
Terahertz spectroscopic characterization of phase separation in polymer blends

1. Introduction

Blends of polymers with differing molecular weight are expected to exhibit separation of phases according to their molecular architecture. Fig. 1 shows IR measurements of two polymers and their 50:50 blend [1]. It can be seen that the absorbance of these polymers scales according to the molecular weight in the higher wavenumber region. IR cannot access the lower frequency region (below 1000 cm^{-1}) but this region is of importance because here the T-ray is sensitive to the resonances of the molecule as a whole, as opposed to just a bond vibration sensed by IR.

The objective of the present investigation is to investigate the behavior of the above materials in terahertz spectral region. Because the interaction of terahertz radiation with a given molecular system is greatly influenced by the characteristic parameters of the molecule such as its molecular weight and vibrational properties, it is expected the terahertz transmission (or equivalently terahertz reflection) will be a function of the molar mass of each species. This hypothesis has been successfully tested on macromolecular systems [2].

In the present study, we have investigated three biodegradable polymers using Terahertz spectrometry. Similar to IR region, THz spectra found clear distinction among the three compositions in the terahertz region. However, unlike IR, THz has reported the presence of many resonance peaks in the lower frequency region that cannot be accessed by IR.

2. Experimental

ARP's terahertz spectrometer system (TeraSpectra©) was used to measure three samples, composed of two polymers, poly(3-hydroxybutyrate) (PHB) and poly(caprolactone) (PCL); both polymers are from Sigma-Aldrich. Two of the samples were pure, PHB 100% and PCL 100%, and the last one is a 50:50 blend of each. The first two polymers have a vast difference in molecular weight; PHB: $M_w = 437000\text{ g/mol}$ and PCL $M_n = 80000\text{ g/mol}$. Due to this, it was expected that their transmittances would be sharply distinct from each

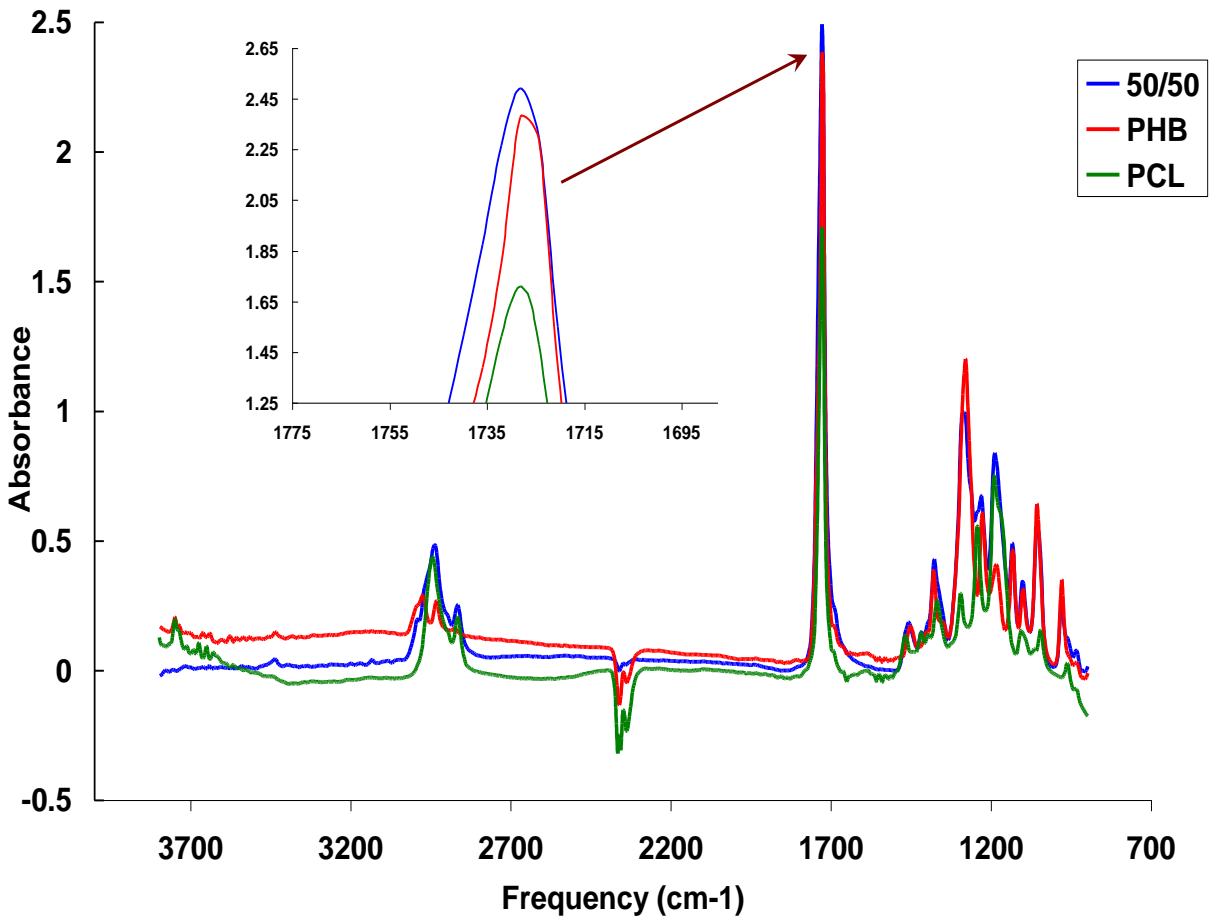


Fig. 1. IR spectra of polymers PHB, PCL, and 50:50 blend generated at Dr. Heinz W. Siesler's Lab [1].

Table 1: Summary of polymer <i>Film</i> sample parameters			
<i>Sample</i>	<i>Thickness (μm)</i>	<i>Sample Weight (g)</i>	<i>Molecular Weight (g/mole)</i>
<i>PCL 100%</i>	5	0.00245	80000
<i>PHB 100%</i>	6	0.00173	437000
<i>50:50</i>	8	0.00326	258500

other; heavier polymer would have a lower transmission. The sample characteristics are summarized in Table 1. Since the last sample consisted of equal parts of each polymer, we were able to estimate the molecular weight by simply calculating the average. The samples configuration, as shown in Fig. 2, were received from HWS's lab [1].

TeraSpectra uses a collimated wide terahertz beam (~1" dia) for uniform exposure of the transmitted beam on the specimen. As shown in Fig. 2, the supplied films were usually less than 1" wide and somewhat of irregular shape. The 100% PCL and 100% PHB samples were more rectangular while the 50:50 blend sample resembling a square. Also the films have irregular creases on their surface presumably due to the transatlantic shipping and handling. As a result, there is significant variation in the effective mass of the portion of the specimens exposed to the beam. This was addressed by normalizing the measured spectra with respect to the sample thickness and its effective mass. The samples were individually measured on a microbalance to determine their weights listed in Table 1.

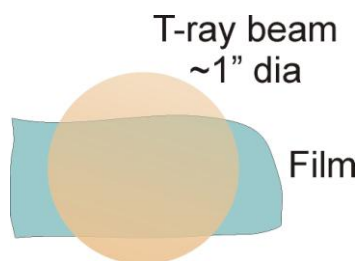


Fig. 2. Sample configuration.

The specimen films were “sandwiched” between two thin Plexiglas sheets that served as a cell for the samples and also kept them fixed during measurements. The cell has 1" dia opening so that the beam interacts only with the film. Additionally, the sample cell was placed on a XYZ stage for fine tuning the film position with respect to the beam. Time-domain spectra for each sample were recorded by the spectrometer front-end (Fig. 3).

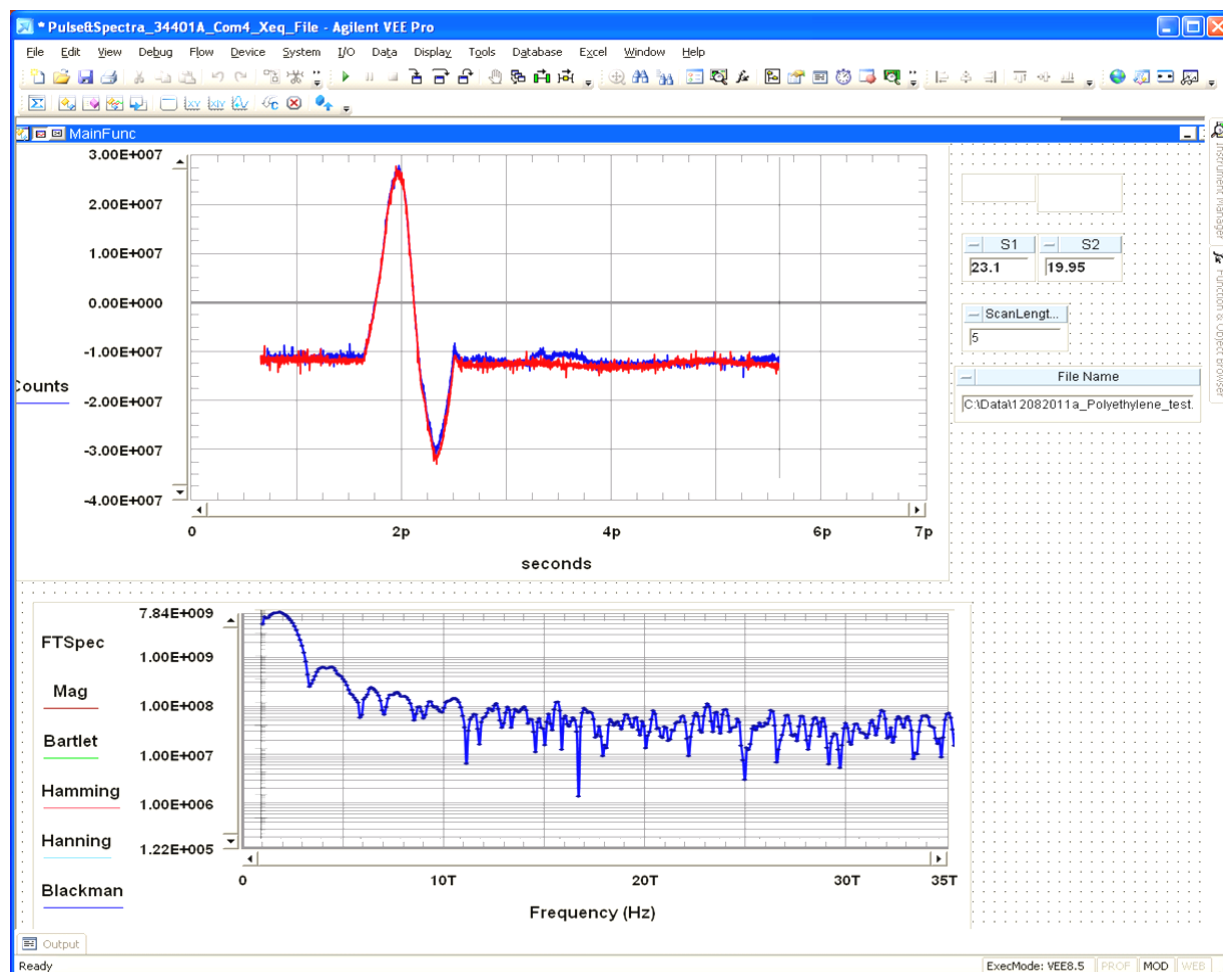


Fig. 3. The data acquisition console (front-end) of TeraSpectra. Interferogram (top) and Fourier transform spectrum (bottom).

3. Results and discussion

Fig. 4 shows the time domain signals (pulse) of three specimens. The pulses were normalized w.r.t. the lowest transmission (PHB 100%) film. As expected, the normalized signals exhibit higher transmission for lower molecular weight and follow an increasing trend with molecular weight. Consequently, their Fourier transform spectra will also exhibit the same trend. This is evident from Fig. 5 where the normalized magnitude is plotted as a function of frequency expressed in cm^{-1} . Contrasting with Fig. 1, it is evident that while IR spectra show only one or two main peaks, THz has reported a number of peaks in the low frequency region; however the order is maintained as predicted by the

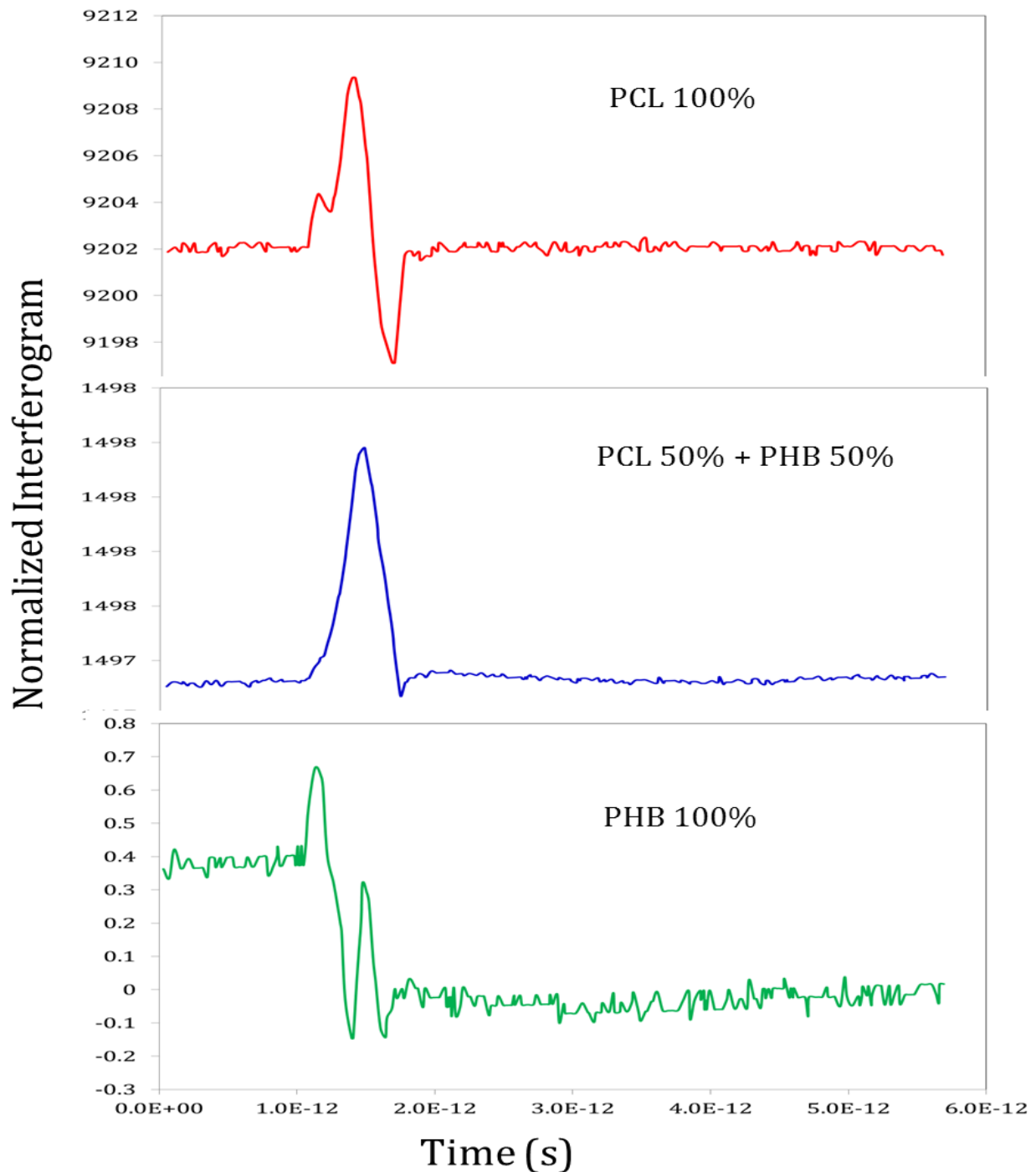


Fig. 4. Representative time domain signals (pulse) of three specimens. The pulses were normalized w.r.t. the lowest transmission (PHB 100%) film. As expected, the normalized signals fall in line according to their molecular weight.

molecular weight dependence. This is most likely a manifestation of the Beer-Lambert's law with the modification that instead of concentration of an analyte, here molecular weight is the variable.

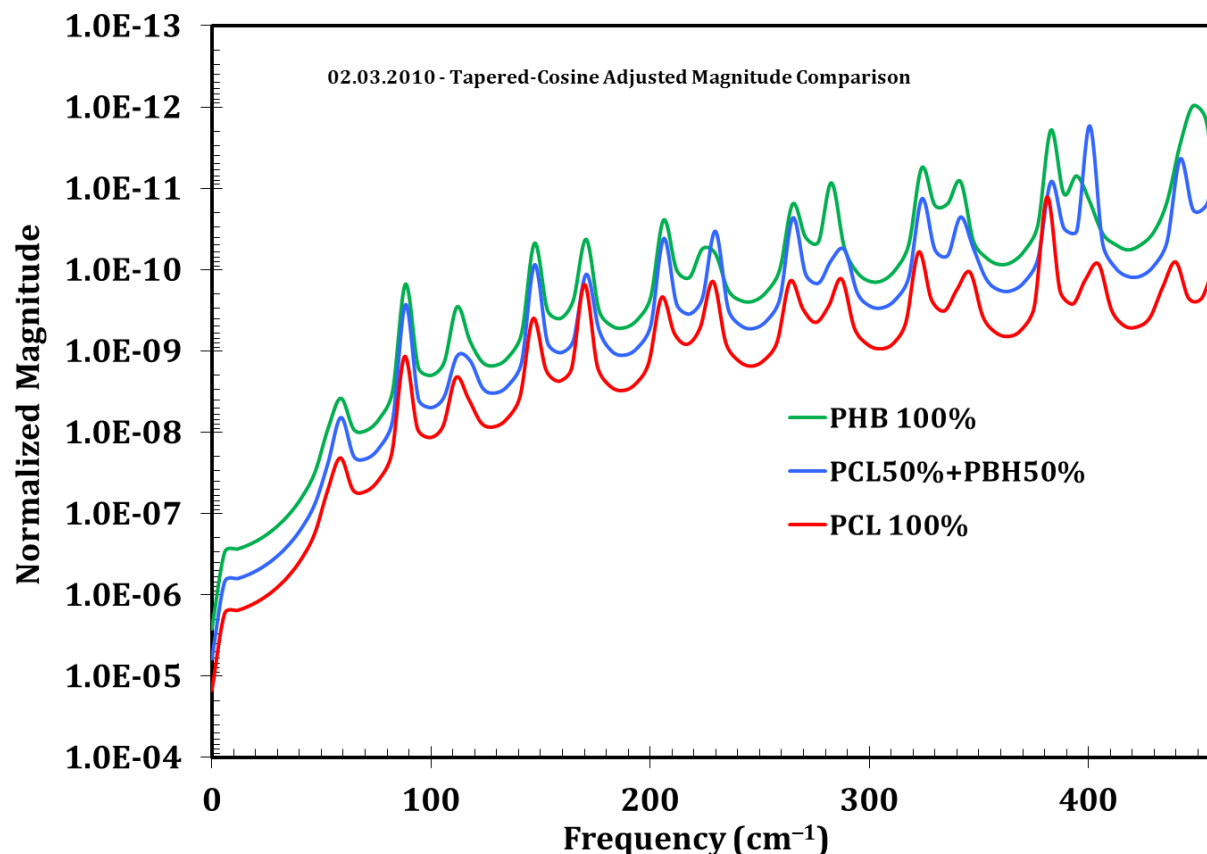


Fig. 5. Fourier transform magnitude spectra of three samples obtained from the signals of Fig. 4 for the respective samples. The transmission expressed in magnitude follows the predicted behavior of molecular weight dependence.

4. Summary

The preliminary investigation reported herein demonstrate that terahertz spectroscopy is capable of identifying phase separation of polymers and polymer blend of different molecular weight.

The normalized time-domain signals of three specimens used in this report exhibit higher transmission for lower molecular weight and follow an increasing trend with molecular weight. Consequently, their Fourier transform spectra will also exhibit the same trend. It was also found that THz spectroscopy finds

a number of resonance peaks in the low frequency region that were not detected by IR. Additionally, the magnitude of transmission follow the same trend as predicted by the molecular weight dependence. This is most likely a manifestation of the Beer-Lambert's law with the modification that instead of concentration of an analyte, here molecular weight is the variable.

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6. References

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