

# Infrared Spectroscopy Method Reveals Hydrogen Bonding and Intermolecular Interaction between Components in Polymer Blends

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**ABSTRACT:** An infrared spectroscopy method was devised to uncover evidence of hydrogen bonding and intermolecular interaction between components in solid poly(lactic acid) (PLA) and poly(hydroxyester ether) (PHEE) blends. The method compares Gaussian/Lorentzian deconvoluted infrared spectra of the polymer blends with deconvoluted spectra of weight ratio-equivalent mixtures of the physically separated polymers. Infrared spectra of polymer blends, where hydrogen bonding exists, differ from spectra of physical mixtures of the polymers. Deconvoluting spectra of the blends into their underlying peaks revealed theoretically expected differences between hydrogen-bonded and nonhydrogen bonded components. The findings are supported by differential scanning calorimetry, scanning electron micros-

copy, and mechanical rheometry studies. The new method, differential spectral deconvolution, afforded a quantitative estimate of the extent of hydrogen bonding between PLA and PHEE and could therefore be used to measure the degree of interaction between components in thermoplastic blends. This technique is superior to conventional spectral subtraction and it should be applicable to intimate mixtures or solid solutions in general. © 2005 Wiley Periodicals, Inc. \* J Appl Polym Sci 97: 813–821, 2005

**Key words:** infrared spectroscopy method; differential spectral deconvolution; hydrogen bonds; polymer blends; biopolymers

## INTRODUCTION

Intermolecular interactions and hydrogen bonding in polymers have been of interest for some time. A large body of literature deals with the structure–property relations in polymers and the role played by hydrogen bonds, which are particularly important for mechanical properties of polymers that contain proton donating (NH, OH) and proton accepting (C=O) functional groups.<sup>1–8</sup> A number of studies of polymer blends have been reported using Fourier transform spectroscopy and differential scanning calorimetry to investi-

gate homopolymer miscibility through formation of hydrogen bonding.<sup>9–13</sup>

Fourier transform infrared spectroscopy (FT-IR) is well established as an analytical technique for the study of hydrogen bonding in polymers, since mid-infrared spectral changes in band intensity and frequency shifts are known criteria for the presence and strength of hydrogen bonds.<sup>1–3,14–16</sup> However, when an infrared absorption band is not a single symmetric band but the asymmetric spectral sum of two or more overlapping peaks, the use of spectral changes as criteria for hydrogen bonding or intermolecular interaction is seriously problematic and can be fatally flawed.

Structure–property relations in polymer blends, which are composed of two or more homopolymers to enhance the properties of the individual component polymers, are, nevertheless, being studied by FT-IR spectroscopy using such criteria.<sup>1,13,17,18</sup> This is occurring despite the realization that spectral investigation of hydrogen bonding in polymer blends is complicated not only by multiple overlapping peaks but also by other band distortions such as those that result from the Christiansen effect<sup>15,19</sup> and by optical disper-

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sion effects when the component polymers have significantly different refractive indices.<sup>14,20,21</sup>

In this article a new FT-IR analytical method, here named differential spectral deconvolution, is presented that removes or cancels out these optical artifacts from the observed spectra to reveal evidence of true intermolecular interactions and hydrogen bonding between components in polymer blends.

## EXPERIMENTAL

### Materials

Starch was Pearl cornstarch (Buffalo 3401) purchased from CPC International, Englewood Cliffs, NJ. Poly(lactic acid) (PLA) was obtained from Cargill Dow LLC, Savage, MN. Poly(hydroxy ester ether) (PHEE) was obtained from the DOW Chemical Company, Midland, MI.

### Preparation of polymer blends (melts)

Two test blends were prepared, one containing two polymers, 50% starch and 50% poly(hydroxyester ether) (50/50 Starch/PHEE MELT), and another containing two polymers, 60% poly(lactic acid) and 40% poly(hydroxyester ether) (60/40 PLA/PHEE MELT). These test blends (melts) were formed in a Brabender mixing bowl under the following conditions: Total polymer weight, 50.0 g; mixer temperature, 190°C; mixing screw speed, 50 rpm; and mixing time, 15 min. All polymers were vacuum dried before use. No plasticizers or other chemicals were added. Samples of pure PLA and pure PHEE treated neat under these same conditions in the Brabender mixer formed melts. Starch treated neat under the same conditions did not form a melt.

### Preparation of polymer mixtures (mixes)

Two control mixtures of the pure (neat) polymers were prepared cryogenically to prevent intermolecular interactions. A mixture of 50% starch and 50% PHEE (50/50 Starch/PHEE MIX) and a mixture of 60% PLA and 40% PHEE (60/40 PLA/PHEE MIX) were made from the neat polymers treated as described above. Required weights of the two polymers were intimately mixed and pulverized by ball-milling (Brinkmann Instruments, Inc., Westbury, NY) in sealed stainless-steel vials under liquid nitrogen for several minutes until virtually homogeneous powders were obtained. Pulverization at liquid nitrogen temperature (−196°C) prevented chemical or molecular changes in the previously treated neat polymers that might alter their infrared spectra and appear in the spectrum of the mix.

### Pure (neat) polymers

Samples of the pure polymers, treated neat and pulverized in the same manner as above, were used to obtain pure component spectra.

### Fourier transform infrared (FT-IR) spectrometry

Samples of the test blends, the control mixtures, and the neat polymers were pulverized with KBr and pressed into transparent disks for analysis by FT-IR spectrometry. Special effort was made to minimize the particle size of the powders to prepare homogeneous and perfectly transparent KBr disks. This was necessary to minimize optical dispersion and ensure compliance with the Beer-Lambert law, which requires the KBr disks show homogeneity approaching that of solid solutions. Also, it was necessary to prevent the normal absorption of moisture by KBr during pulverization, to minimize interference from water bands in the spectra.

To meet these requirements, a typical test sample (50 mg) was pulverized repeatedly at liquid nitrogen temperature in a sealed stainless-steel vial containing a stainless-steel ball bearing for a total of 5 min on a Wig-L-Bug amalgamator (Crescent Dental Manufacturing, Lyons, IL). The vial was allowed to warm to room temperature before KBr (50 mg) was added. The KBr/sample mixture was pulverized at liquid nitrogen temperature in the same vial with the same ball bearing on the amalgamator for just 5 s. The vial was again allowed to warm to room temperature before 75 mg of the KBr/sample mixture was removed and discarded. Fresh KBr (125 mg) was added to the vial containing the remaining 25 mg of the KBr/sample mixture with the ball bearing. After shaking this KBr/sample mixture by hand, the ball bearing was removed and the vial was mixed on the amalgamator without the ball bearing for 5 s at room temperature. Of the 150 mg KBr/sample, 25 mg was transferred to a second stainless-steel vial containing 725 mg of fresh KBr and mixed on the amalgamator without a ball bearing for another 5 s at room temperature. Finally, 300 mg of the 750 mg KBr/sample mixture was transferred to a KBr die (Perkin-Elmer Corp. Norwalk, CT) and pressed under vacuum at 110 MPa on a laboratory press (Fred S. Carver, Menominee Falls, WI).

FT-IR spectra were measured on an FTS 6000 spectrometer (Bio-Rad, Digilab Division, Cambridge, CT) equipped with a DTGS detector. Absorbance spectra were acquired at 4 cm<sup>−1</sup> resolution and signal-averaged over 32 scans. Interferograms were Fourier transformed using triangular apodization for optimum linear response. Spectra were baseline corrected, truncated to span only the carbonyl band range (1650–1850 cm<sup>−1</sup>), smoothed by a Savitski-Golay algorithm, and scaled to adjust for small differences in sample weights.

### Deconvolution of FT-IR spectra

Spectral deconvolution was done with a curve-fitting routine provided in GRAMS/32 software (Galactic Industries, Salem, NH). Three or four combination (hybrid) Gaussian/Lorentzian peaks were fitted to the measured carbonyl band, which invariably exhibited pronounced asymmetry with one or two shoulders on each side. The combination peaks, which are symmetric, overlapped and their summation was equal in area and shape to the measured carbonyl band. The number of overlapping peaks was determined by the software and the peaks were automatically located by the GRAMS/32 curve-fitting routine. All peaks were allowed to wander freely in position and to change freely in height and width until the process converged at the best possible fit to the measured carbonyl band.

### Differential spectral deconvolution

The method proposed here is based on the hypothesis that infrared spectra of polymer blends exhibit absorption bands that differ in shape and intensity from the same absorption bands in the neat homopolymers for the following three reasons:

1. The spectrum of a polymer blend is composed of overlapping bands from each of the component polymers and, consequently, the spectral profile of the blend depends on the relative concentrations of each polymer. That is, the particular shape of a given spectral band may result from the simple spectral addition of two or more underlying bands that vary with concentration. Figure 3 shows the carbonyl bands from two neat polymers digitally overlaid. In a blend these two bands overlap and sum to a band whose shape reflects the relative concentrations of each polymer. According to the Beer-Lambert law, the resulting band is the exact sum of the overlapping component bands, unless molecular interactions or hydrogen bonds exist between the polymers.
2. An absorption band that is the sum of overlapping asymmetric bands from two or more different polymers can, and often does, appear as a single asymmetric band skewed to the right or left of the center of the overlapping bands. Therefore, an observed change in the position or intensity of such a composite band from the position or intensity of any one of the component bands does not necessarily indicate interaction or hydrogen bonding between the component polymers, as the observed change might be the mere arithmetic sum of spectrally unchanged absorption bands.
3. When an absorption band is the sum of overlapping asymmetric bands from two or more differ-

ent polymers it can be, and often is, distorted by optical dispersion effects such as the Christiansen effect and differences in the refractive indices of the component polymers. FT-IR spectra of polymer blends sampled as powders (as in KBr disks) are frequently beset with such band distortions, especially when the sample particle size is in the order of the infrared wavelength. Observed changes in band intensities as well as band shifts from a component absorption band center in both positive and negative directions can result purely from optical dispersion effects.

Therefore, by this hypothesis, it is necessary to determine experimentally whether observed spectral changes in polymer blends merely reflect concentration changes and/or optical artifacts or whether they instead arise from true intermolecular interactions and hydrogen bonding between the component polymers.<sup>14</sup>

To accomplish this, the infrared spectrum of the polymer blend (melt) must be deconvoluted and compared with the deconvoluted spectrum of the polymer mixture (mix) prepared cryogenically as described above. As depicted in Figure 1, the control sample (mix), composed of microscopic particles of two polymers in the same concentrations as in the test sample but with the particles physically separated from each other in a pressed KBr disk, is placed in the infrared beam and its spectrum is recorded. As depicted in Figure 1, the test sample (melt) contains the same concentration of each polymer as in the control (mix), but when the two polymers are miscible or compatible, some fraction of the particles will exist as solid solutions of both polymers. In Figure 1 the solid solution particles are shaded gray to illustrate they are combinations of the two homopolymers (black and white). When a pressed KBr disk containing this sample (melt) is placed in the infrared beam and its spectrum is recorded, the observed spectral differences between the melt and the mix will reflect the presence of the solid solution particles in the melt. Figure 2 shows the small differences in the shape and intensity of the carbonyl band between a typical polymer blend melt and its cryogenic mix.

If solid solution particles exist in the sample it is likely that the polymer blend (melt) spectrum will contain evidence of hydrogen bonding and intermolecular interactions. To detect this evidence, both the mix spectrum and the melt spectrum must be deconvoluted into their underlying absorption peaks.

According to the mathematics of Fourier transform theory of spectral band formation,<sup>15</sup> the shape of a single absorption band is, of necessity, symmetric about its peak center. Therefore, barring optical dispersion effects, any shift in the position of the band to higher or lower wavenumber must result from

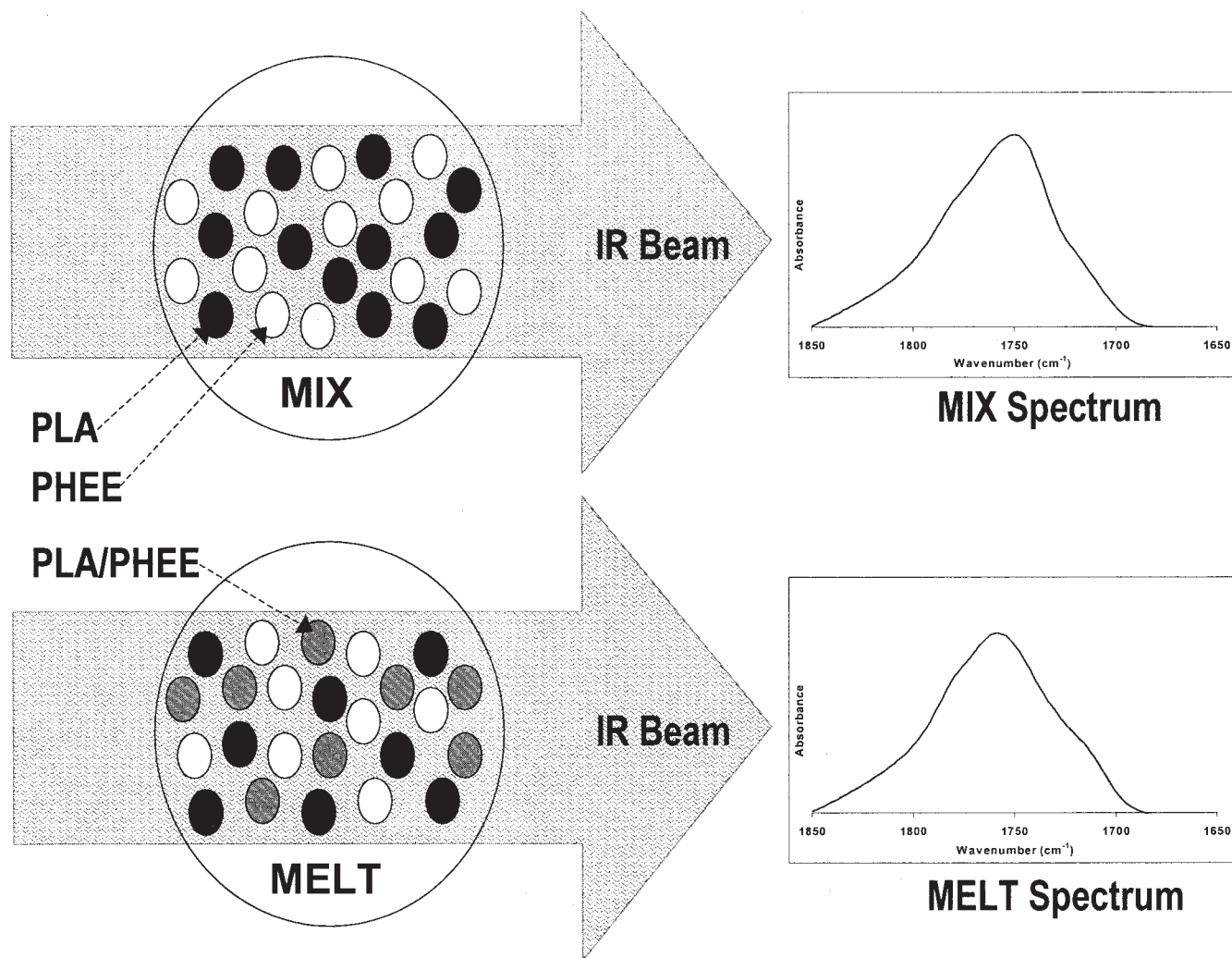


Figure 1 Schematic of sampling technique for differential spectral deconvolution method.

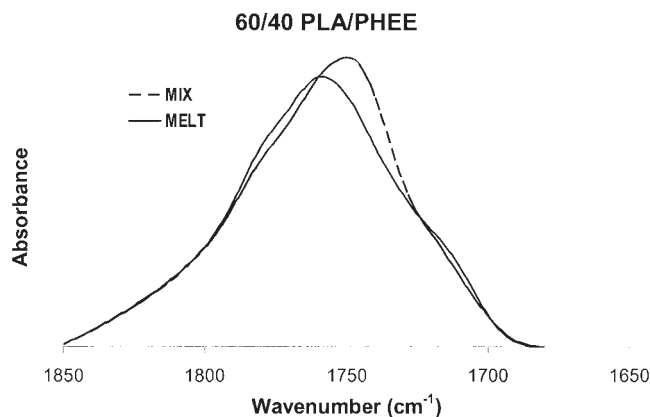


Figure 2 Comparison of blended PLA/PHEE melt spectrum with blended PLA/PHEE mix spectrum.

changes in force constants in the absorbing molecules. Hence, it is the single symmetric bands that contain the most reliable and accurate information about molecular and intermolecular forces. Conveniently, with recent advances in computational chemistry, these underlying symmetric bands can be mathematically extracted from asymmetric bands using available spectral deconvolution software. Note: Hereinafter, a single deconvoluted band will be called a peak to designate it differently from the asymmetric spectrum band from which it is extracted.

When spectral bands such as those in Figure 2 are deconvoluted into their underlying peaks, the ratios of the peak areas in each band represent relative concentrations of different vibrational modes of the carbonyl functional groups in the respective polymer. Therefore, peak area ratios from the deconvoluted polymer melt band can be compared with corresponding peak area ratios from the deconvoluted polymer mix band.

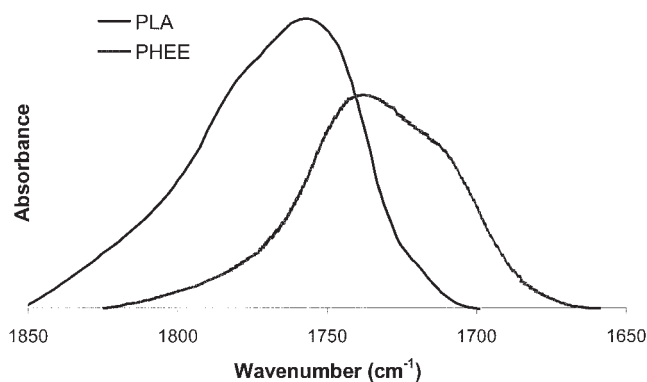


The polymer mix peak ratios serve as controls for the polymer melt peak ratios to cancel out all spectral artifacts and leave only measures of true intermolecular interactions. A series of polymer melt spectra can thus be normalized against mix spectra to remove interference from noninteraction effects and reveal hydrogen bonding or residual interactions even in the presence of overwhelming noninteraction.

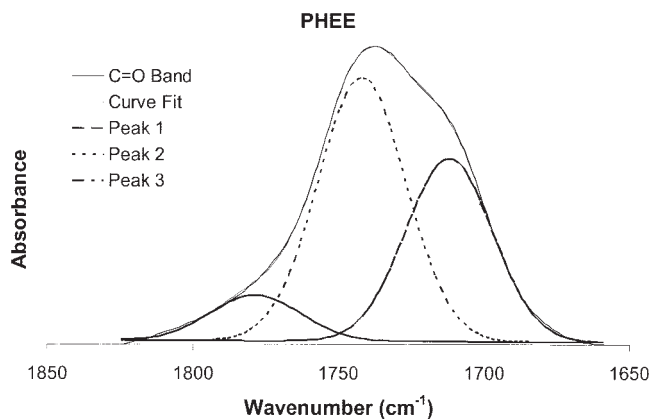
In fact, with multicomponent blends, the system is optimal for estimating interactions and hydrogen bonds by the proposed method when these exist at relatively low levels. This is because the difference between the concentrations of noninteracting polymers in the melt versus the mix is small enough to be neglected in the calculations. In systems where this concentration difference is too large to be neglected, a decidedly more mathematical (chemometric) approach than the one proposed here is required to extract and accurately estimate the interaction component.

## RESULTS AND DISCUSSION

Before becoming embroiled in the details of the results, it is worthwhile to restate a point made earlier. As mentioned in under Experimental, it is known qualitatively that, because of optical dispersion effects, the mere observation of a spectral band shift or intensity change reveals nothing about polymer interaction or hydrogen bonding in blends. Indeed, if it were possible to draw such information directly from spectral bands of blends, an apparent anomaly with theory would exist in the example in Figure 2, which clearly shows the melt carbonyl band shifted to higher wavenumbers than the mix carbonyl band. Since the polymer melt is presumed to contain more hydrogen bonds than the cryogenic polymer mix (Recall, the polymers in the mix were also neat melts prior to the cryogenic treatment.), this shift appears to be in the wrong direction, as hydrogen bonding theory predicts



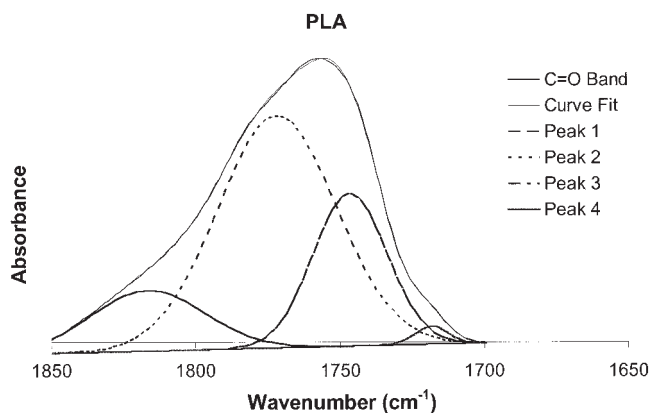
**Figure 3** Digital overlay of carbonyl bands from PLA and PHEE.



**Figure 4** Deconvoluted spectrum of carbonyl band in neat PHEE.

the shift should be to lower, not higher, wavenumbers.<sup>11–17,22</sup> In fact, the observed spectral change in Figure 2 is inexplicable by any molecular interaction interpretation. It will be seen later how this apparent anomaly vanishes when the bands are deconvoluted by this method and the underlying peak relationships become clear.

First, to better understand the strategy employed in the differential spectral deconvolution method, it is instructive to look at deconvolution spectra of the neat polymers used in the Starch/PHEE and PLA/PHEE blends used in this work. Since only carbonyl bands were studied, the spectrum of starch, which is virtually devoid of carbonyl groups, was not deconvoluted. The carbonyl band in PHEE differs in position, shape, and intensity from the carbonyl band in PLA as shown in Figure 3. The deconvoluted carbonyl bands from neat PHEE and neat PLA are shown in Figures 4 and 5. PHEE shows two strong peaks (peak 3 at  $1710\text{ cm}^{-1}$  and peak 2 near  $1740\text{ cm}^{-1}$ ) and one weaker peak (peak 1 near  $1780\text{ cm}^{-1}$ ). These peaks represent three different carbonyl vibrational modes in neat PHEE.



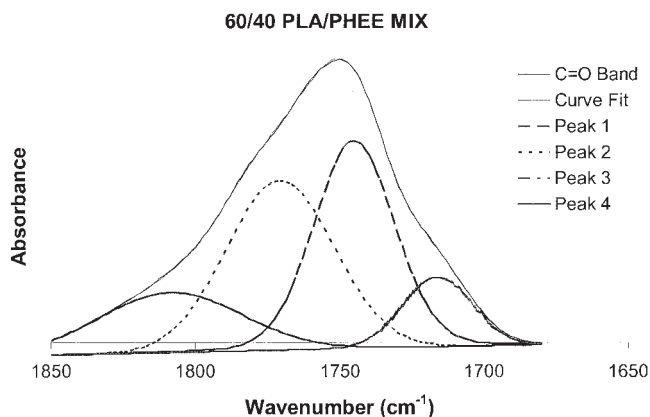
**Figure 5** Deconvoluted spectrum of carbonyl band in neat PLA.

PLA also shows two strong peaks (peak 2 near 1770  $\text{cm}^{-1}$  and peak 3 at 1740  $\text{cm}^{-1}$ ), but PLA also contains two weaker peaks (peak 1 near 1810  $\text{cm}^{-1}$  and peak 4 at 1720  $\text{cm}^{-1}$ ). These peaks represent four different carbonyl vibrational modes in neat PLA.

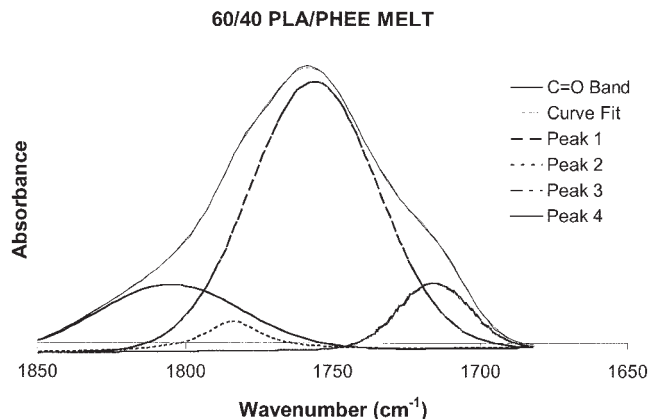
The vibrations that give rise to each peak are distributed symmetrically across a range of frequencies. This range is considerably broader in polymers than in monomers because of the complexity and multiplicity of inter- and intramolecular environments surrounding the carbonyl groups in polymers.<sup>23</sup> The fact that peaks overlap indicates that many frequencies are common to each vibrational mode, as would be expected.

Thus, it should be realized that any change in a peak position or shape means a change has occurred in the distribution of frequencies included in that particular vibration mode. While this may seem to be a trivial fact, it can be important for interpretation of multiple polymer bands in blends where multiple peaks overlap strongly. It compels an objective deconvolution strategy that allows peaks to form and wander at will into whatever distribution pattern best fits the measured spectral band. Since the molecular environment in polymer blends is necessarily complex and undefined, no attempt should be made to force peak parameters to agree closely with literature values or to force the peaks to appear in expected positions.

With polymers, the actual wavenumbers at which peaks appear are not as significant as their positions relative to each other. For example, the fact that PHEE and PLA both show a peak at 1740  $\text{cm}^{-1}$  does not mean the two peaks necessarily arise from the same vibrational mode. However, it can be reasonably assumed that a peak at 1710  $\text{cm}^{-1}$  in PHEE likely arises from more hydrogen bonded carbonyls than those giving rise to the peak near 1740  $\text{cm}^{-1}$  in PHEE. And, it can be assumed the peak at 1720  $\text{cm}^{-1}$  in PLA represents more hydrogen bonded carbonyls than



**Figure 6** Deconvolution spectrum of 60/40 PLA/PHEE blend prepared by cryogenic mixing.



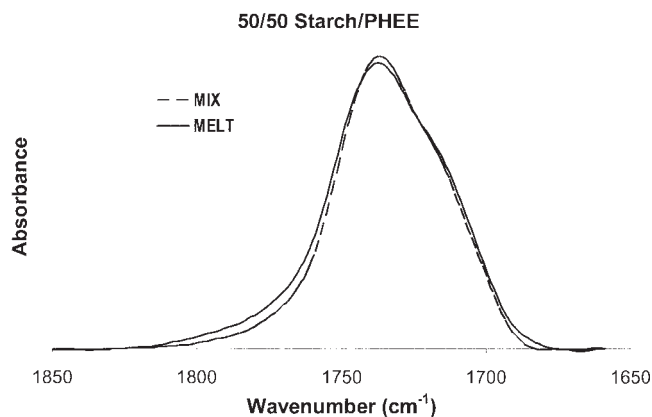
**Figure 7** Deconvolution spectrum of 60/40 PLA/PHEE blend prepared by melting at 190°C.

those represented by the other three peaks at higher wavenumbers in PLA. It is because of this relativity and lack of exact wavenumber correspondence that all carbonyl peaks are labeled in the figures by number (1, 2, 3, and 4) in order of increasing hydrogen bonding or interaction (decreasing wavenumber) and not labeled by the wavenumbers themselves.

Applying the differential spectral deconvolution strategy to the 60/40 PLA/PHEE blend produced Figures 6 and 7. The deconvoluted mix spectrum (Figure 6) gives the ratio of the area of peak 3 to the area of peak 2 as 0.941. The deconvoluted melt spectrum (Figure 7) gives the ratio of the areas of the corresponding peak 3 and peak 2 as 15.12. This suggests the 60/40 PLA/PHEE blend experienced a large increase ( $15.12/0.941 = 16.08$ ) in the second most hydrogen bonded carbonyls relative to the third most hydrogen bonded carbonyls when the PLA and PHEE were melted together. When these peak ratios are used to compute the amount of carbonyls involved in the interaction, the data indicate that 33.8% of the total carbonyls shifted from peak 2 to peak 3 in the melt spectrum. Such a large shift from the cryogenically prepared polymer mixture proves PLA and PHEE are highly compatible in the melt phase.

The direction of the peak shift to lower wavenumbers indicates the compatibility is due, at least in part, to hydrogen bonding between the two polymers. Therefore, the deconvoluted peaks are in complete agreement with established hydrogen bonding theory, even though the observed spectral band for the melt clearly shifted in the opposite direction (Figure 2).

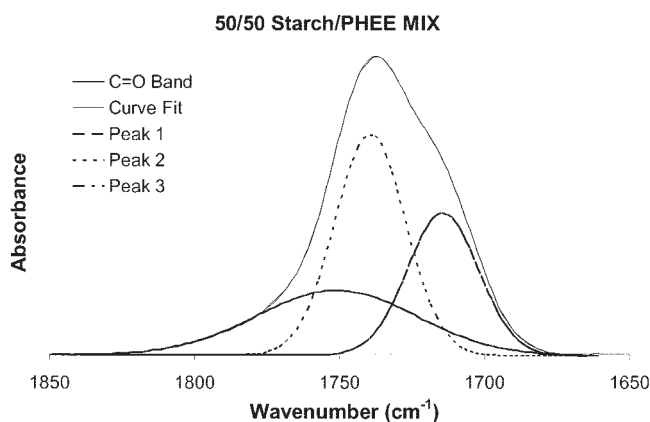
In Figures 6 and 7 it can also be seen from peak 4 and peak 1 that the relative concentrations of the most hydrogen bonded carbonyls and the least hydrogen bonded carbonyls, respectively, did not change appreciably compared to the total carbonyls in the 60/40 PLA/PHEE blend. While it is known that increasing temperature converts bonded carbonyls to free car-



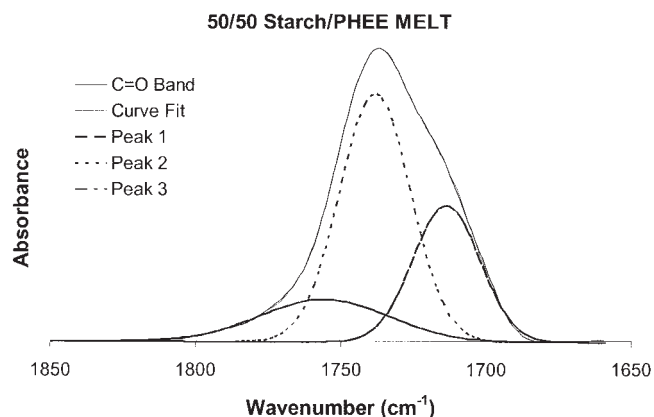
**Figure 8** Comparison of blended Starch/PHEE melt spectrum with blended Starch/PHEE mix spectrum.

bonyls<sup>24</sup> and *vice versa*, interpretation of this interesting result was not attempted here and is left to research in polymer conformation.

Figure 8 shows the slight differences in the shape and intensity of the carbonyl band between the 50/50 Starch/PHEE melt and its cryogenic mix. Applying the differential spectral deconvolution strategy to this Starch/PHEE blend produced Figures 9 and 10. The deconvoluted mix spectrum (Figure 9) gives the ratio of the area of peak 3 to the area of peak 2 as 0.517. The deconvoluted melt spectrum (Figure 10) gives the ratio of the areas of the corresponding peak 3 and peak 2 as 0.646. This suggests the 50/50 Starch/PHEE blend experienced a significant increase ( $0.646/0.517 = 1.25$ ) in the most hydrogen bonded carbonyls relative to the second most hydrogen bonded carbonyls when PHEE was melted with starch. When these peak ratios are used to compute the amount of carbonyls involved in the starch-PHEE interaction, the data indicate that 3.99% of the total carbonyls shifted from peak 2 to peak 3 in the melt spectrum. This shift from the cryogenically prepared starch/polymer mixture proves



**Figure 9** Deconvolution spectrum of 50/50 Starch/PHEE blend prepared by cryogenic mixing.



**Figure 10** Deconvolution spectrum of 50/50 Starch/PHEE blend prepared by melting at 190°C.

starch and PHEE are partially compatible when heated, and it indicates part of this interaction is due to a small but significant amount of hydrogen bond formation.

An estimate of the hydrogen bonding layer in starch-PHEE blends can be calculated from the specific surface area of starch ( $10^3 \text{ m}^2/\text{kg}$ ), the specific volume of PHEE ( $8 \times 10^{-4} \text{ m}^3/\text{kg}$ ) taken from the literature, and the radius of gyration of PHEE ( $10^{-8} \text{ m}$ ) measured by light scattering. Using these figures, the relative volume of the hydrogen bonding layer in a 50/50 Starch/PHEE blend is calculated as approximately 1.0%, which is in good agreement with the 3.99% result obtained above by differential spectral deconvolution: It may indicate that, while 3.99% of the total PHEE carbonyls were changed by heating and forming the melt, approximately 1.0%, or about one-fourth of the change, was caused by hydrogen bonding with starch. However, it is more likely that the two computed figures are within experimental error of each other, showing significant hydrogen bond formation.

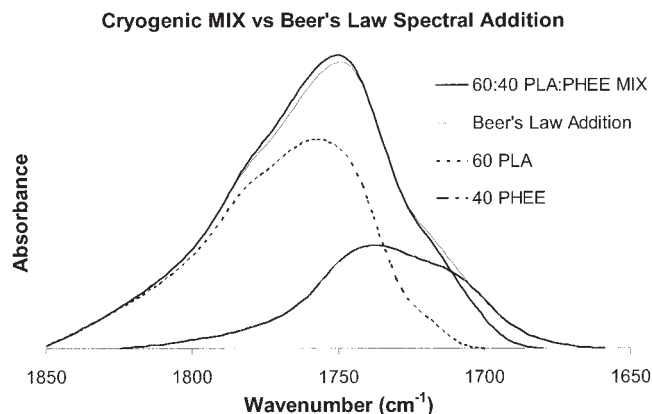
This result was not expected and would not have been evident from direct observation of the difference between the carbonyl bands of the polymer melt and the polymer mix shown in Figure 8. The carbonyl band of the polymer melt did not appear shifted significantly from that of the cryogenically prepared polymer mix. Yet, differential spectra deconvolution revealed the underlying peaks were clearly shifted in the direction expected for increased hydrogen bonding. Further evidence of molecular interaction and hydrogen bonding between the homopolymers in the blends used in this work was obtained by differential scanning calorimetry (DSC). The combination of FT-IR spectra and DSC thermograms provides positive evidence and information about specific molecular interactions and hydrogen bonding between homopolymers in blends, both qualitatively and quantitative-

ly.<sup>13</sup> A strong correlation was seen between FT-IR spectral deconvolution results and DSC measurements (glass transition and crystalline melting temperatures), which suggested hydrogen bonding occurred in cornstarch/PLA/PHEE blends.<sup>9</sup> DSC heating and cooling cycles repeated on PLA/PHEE blends revealed that the blends are phase separated and thus hydrogen bonding can only occur at the interface regions of the domains,<sup>10</sup> which is in very good agreement with the degree of interaction obtained for the 60 : 40 PLA/PHEE blend by the present differential spectral deconvolution method. Preliminary results of subsequent DSC runs and FT-IR spectra indicate the present method makes it possible to monitor increases in the degree of interaction between homopolymers as the number of DSC cycles increases and the phase-separated domains disappear.

Other workers have studied the interactions of PLA, PHEE, and cornstarch and have found evidence that supports the results reported here. Scanning electron microscopy (SEM) of Starch/PHEE blends following elongation to break tests reveal the fracture path includes broken starch granules.<sup>25</sup> This suggests good adhesion of the PHEE matrix to the starch granules, as would be expected if hydrogen bonding occurs at the interface of the two homopolymers. SEM revealed that addition of PHEE increased the adhesion between starch granules and PHEE in blends, presumably by hydrogen bonding.<sup>26</sup>

Mechanical and rheometric properties of various blends of PLA, PHEE, and cornstarch also support the present findings. Good adhesion between starch granules and PHEE was evident, as debonding did not occur in stress-strain tests of Starch/PHEE blends.<sup>27,28</sup> As a result of this adhesion, there was a general increase in tensile strength and Young's modulus as starch content increased. Fair adhesion was also observed in starch-filled PLA/PHEE blends. Similar evidence of interaction was observed in the mechanical properties of PLA/PHEE blends.<sup>26</sup> This behavior was likely the result of increased hydrogen bonding between the starch granules and the PLA/PHEE matrix in composites of these homopolymers.

Infrared spectroscopists have established and accepted the method of spectral subtraction to study the interaction of two homopolymers in blends.<sup>14,29</sup> An interaction spectrum is generated by double subtraction of the spectra of the two neat polymers from the spectrum of the blend using Beer's law. Although this method has become the convention, there is reason to question its accuracy. For example, in a cryogenic mixture of two homopolymer polymers, where there can be no interaction possible, Beer's law predicts that, when the two neat polymer spectra are added together, their sum will be exactly equal to the mixture spectrum. To test this in this work, the spectrum of a cryogenic mixture of neat PLA and neat PHEE (60 : 40)



**Figure 11** Comparison of Beer's law spectral addition with cryogenic mixture spectrum.

was compared with a spectrum obtained by Beer's law addition of the spectrum of neat PLA to the spectrum of neat PHEE. As can be seen in Figure 11, the sum of the two neat polymer spectra and does not exactly match the cryogenic mix spectrum. The cause of this, slight nonlinearity in the infrared spectrometric response, is well known as deviation from Beer's law. Spectral subtraction wrongly assumes linearity and thus no deviation. Therefore, spectral subtraction cannot be expected to be as accurate or reliable as this differential spectral deconvolution method that cancels out deviations from Beer's law.

Attempts to extract interaction spectra from the polymer blends in this work using the conventional subtraction of the two neat polymer spectra from the blend spectrum failed to give the definitive evidence of hydrogen bonding reported here and provided no estimate of the degree of intermolecular interaction revealed by the differential spectral deconvolution method developed in this study.

## CONCLUSIONS

An FT-IR spectroscopy method was devised that revealed evidence of hydrogen bonding and other intermolecular interactions between components of solid blends of PLA and PHEE. The method directly compares hybrid Gaussian/Lorentzian peaks from deconvoluted FT-IR spectra of the polymer blends, prepared as melts, with peaks from similarly deconvoluted spectra of equivalent mixtures of the physically separated polymers prepared cryogenically to prevent interaction. Infrared spectra of melted polymer blends, when hydrogen bonding existed, differed from spectra of physical mixtures of the cryogenically prepared polymers. Thermoplastic blends of PLA and PHEE show spectral differences, which, on first inspection, appear anomalous with hydrogen bonding theory. However, differential deconvolution of the spectra



into their underlying component peaks reveals the spectra are not at all anomalous and do actually show theoretically expected differences between hydrogen-bonded and nonhydrogen bonded components. Differential spectral deconvolution afforded a quantitative approximation of the extent of hydrogen bonding and intermolecular interaction between the polymers. The technique was used to estimate the degree of interaction between PLA and PHEE and between starch and PHEE in thermoplastic blends. This was the first reported direct evidence of hydrogen bond formation in thermoplastic blends of starch and PHEE. The findings are supported by earlier and ongoing DSC, SEM, and mechanical rheometry studies. The method was found to be more definitive and quantitative than conventional spectral subtraction and it should be applicable to intimate mixtures of solid materials in general.

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## References

1. Urban, M. W.; Craver, C. D., Eds. *Structure-Property Relations in Polymers: Spectroscopy and Performance*, Advances in Chemistry Series 236, American Chemical Society: Washington, DC, 1993.
2. Koenig, J. L. *Adv Polym Sci* 1983, 54, 87.
3. Siesler, H. W.; Holland-Moritz, K. *Infrared and Raman Spectroscopy of Polymers*; Marcel Dekker: New York, 1980.
4. Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectroscopy and Its Applications to Polymeric Materials*; Wiley-Interscience: New York, 1982.
5. Schuster, P.; Zundel, G.; Sandorfy, C., Eds. *The Hydrogen Bond*; North-Holland: New York, 1976.
6. Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van-Nostrand Reinhold: New York, 1972.
7. Skrovanek, D. J.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1986, 19, 669.
8. Burkle, K. R. Ph.D. Thesis, University of Berlin, Berlin, Germany, 1988.
9. Cao, X.; Gordon, S. H.; Willett, J. L.; Sessa, D. J. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2001, 42, 623.
10. Cao, X.; Mohamed, A.; Gordon, S. H.; Willett, J. L.; Sessa, D. J. *Proceedings of the 29th North American Thermal Analysis Society Conference*, September 24-26, 2001; p 340.
11. Wang, F. C.; Feve, M.; Lam, T. M.; Pascault, J. J. *Polym Sci B Polym Phys* 1994, 32, 1305.
12. Wang, F. C.; Feve, M.; Lam, T. M.; Pascault, J. J. *Polym Sci B Polym Phys* 1994, 32, 1315.
13. Kuo, S. W.; Huang, C. F.; Chang, F. C. J. *Polym Sci B Polym Phys* 2001, 39, 1348.
14. Koenig, J. L., *Spectroscopy of Polymers*; Elsevier Science: New York, 1999.
15. Griffiths, P. R.; deHaseth, J. A. *Fourier-Transform Infrared Spectroscopy*; Chemical Analysis Series 83; Wiley: New York, 1986.
16. Katime, I.; Parada, L.; Meaurio, E.; Cedsteros, L. *Recent Res Dev Polym Sci* 1997, 1, 91.
17. Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C. *Macromolecules* 1988, 21, 59.
18. Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* 1988, 21, 66.
19. Saperstein, D. D. *J Phys Chem* 1987, 91, 6659.
20. Greenler, R. G.; Rahn, R. R.; Schwartz, J. P. *J Catal* 1971, 23, 42.
21. Zhou, Z.; Choi, B.; Flik, M. I.; Fan, S.; Reif, R. *J Appl Phys* 1994, 76, 2448.
22. Paul, D. R.; Bucknall, C. B., Eds. *Polymer Blends; Volume 1: Formulation*; John Wiley & Sons: New York, 2000.
23. Painter, P. C.; Pehlert, G. J.; Hu, Y.; Coleman, M. M. *Macromolecules* 1999, 32, 2055.
24. Skrovanek, D. J.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1986, 19, 699.
25. Landel, R.F.; Neilsen, L.E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994; ed. 2, p 377.
26. Garlotta, D. V.; Doane, W. M.; Shogren, R. L.; Lawton, J. W.; Willett, J. L. *J Appl Polym Sci* 2003, 88, 1775.
27. St. Lawrence, S.; Willett, J. L.; Carriere, C. J. *ANTEC Proc* 2000, 58, 3640.
28. St. Lawrence, S.; Willett, J. L.; Carriere, C. J. *Polymer* 2001, 42, 5643.
29. Sargent, M.; Koenig, J. L. *Vib Spectrosc* 1991, 2, 21.