APPLICATION NOTE

FT-IR Spectroscopy

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Investigating Phase Transitions with Variable Temperature ATR

Introduction

Heating and cooling cause phase changes in many materials with consequent effects on their physical properties. IR spectroscopy is a powerful tool for studying these changes since the spectra are sensitive to variations in both intermolecular and intramolecular interactions. Changes in the IR spectra due to temperature variations can be correlated with structural changes and the spectra can be associated with specific crystalline forms. For example, any transition from a crystalline to an amorphous phase results in a broadening of bands as the molecules are in more varied environments. In crystalline materials, a change from one polymorph to another generally causes band shifts and splitting. For many materials transmission and external reflection measurements are not practicable without some sample preparation but ATR can often be used directly. In this note we illustrate the use of heated ATR to follow thermal changes in chocolate, which is largely a suspension of sucrose and cocoa solids in a matrix of cocoa butter. Chocolate and cocoa butter both have several polymorphs with melting points between 17 and 37 °C.[1] The polymorphic form has to be carefully controlled in manufacture because of its importance for storage and its major contribution to the sensory experience when eating chocolate.

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Experimental

Spectra were measured with a Frontier FT-IR spectrometer using a single bounce PIKE ATR accessory with a ZnSe crystal that could be heated at a controlled rate up to 135 ˚C. The heating rate was usually 1 degree C/minute with 4 cm^{-1} spectra collected at 15 second intervals using PerkinElmer® TimeBase™ software (Figure 1). The materials used were cocoa butter and a commercial dark chocolate product containing 85% cocoa and about 15% sucrose with other minor constituents.[2]

Results

Caution is needed in interpreting ATR spectra because they come from the first few microns depth of material in contact with the crystal. Because of this, ATR spectra may differ from those of the bulk material. The penetration depth is proportional to wavelength which means that relative band intensities in different regions may change if the degree of contact with the crystal changes. In this case the bands used to generate band ratios were separated by less than 20 cm^{-1} so the difference in penetration depth is insignificant.

Typical ATR spectra of chocolate and cocoa butter are shown in Figure 2. The chocolate spectrum is dominated by the cocoa butter which is largely a mixture of di and triglycerides of stearic, palmitic and oleic acids, and by sucrose. As the sample is heated (Figure 3) the features associated with cocoa butter broaden and shift while the sucrose bands are unchanged. Melting causes an overall increase in band intensities because of improved contact with the ATR crystal. At the same time there is a reduction in the intensities of all the sucrose bands relative to those of the cocoa butter. This is attributed to the liquid cocoa butter flowing around the sucrose crystals on to the surface of the crystal.

Although there are changes occurring in many regions of the spectra they are seen most clearly in the complex C=O absorption around 1740 cm^{-1}. The C=O feature of three samples of the same chocolate with different thermal histories at about 20 ˚C are seen in Figure 4. Three peaks are seen in the original material but their relative intensities are affected by heating and cooling. After melting and cooling there is a broad unresolved band. The changes with temperature can be followed by monitoring appropriate band intensities within this region or, in more detail by using principal components analysis (PCA).

TimeBase software provides several different ways of presenting the data, as individual spectra or a stacked plot. The changes with temperature can be examined as the intensities at specific frequencies or as ratios of pairs of peak heights or band areas that can be chosen interactively. The use of band intensity ratios is especially appropriate for ATR data as the overall intensities can be affected by changes in the contact with the ATR crystal. Figure 5 shows typical TimeBase screen displays.

In Figure 6 the ratio of intensities at different frequencies within the C=O band for chocolate is compared with the same ratio for a cocoa butter as each is heated to above its melting point. There appears to be a single smooth transition for cocoa butter while the chocolate melting appears more complex. PCA of the chocolate spectra identifies several significant principal components. Combinations of the scores for the first two PC's separate one process that appears complete at 25 ˚C from a second that occurs between 25 and 30 ˚C (Figure 7). Identifying the specific polymorph changes associated with these transitions would require reference spectra of the individual polymorphs which were not available at the time of this study.

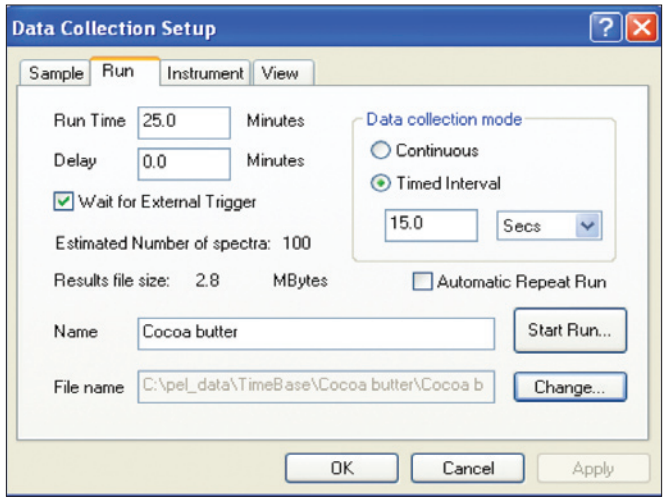

Figure 1. Set-up screen for TimeBase.

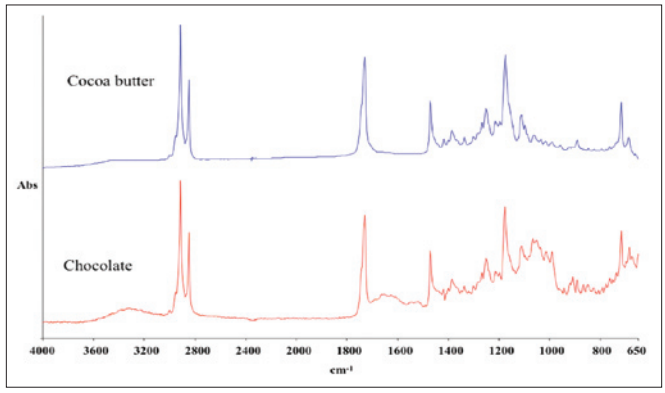

Figure 2. Spectra of chocolate and cocoa butter.

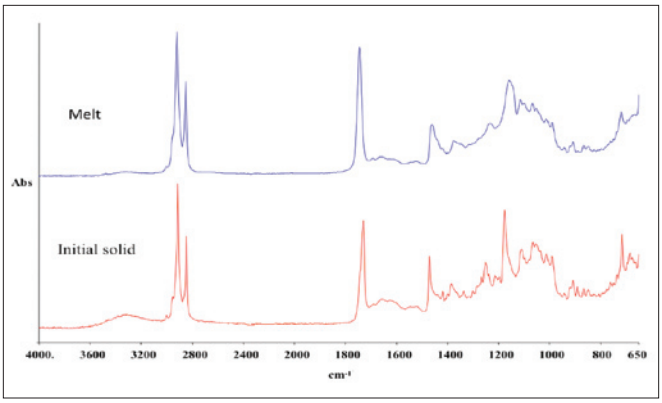

Figure 3. Chocolate solid and melt.

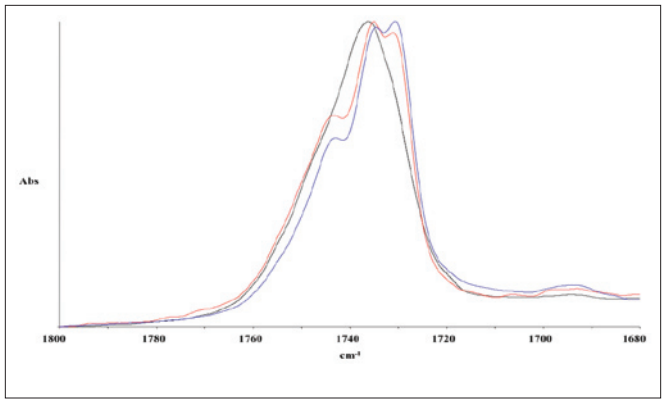

Figure 4. C=O region for chocolate with different thermal histories.

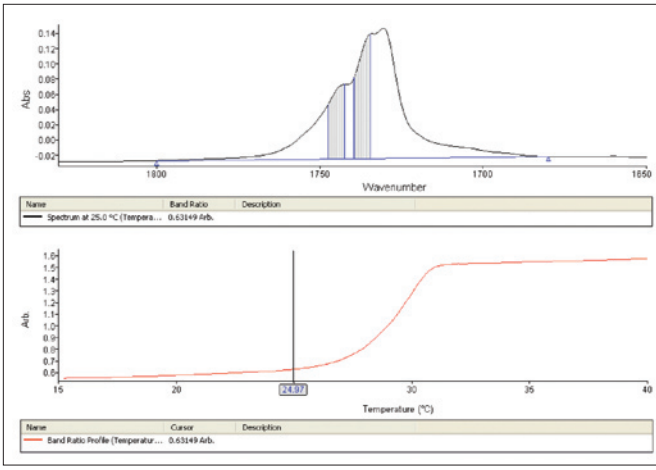

Figure 5a. TimeBase spectral display and band ratio profile for cocoa butter.

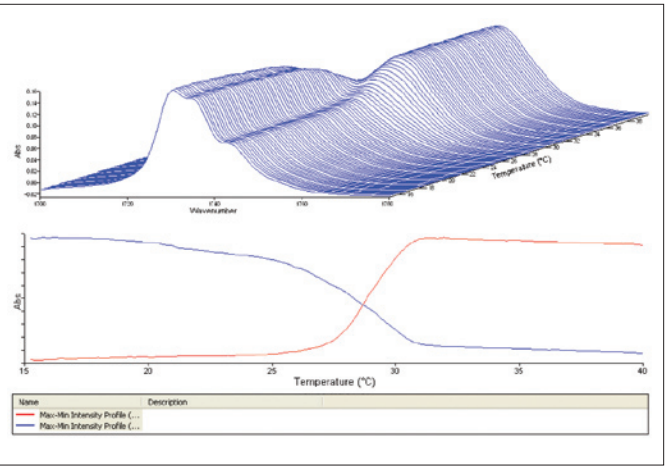

Figure 5b. TimeBase stacked plot and specific band intensity profiles for cocoa butter.

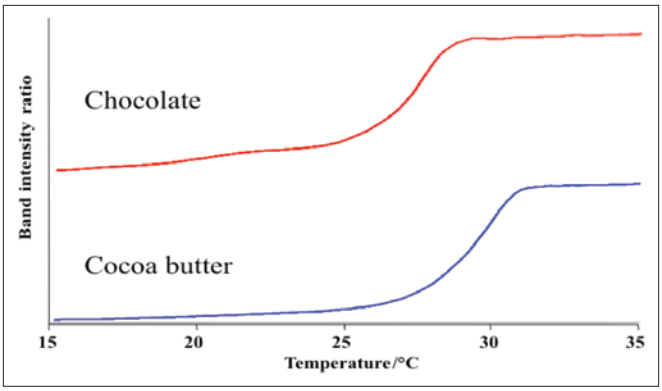

Figure 6. Band intensity ratios for chocolate and cocoa butter.

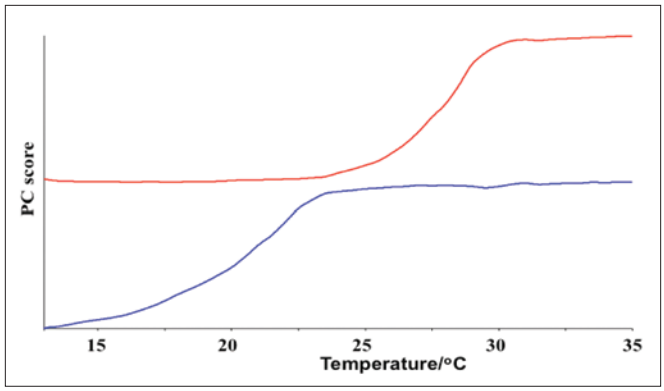

Figure 7. PCA scores for chocolate showing successive transitions.

Summary

These data show how variable temperature IR measurements can be used to monitor complex phase transitions. The transitions in chocolate are more complex than that seen in cocoa butter. Because the transitions have different spectral signatures they can be separated by choosing to look at different band intensity ratios, or more systematically by using PCA. The spectra at 20 ˚C show how the thermal history affects the spectra observed at ambient temperatures. Any systematic study to identify the polymorphic changes would require materials with well characterized thermal histories, for example by using Differential Scanning Calorimetry.[1]

As the temperature is raised there is an observable reduction in the intensity of bands due to sucrose compared to those from the cocoa butter. This implies that the cocoa butter concentration at the crystal surface increases, displacing sucrose.

References

1. 'Characterization of Chocolate Using Power Compensated DSC' PerkinElmer Thermal Analysis Application Note. PETech-43.

2. Lindt & Sprüngli AG, Kulrich, Switzerland, courtesy of W. Böttcher.

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