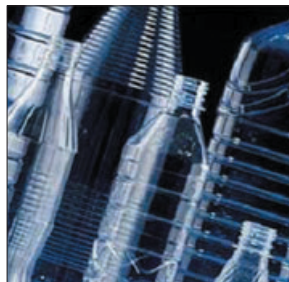


# A Study of Polymer Crystallinity Using the RamanStation 400F

## Introduction



The study of polymer crystallinity is important as the degree of crystallinity is directly related to the ruggedness and impact resistance of many polymers. A good example of this is Polyethylene Terephthalate or PET.

PET is commonly used in beverage containers, particularly those used for carbonated soft drinks. These containers are produced in very large quantities. A better understanding and increased control of the crystallization process could result in thinner bottles that retain the same strength. A reduction in the amount of polymer feedstock used could not only provide a large economic benefit, but could also potentially reduce environmental impact.

PET beverage containers are stretch blow molded from an amorphous plastic plug. The expanding polymer comes in contact with a cold metal mold and rapidly takes its final form. This process can result in strain-induced crystallinity. As the polymer is non-uniformly stretched during the process, different regions of the PET container have varying crystallinity.

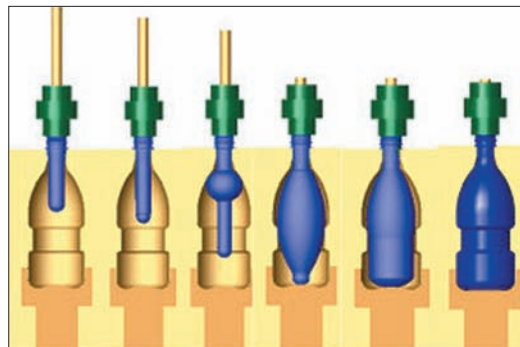


Figure 1: The stretch blow molding process

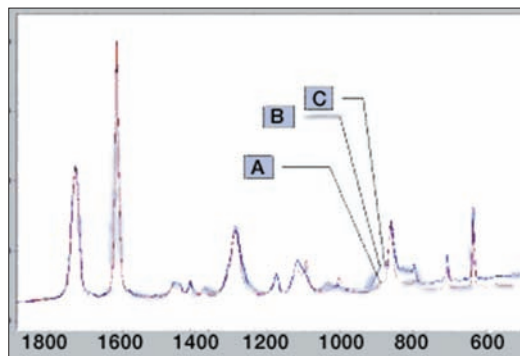


Figure 2: Raman spectra from top (B), middle (A) and bottom (C) of PET bottle

## Raman Analysis of PET Bottles

Figure 2 shows the fingerprint region of Raman spectra taken from three places on a PET bottle using a PerkinElmer® RamanStation™ 400F. No sample preparation was necessary and no pieces of the bottle were removed for this analysis.

It has been reported that the crystalline content of semi-crystalline PET can be determined from Raman spectra in at least two ways. The first of these is the peak ratio of bands at approximately  $1,120\text{ cm}^{-1}$  and  $1,100\text{ cm}^{-1}$  Raman shift.

Figure 3 shows the details of the Raman spectra in the region of interest ( $1,060\text{ cm}^{-1}$  to  $1,220\text{ cm}^{-1}$  Raman shift). The spectra indicate a range of degrees

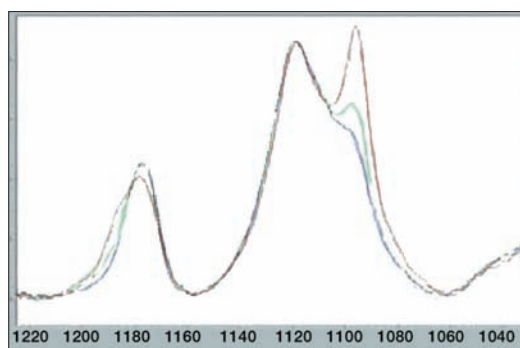


Figure 3: Details of the Raman spectra in the  $1,060\text{--}1,220\text{ cm}^{-1}$  region

of crystallinity. Highly crystalline samples exhibit a large peak at  $1,095\text{ cm}^{-1}$ ; whereas amorphous samples simply show a shoulder on the  $1,120\text{ cm}^{-1}$  peak.

The second technique involves consideration of the peak width of the Raman emission at  $1,730\text{ cm}^{-1}$ . This is shown in Figure 4.

Again, the spectra result from a range of samples with varying degrees of crystallinity. The highly crystalline samples give a narrow peak; whereas the amorphous bandwidth is demonstrably broader.

In the next study, the peak ratio technique was used to compare the crystallinity of a PET bottle along its length.

The graph in Figure 5 illustrates the variation in the ratio of Raman peaks at  $1,096\text{ cm}^{-1}$  and  $1,119\text{ cm}^{-1}$  showing a large change in crystallinity along the length of the bottle. The data shows the material is essentially amorphous in the threaded top portion and the bottom of the bottle, whereas it is relatively crystalline in the rest of the bottle. Moreover, the degree of crystallinity is quite constant over the length of the bottle except for two transition regions near the top and the bottom, where there is a rapid increase in crystallinity.

### Industrial Application

It has been shown that, using the RamanStation 400F spectrometer, a rapid assessment of crystallinity in fabricated PET bottles can be achieved, quickly and easily. This has obvious applications in the design of mold tools for PET products as well as on-line QC monitoring in production environments.

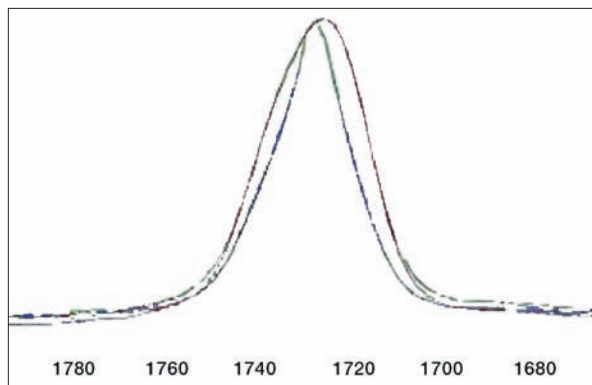


Figure 4: Raman bands at  $1,730\text{ cm}^{-1}$

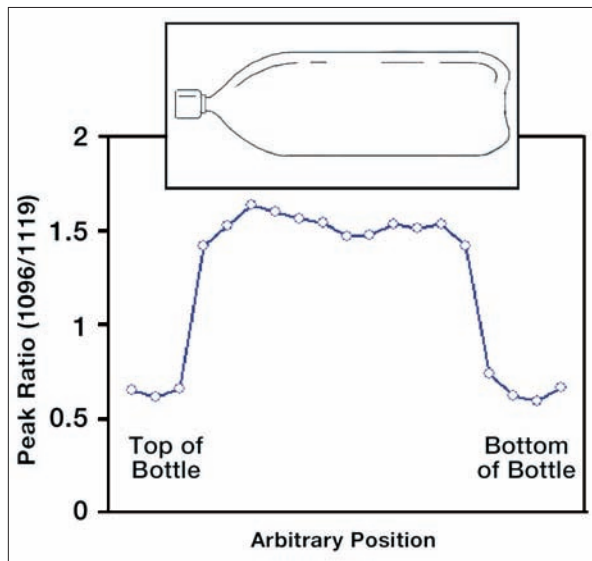


Figure 5: Variation of Raman peak ratio associated with crystallinity along the length of a PET bottle