV and NIR regions. These chemicals provide strong UV absorptions, and viability was assessed of using UV spectroscopy as an alternative and in conjunction with NIR spectroscopy for in-line monitoring. Correlation spectroscopy was introduced with intent to explore better physical interpretations of spectral features from the combined NIR and UV regions. Recent developments in instrumentation, such as linear array-based detectors and better fiber-optics, makes feasible in-line UV measurements of polymer additives. Quantitative results for both additive systems were validated by more than one multivariate regression technique.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

This research has made significant contributions in the use of fiber-optic spectroscopic techniques as tools for monitoring chemical-polymer processes in-line. The experimental studies conducted in this research have demonstrated that these techniques, in conjunction with powerful multivariate statistical analysis, can be utilized for extracting important information pertaining to (1) estimation of molten polymer rheological properties and (2) polymer additive levels.

In the first category, an elegant methodology was proposed for simultaneous, in-line monitoring of polymer rheological properties, such as melt index and $|\eta^*(\omega)|$, and chemical composition, from their NIR absorption spectra. These measurements were carried out on a random copolymer system of ethylene-vinyl acetate (EVA) during a single-screw extrusion process. Such correlations of rheological properties with absorption spectra utilized differences in orientation and orientation distribution (in the optical measurement volume) of a flowing polymer melt with varying molecular weight parameters. These rheological flow effects on the NIR spectra are lower-order magnitude effects as compared to the strong, primary effects due to chemical composition. Therefore, development of robust calibration models required a detailed analysis using chemometric methods, such as partial least squares regression. In

addition to robust calibration models for quantitative predictions for comonomer content, MI, and $|\eta^*(\omega)|$, these methods provided useful qualitative interpretation. Such physical interpretation was used for identifying the origins of rheological behavior and comonomer concentration in the NIR absorption spectra.

The primary disadvantage in the above work was the use of isotropic light for conducting these studies. Because the rheological effects due to anisotropy in flow are only subtle effects with isotropic NIR radiation, considerable mathematical analysis was required before these results could be applied for real-time measurements [97,98].

(1) One direction for future work could use NIR spectropolarimetry, which involves the use polarized radiation instead of isotropic radiation. It is expected that the use of polarized radiation would capture information, that has *strong, physical dependence* on the molecular weight parameters [113]. This technology can be used for measurements of flow birefringence or dichroism, which are direct indicators of molecular anisotropy. Because this methodology would use the NIR region, simultaneous in-line predictions can be obtained for both composition and polymer rheological properties.

(2) In the current study, the deconvolution of spectral effects due to rheological flow and chemical composition for the EVA random copolymer system was not a trivial task and required considerable multivariate analysis. An alternative system involving homopolymers, such as a system of polyethylenes with varying molecular weight parameters, so that rheological effects are the *only* cause of variation in the absorption spectra.

(3) A better qualitative understanding is required of the phenomena underlying these rheological flow effects. In this research, an attempt was made to understand the physical origin of these effects by identifying spectral origins that showed strong correlations with the rheological properties. Some hypotheses were proposed utilizing this information in conjunction with the theories of polymer science. An additional study involving quantum physics is required that would utilize better spectral assignation techniques, and thereby, a better theoretical understanding for the physical origin.

In the current research, another interesting problem, involving in-line monitoring trace level additive concentrations, was explored; and significant results and useful recommendations were outlined based on experimental studies. The suitability was examined of using fiber-optic NIR spectrometry for the analysis of erucamide additives in EVA copolymers. The study demonstrated that such applications can be enhanced by incorporating exploratory data analysis methods for identifying sample clusters. This study is the first attempt of its kind for applications to trace-level polymeric systems. These cluster analysis methods also help in subsequent development of calibration models. A second additive system, of hindered amine additives in polypropylene, was chosen for examining the feasibility of utilizing the ultraviolet (UV) region for in-line process measurements. A correlation spectroscopy methodology, using multivariate analysis, was introduced, which used combined NIR and UV measurements for spectral deconvolution of overlapping peaks and identification of unknown spectral effects. This approach has potential application in interpretation and assignation of unknown spectral

peaks to specific chemical moieties. Another potential application of this technique is in instrument standardization during optical multiplexing, which involves process monitoring with several analyzers that provide simultaneous spectral information from different regions of the electromagnetic spectrum. In the experimental set up, two sets of fiber-optics can be installed in the flow cell, and spectra can be collected simultaneously in the UV and NIR regions. With such optical multiplexing, based on the sensitivity of the signal in different wavelength regions, UV or NIR spectrometry can be chosen for monitoring a given chemical species. The aforementioned research was by no means an exhaustive study, but led to significant results and conclusions about the applicability of using spectrometric techniques for in-line monitoring.

A definitive system, involving variations in several additive levels can be developed, with intent to explore key concepts of spectral deconvolution, overlap effects, quantitative limits of detection, *et cetera*. The preliminary results obtained in the above studies provide valuable insights into this area of research of additive monitoring. Thus, the UV region offers tremendous potential for such applications. With the availability of improved instrumentation in the form of acousto-optic-tunable-filters (AOTF) and linear-array based detectors, fiber-optic spectrometric applications are more amenable to the research areas of optical spectropolarimetry and ultraviolet monitoring. New instrumentation also lends itself to applications where several processes are monitored simultaneously, and thereby, the concept of optical multiplexing would be more feasible. For these measurements using UV spectroscopy, research is required for instrumentation that can incorporate measurements in

wavelength range of 190-230 nm (which has a wealth of information); and in the development of better fiber-optics. The development of multivariate analysis techniques has to go hand-to-hand with better instrumentation; and this implies research in chemometrics for more robust neural network (NN) and genetic algorithms.

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