BRIDGE

Application Note

Determination of the Degree of Crystallinity of Plastics using Solid-state Nuclear Magnetic Resonance (NMR) Spectroscopy

Background

The degree of crystallinity of a plastic strongly affects, amongst other things, the plastic's mechanical properties and is therefore one of the most important determinants of the end use of the plastic.

Variation in manufacturing conditions can affect the degree of crystallinity of a plastic and the resultant final product properties. Being able to determine the degree of crystallinity within plastic materials quickly and robustly improves product quality and would offer a beneficial process to determine this important property for plastic manufacturers and suppliers.

Traditionally, determination of crystallinity has been carried out using thermal analysis which is time consuming. The method outlined here presents a significant saving of time when compared to thermal analysis methods.

Solid-state NMR

At the Bridge, the Bruker Avance III HD NMR spectrometer operating at a proton Larmor frequency of 500 MHz, is capable of handling both liquid and solid-state samples reducing the need for sample dissolution and increasing the number of applications available.

Figure 1: NMR instrumentation at the Bridge @ University of Lincoln.

Solid-state NMR can be used to determine the degree of crystallinity in a time-efficient manner. A small amount of plastic material is milled to produce an even powder via cryomilling.

The powdered material is then loaded into an NMR rotor, with an internal capacity of 106 µL. This rotor is then loaded into the spectrometer (Figure 1) and analysed.

The NMR analysis is rapid, with multiple sample analysis possible using an autosampler allowing for high throughput analysis.

NMR spectroscopy is an analytical technique in which a wide range of chemicals can be studied and is particularly well-suited to organic compounds. The technique works by exposing chemicals to a powerful magnetic field, causing certain atomic nuclei to spin.

Careful analysis of the speeds at which the nuclei spin can elucidate both specific chemicals and broad groups of chemical compounds (e.g., sugars, aromatic hydrocarbons etc.) present in the sample.

Outcomes

Crystalline plastic polymer is rigid and therefore gives rise to a broad 1H NMR peak (Figure 2, grey line) whilst amorphous plastic polymer is more flexible, producing a narrower peak (Figure 2, red line) due to the averaging out of dipolar interactions between the nuclei.

Thus, the crystalline and amorphous phases are easily differentiated by NMR and fitting the collected experimental data to the theoretical crystalline and amorphous peaks allows the crystalline content to be determined. The example shown in Figure 2 was determined to have a crystalline content of ca. 90%, typical of polypropylene.

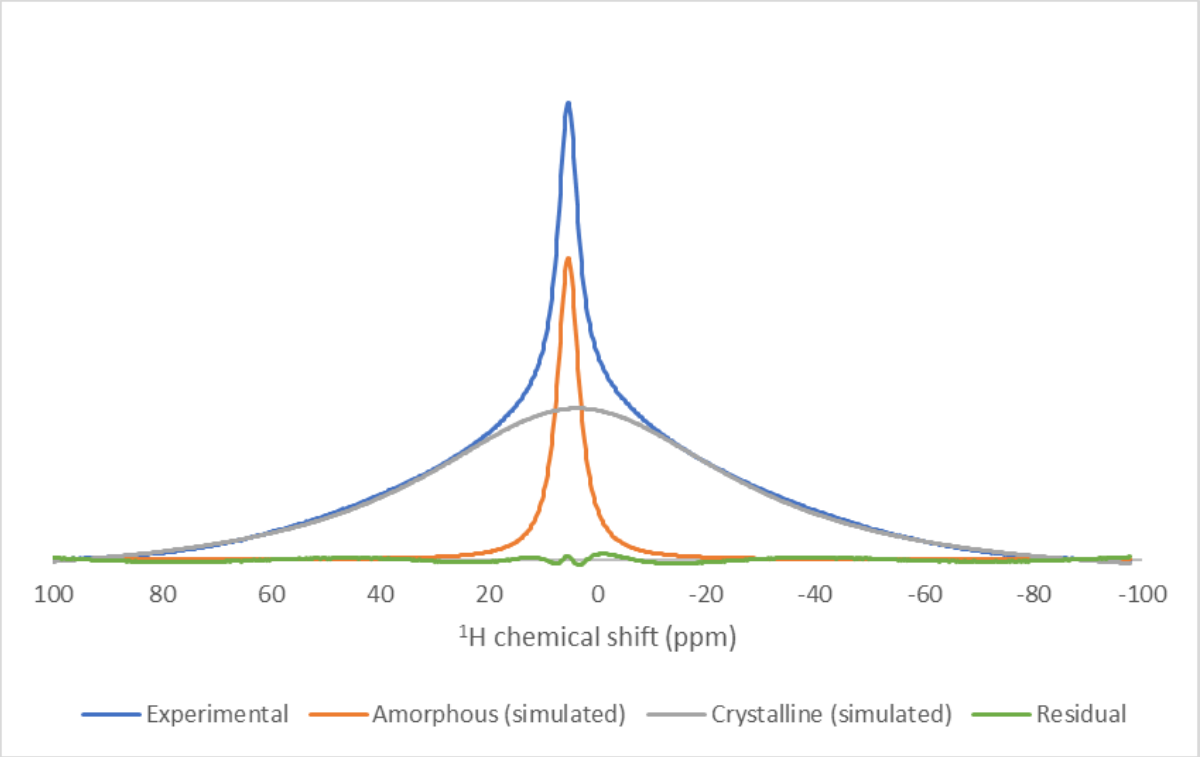

Figure 2: Experimental (blue line) and fitted (red and grey lines) of cryomilled polypropylene sample. Residual (green line) shows excellent agreement between experimental and theoretical model.

Summary

It has been demonstrated that solid-state NMR is an effective and efficient approach to determine the degree of crystallinity in plastic samples.

The method is rapid, taking only 5 – 10 minutes, and can therefore be utilised to give almost real-time feedback for R&D samples and for new product development.

The method can also be applied generally where polymer crystallinity is of interest as a viable alternative to the traditional thermal methods.

This method could be utilised for any industry that needs to understand the degree of crystallinity in plastics when this is critical to the properties of their manufactured goods.

It would also be of benefit if it was a requirement to analyse potential degradation of plastics or to determine the efficacy of new and novel antioxidants, including bioderived solutions, when developing new materials or new antioxidants.

It would also be of benefit to ensure that ductile properties of materials were maintained when moving to new, more sustainable materials and/or manufacturing methods.

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