Determination of Xylene Solubles in Polypropylene

Application Note 16

Summary

- Fast, accurate and repeatable
- No sample preparation
- Simple linear calibration
- Easiest, most reliable technique available; suitable for unskilled personnel

Application

Xylene solubles' (XS) is a historically established term denoting the percentage of soluble species in polypropylene homo- and co-polymers. In practice, this measurement is widely used for product quality control and monitoring physical properties of the polymer during synthesis and processing.

Advantages of NMR

The xylene extraction method (ASTM D5492, technically equivalent to the standard ISO 16152) is commonly employed to determine the xylene solubles content by weight. However, this method requires dissolution of the products in a harmful solvent, high temperatures (135 and 150°C), large sample sizes (to guarantee reliable reproducibility), highly skilled analysts, and long measurement times. The xylene solubles can also be measured using a Fourier transform infrared technique (FTIR). Although this method significantly reduces the analysis time, it requires delicate sample preparation and a highly skilled operator.

In contrast to the standard wet chemistry method and FTIR technique, low resolution Nuclear Magnetic Resonance (NMR) provides a fast, direct and user friendly method for determination of the xylene solubles content in polypropylene products.

The **MQC+** benchtop NMR analyser provides an alternative method which is quick and easy to perform, simple to calibrate, and requires minimal sample preparation. As such it is ideal for routine operation either in a laboratory or production environment without any requirement for additional chemicals or specialist operator training.

Method

Benchtop NMR is able to distinguish between signals from solid (dense, ordered crystallites) and amorphous regions within samples. This is because the solid signals decay rapidly (in the order of a few tens of microseconds), whereas the amorphous signals prevail for much longer (many hundreds of microseconds).

This measurement is based on measuring the NMR response obtained from the amorphous part of the material which is proportional to xylene solubles content, and quantification by calibration with known standards.

Calibration

Ultimately, only two well known standards are required to calibrate the instrument as the calibration is linear. However, it is recommended that initially the instrument is calibrated by 3-6, or more standards with known xylene solubles contents evenly spread over the range of interest. NMR is a comparative technique and therefore cannot be more accurate than the reference technique against which it is being compared; confidence in the calibration is increased by analysing more reference samples.

Measurement

Polypropylene samples are poured into 18 mm glass NMR tubes up to a predefined mark and weighed. The sample tubes are placed in a temperature controlled conditioning block at 60°C for 20 minutes prior to analysis. Measurement time is 20 seconds per sample.

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Results

Figure 1 shows an example of a calibration for polypropylenes with xylene solubles content ranging from 0.9 to 4.3 % by weight (wt.-%). As seen in this figure, NMR gives an excellent linear correlation between the NMR response and the concentration of xylene solubles in the products. The technique is not limited to precise measurement of low concentrations and may be used up to at least 30% xylene solubles content.

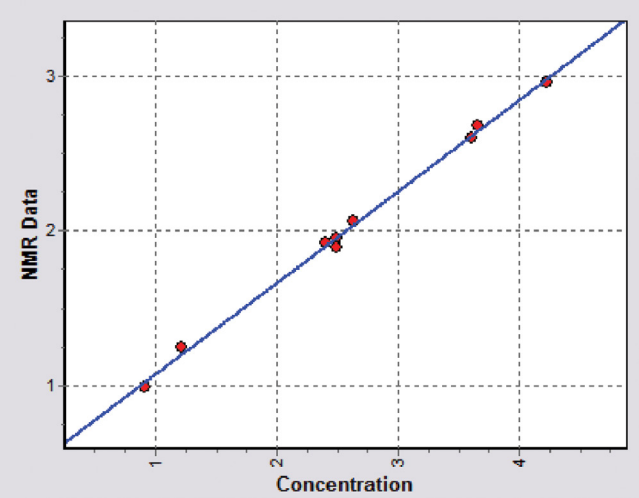


Figure 1: *Calibration obtained for xylene solubles in polypropylene standard deviation of the linear fit is 0.06 wt.-%, correlation coefficient R^2 = 1.00. Measurements were made using Oxford Instruments* ***MQC+****23 benchtop NMR analyser fitted with an 18 mm diameter probe.*

The repeatability was tested by measuring one sample ten times. After every test measurement, the sample was transferred from the magnet bore back to the conditioning block for 20 min to be conditioned at 60°C and then measured again.

Table 1. *Results of measurement repeatability test*

Given XS Value, wt.-%	Results (wt.-%) of Repeat Measurements										Mean XS Value, wt.-%	Standard Deviation wt.-%
0.92	0.94	0.87	0.90	0.94	0.92	0.91	0.93	0.89	0.92	0.91	0.91	0.02

Conclusion

- NMR is very stable over the long term and rarely needs calibration adjustment
- NMR is insensitive to the air voids between the pellets or grains of powder
- Measurement precision is good compared to wet chemical methods
- Sample measurement is rapid
- The NMR technique is non-destructive so the same sample may be measured several times before being analysed by other techniques
- The NMR instrument may be used for the measurement of other extractables

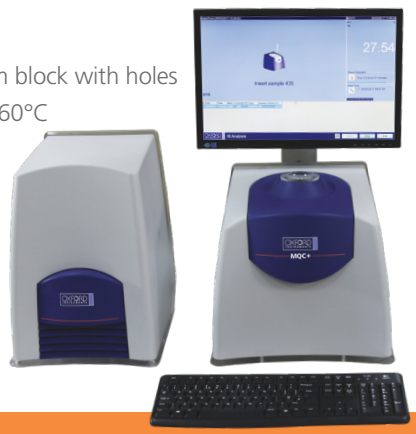
Complete Package

Oxford Instruments offers a package especially tailored to the measurement of Xylene Solubles in Polypropylene.

- Oxford Instruments **MQC+**23 NMR Analyser
  - 0.55 Tesla (23 MHz) high homogeneity magnet
  - Probe for 18 mm diameter sample tubes (7 ml sample volume)
  - Integrated system controller (no external PC required)
  - Integrated flat-screen display
- **MultiQuant** software including **RI Calibration**, **RI Analysis**, and the **EasyCal** 'Xylene Solubles in Polypropylene' application
- Test/tuning sample
- 18 mm glass tubes
- PTFE stoppers
- Stopper insertion/removal tool
- User manuals
- Method sheet

Optional items are:

- A dry heater and aluminium block with holes for sample conditioning at 60°C
- A precision balance



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