Technical Note

TN2

How does the identiPol QA2 work and what does it measure

Introduction

The identiPol QA2 is a machine that has been developed for the rapid measurement of thermoplastic materials in the manufacturing / quality assurance departments. It is based on fundamental scientific principles and has its origins in the field of thermal analysis. Thermal analysis is a collection of techniques that measure the property of a material as a function of temperature[1]. One technique measures length as a function of temperature, another measures dielectric properties as a function of temperature, and so on. The typical output from a thermal analysis instrument is a graph with temperature along the x-axis and the property being measured as the y -axis. So, length would be plotted against temperature to give a graph that shows how a material might expand, soften or melt as it was heated.

Two of the most popular thermal analysis techniques used in the characterisation of thermoplastic polymers are Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). A DSC measures heat flow based upon a temperature difference between a sample and inert reference and the resulting data can be used to measure melting, oxidation, cross-linking and glass transition (softening) temperature. A DMA measures the modulus (stiffness) of a material. The utility of these techniques to the characterisation and analysis of polymeric materials is well documented[2].

The identiPol QA2 combines aspects of both DSC (or more closely, Differential Thermal Analysis – DTA) and DMA into a single system. The combination of thermal techniques is quite common and often involves a compromise in performance when compared to the separate individual techniques. This may be a concern in the research laboratory where detection limits, resolution

The identiPol QA2

and precision are key factors – but are of less concern in the pragmatic manufacturing environment where the main focus is on productivity and quality. By combining DSC / DMA type measurements into a single unit a powerful system is created for the rapid analysis of thermoplastics. These measurements can then be used in three different modes of operation.

- Identification Mode = What type of plastic is this?
- Confirmation Mode = Is this batch acceptable for the production line?
- Comparison Mode = Is this material equivalent to our current supplier?

The Production Line vs. The Scientific Laboratory

For those who work mainly in the manufacturing and production area, the tools available for the analysis and characterisation of thermoplastics is somewhat limited. They range from the very simple such as burning and smelling, will it float or sink (a simple density measurement) to the slightly more sophisticated Heat Deflection

Temperature (HDT) or Melt Flow Index (MFI) which measure mechanical or flow properties as a function of temperature. The trouble with these sorts of measurements is they often yield a single number or value that is used to asses manufacturing parameters and are not, in themselves, a measure of the materials full properties across the entire temperature range they will experience during manufacture. Consequently, two very different plastic materials could have the same MFI value but be entirely different plastics.

The problems raised by using MFI, HDT and other simple (but cost effective) tests are easily overcome by using the thermal analysis techniques of the product development or research laboratory. These sophisticated instruments can detect very subtle differences between material properties and, in the hands of an experienced scientist, be used for a thorough investigation into material failure or structure / property relationships. However it would not be unusual for a laboratory to spend around $100,000 - $150,000 on a DMA and DSC to make these measurements and then, of course, there is the salary of the scientist to operate them to consider. This cost and expertise is outside the budget afforded to most manufacturing sites.

The identiPol QA2 is positioned between these two extremes. It is a more sophisticated instrument than the HDT and MFI type of measurements and it does not have the research and development specifications and costs associated with a DSC / DMA combination. It is priced accordingly and has been designed to be used by non-technical staff.

How does it work?

The identiPol QA2 uses a form of thermo-mechanical analysis (TMA) that has a strong relationship to both DMA and DTA, but is neither. It is simply a means of producing a reproducible thermo-mechanical fingerprint of the material being tested. In order to improve reproducibility and sample handling the plastic material (typically a granule or two) is placed onto a patented sample holder and placed into the moulding station within the machine.

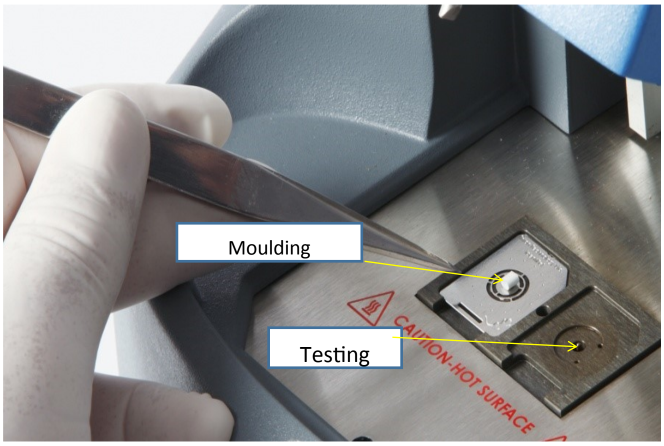


Figure 1 - identiPol QA2 sample moulding and testing stations.

The plastic is then automatically moulded within the machine to produce a highly reproducible test sample for measurement. Being in such close contact with the metal holder also allows high heating rates and ensures that the plastic sample heats rapidly. The operator then transfers the sample to the testing side where it is reheated to measure the thermo-mechanical fingerprint of the material. As the heating block is reheated at 30°/min, the sample area is vibrated by a force motor that contains a temperature sensor at its tip. These signals are used to calculate the stiffness, loss modulus and temperature difference for the sample during the test. These signals constitute the materials thermo-mechanical fingerprint.

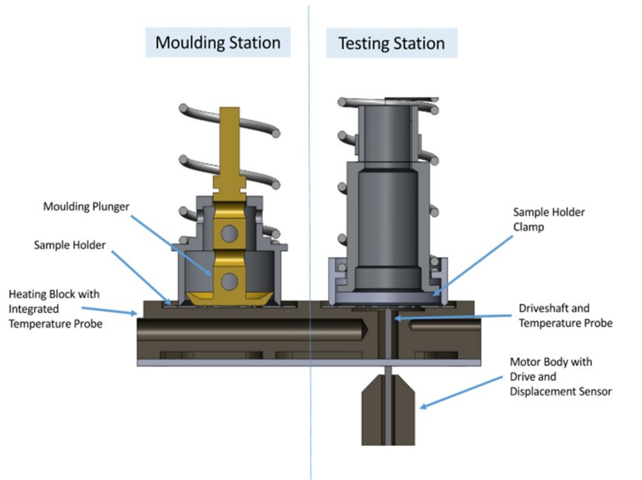


Figure 2 - Schematic of the key components within the identiPol QA2

The ‘thermo-mechanical’ fingerprint (Figure 3.) that is finally measured consists of a number of parameters and three that will be very familiar to the thermal analyst are Stiffness, Tan Delta and Delta T. The test parameter results from the measurement of a piece of polypropylene are shown below.

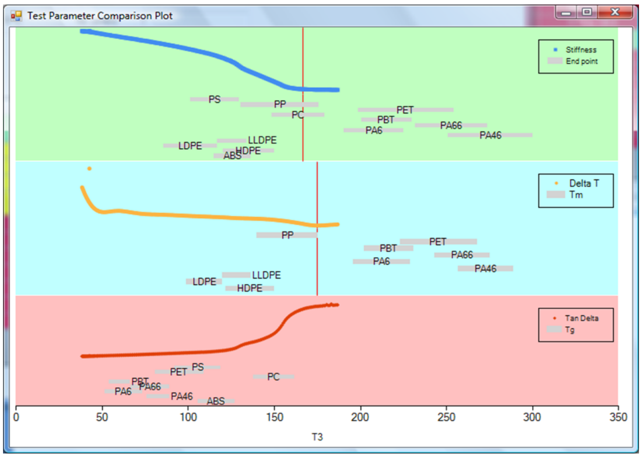


Figure 3 - raw data from the identiPol QA2 for a polypropylene sample

What is measured?

From the measure signals, a number of transition temperatures are automatically recorded within the system software. These are:

Glass Transition Temperature = the softening of any amorphous material

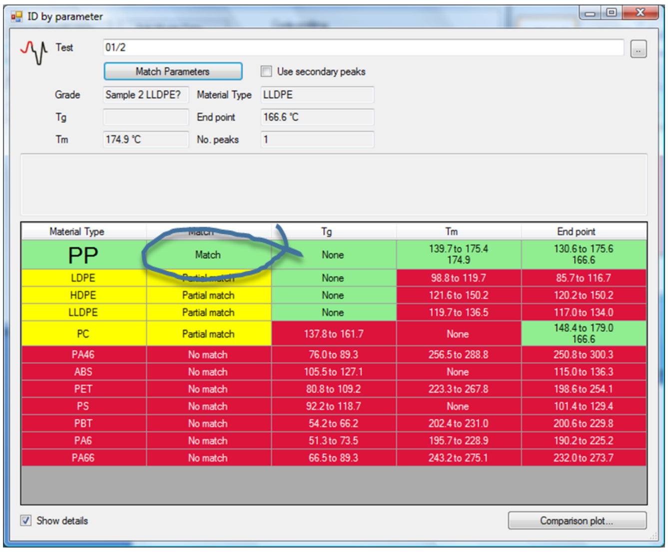
Melting Point Temperature = the melting of any crystalline material

End Point = the temperature at which mechanical integrity is lost

These transition temperatures, along with the raw signal data, are stored for each measurement made and are then interrogated by the system software to enable the three modes of operation outlined on Page 1.

Identification Mode

In this mode all of the transition temperatures measured by the identiPol QA2 are compared to a built in library of known thermoplastic materials. The temperature range where these common plastics soften and melt are highlighted (as grey zones) in Figure 2. Although the operator can view these curves, typically the system software would calculate the transition temperatures and compare them to the library and look for a match. The results are presented as a table with the closest match at the top, if a perfect match is found the word “MATCH” is displayed. Figure 4 shows such a table for the Polypropylene sample whose thermo-mechanical fingerprint is shown in Figure 3.



Material Type	Match	Tg	Tm	End point
PP	Match	None	139.7 to 175.4 174.9	130.6 to 175.6 166.6
LDPE	Partial match	None	98.8 to 119.7	85.7 to 116.7
HDPE	Partial match	None	121.6 to 150.2	120.2 to 150.2
LLDPE	Partial match	None	119.7 to 136.5	117.0 to 134.0
PC	Partial match	137.8 to 161.7	None	148.4 to 179.0 166.6
PA46	No match	76.0 to 89.3	256.5 to 288.8	250.8 to 300.3
ABS	No match	105.5 to 127.1	None	115.0 to 136.3
PET	No match	80.8 to 109.2	223.3 to 267.8	198.6 to 254.1
PS	No match	92.2 to 118.7	None	101.4 to 129.4
PBT	No match	54.2 to 66.2	202.4 to 231.0	200.6 to 229.8
PA6	No match	51.3 to 73.5	195.7 to 228.9	190.2 to 225.2
PA66	No match	66.5 to 89.3	243.2 to 275.1	232.0 to 273.7

Figure 4 - Identification Mode showing a perfect match for Polypropylene

Consequently, an unskilled operator – with little or no scientific knowledge – can quickly and accurately identify an unknown thermoplastic material.

Confirmation Mode

This mode is designed to help manufacturing personnel quickly decide if a new batch of material from their supplier is consistent with previously delivered good material. In the analytical laboratory the raw data (Figure 2) for a good batch and a new batch would be compared to answer the question “is this material the same, or similar enough, so that we can safely recommend that it be used on the production line?” If the results are close, repeat experiments on known good batches would be made to assess the spread and reproducibility of results before comparing curves. This is the approach taken in the identiPol QA2 – multiple good batches are run – and the software makes the comparison between these replicates and the incoming new batch.

Around 15-20 measurements are required to create a "reference set" of known good material. Running a number of samples allows for a measurement of the statistical spread of results to be stored. Rather than have the operator make a visual comparison of the incoming new batch with the reference set, a statistical analysis is employed based upon a chemometric model, to produce a measure of similarity. This reduces operator error and provides an objective measure of similarity that is a single number that ranges from 0 (the materials are totally different) to 10 (the materials are totally identical). This number is called the Quality Index Score, or QIS for short. The QIS range is not linear and is very sensitive to small differences, so that a QIS value down to 7 still means that the material is sufficiently similar to be processed successfully. Values under 7 and down to 4 indicate that the material is the same, but there may be some contamination, which causes a small difference, or a key property may be slightly different. A value of under 4 means that it is likely to be a different material.

The chemometric model used in the identiPol QA2 is the result of joint research between Lacerta Technology and the University of Bristol [3,4,5]. The method is based upon the analysis of the damping factor (tan δ) as a function of temperature using a 2 component multivariate analysis. One benefit of using this signal is that tan δ is a dimensionless quantity (it is the ratio of the Loss and Storage modulus) and so the sample being placed into the identiPol QA2 does not need to be weighed or measured. This adds to the rapid measurement time and simplicity of the system.

Typical QIS results for a series measurements on batches of a Nylon blend are shown in Figure 4 below.

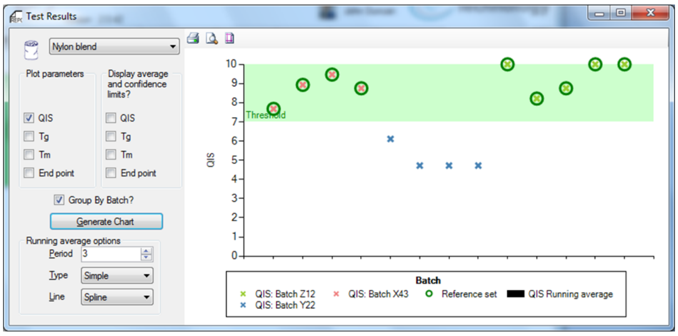
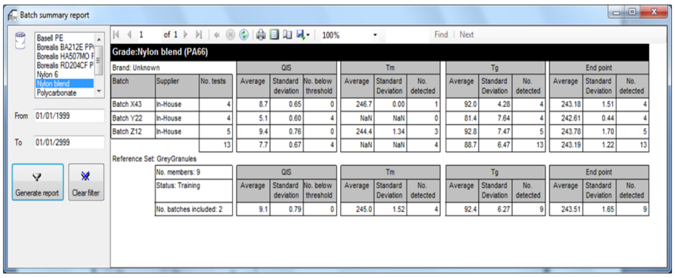


Figure 5 - QIS results for a series of Nylon batches

The QIS value is plotted along the Y-Axis and different measurements along the X-Axis. In this example replicate measurements of three batches (Batch Z12, X43 & Y22) are displayed. The "Pass Zone" is shaded green for QIS results of 7 or higher. The "Fail Zone" is white for those results that are below 7. Reading left to right, the first four measurements (red cross in a green circle) are from Batch X43 and as all four measurements are in the green shaded area, this batch passes and is clear to be used in manufacturing. The next four measurements (blue cross) are from Batch Y22 and all results fall within the fail region indicating that this material should not be used on the production line and should be queried with the supplier. Finally, the last five measurements are from Batch Z12 (green cross in a green circle) and all of these results fall within the pass zone and so this batch should give no problems on the production line.



Batch summary report

Grade:Nylon blend (PA66)

Brand: Unknown

Batch	Supplier	No. tests	QIS Average	QIS Standard deviation	QIS No. below threshold	Tm Average	Tm Standard Deviation	Tm No. detected	Tg Average	Tg Standard Deviation	Tg No. detected	End point Average	End point Standard Deviation	End point No. detected
Batch X43	In-House	4	8.7	0.65	0	246.7	0.00	1	92.0	4.28	4	243.18	1.51	4
Batch Y22	In-House	4	5.1	0.60	4	NaN	NaN	0	81.4	7.64	4	242.61	0.44	4
Batch Z12	In-House	5	9.4	0.76	0	244.4	1.34	3	92.8	7.47	5	243.78	1.70	5
		13	7.7	0.67	4	NaN	NaN	4	88.7	6.47	13	243.19	1.22	13

Reference Set: GreyGranules

	QIS Average	QIS Standard deviation	QIS No. below threshold	Tm Average	Tm Standard Deviation	Tm No. detected	Tg Average	Tg Standard Deviation	Tg No. detected	End point Average	End point Standard Deviation	End point No. detected
No. members: 9 / Status: Training / No. batches included: 2	9.1	0.79	0	245.0	1.52	4	92.4	6.27	9	243.51	1.65	9

Figure 6 - Statistical summary of key properties measured in Confirmation mode.

Although there is a substantial quantity of data and statistical methods underlying the principle of analysis within the identiPol QA2, the end result is a simple Pass / Fail indicator for the busy manufacturing operative.

For the more experienced operator, or senior manager, a summary report can be produced showing the statistical analysis of the multiple tests upon these three batches.

Comparison Mode

This mode of operation of the identiPol QA2 permits the comparison of multiple grades of material. It is worth differentiating between a "batch" and a "grade" at this point. The grade is a 'type' of material, it might be the Manufacturer's type number, a commercial name or product code. So, for example, Zytlel® is Du Pont's commercial name for their range of Nylon resins. Zytel is available in a number of grades: Zytlel ® PA, Zytel®PLUS, Zytel®HTN and so on. A 'batch' is produced from a specific manufacturing run of the material. Typically, each delivery to a manufacturing plant will be made up of one or more batches, of a single grade of material for a particular production run.

If you have standardised your production process on a particular grade of material – and another supplier claims to have an 'equivalent' material – you can use the Comparison mode to confirm, or otherwise, their claims.

In the example for Makrolon PC below, the chart shows that only two samples fall below the normal threshold level of 7. All of the batches of material represented by samples scoring over 7 would be acceptable for processing.

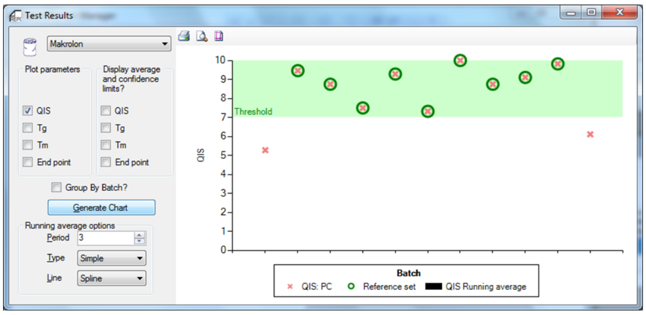


Figure 7. QIS values for a number of Makrolon batches

Once data for a particular grade has been collected the Comparison Mode may be used to check for differences between grades. The "Radar" style plot below shows a two dimensional version of the QIS shown above. Data are plotted from zero (circle centre) to a maximum value of 10 (circle circumference).

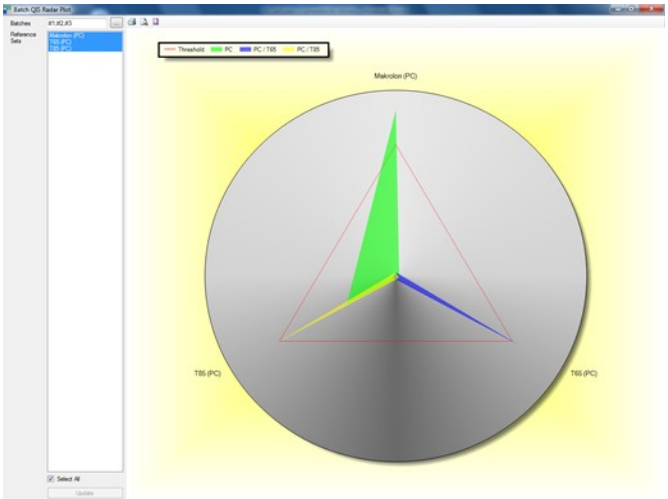


Figure 8—Batch QIS values Radar Plot

For example the plastic grades used for this Batch Comparison Mode test are listed in the table below. They contain varying amounts of Acrylonitrile-Butadiene-Styrene (ABS) blended with Polycarbonate (PC).

The actual value plotted is the QIS value compared to each grade. Therefore in the example below, each grade scores highly against itself, which is expected. The Makrolon PC shows some similarity to the T85 grade, but is quite different to the T65 material. Again this would be expected, since the latter has more ABS present.

Since both PC and ABS are non-crystalline, or amorphous, there is no melting point to measure in these samples. However the glass transition temperature, Tg and the end pont will give useful insights into the materials' properties. The table below shows these two parameters for each sample tested.

Grade	Polycarbonate (%)	Tg (°C)	End point (°C)
PC	100	148.2	159.2
T85	85	148.2	158.1
T65	65	143.5	153.2

Conclusions

The identiPol QA2 is a cost effective unit that has been designed for non-technical staff to operate in the production environment to assess the quality and suitability of polymeric raw materials in the manufacture of plastic components. Although soundly based on research grade instrumentation and advanced chemometric analysis, it remain simple to operate and understand. The system has been designed to a “step-up” from simple HDT and MFI techniques and provide a sophisticated tool kit for the plastic engineer or manufacturing operator.

References

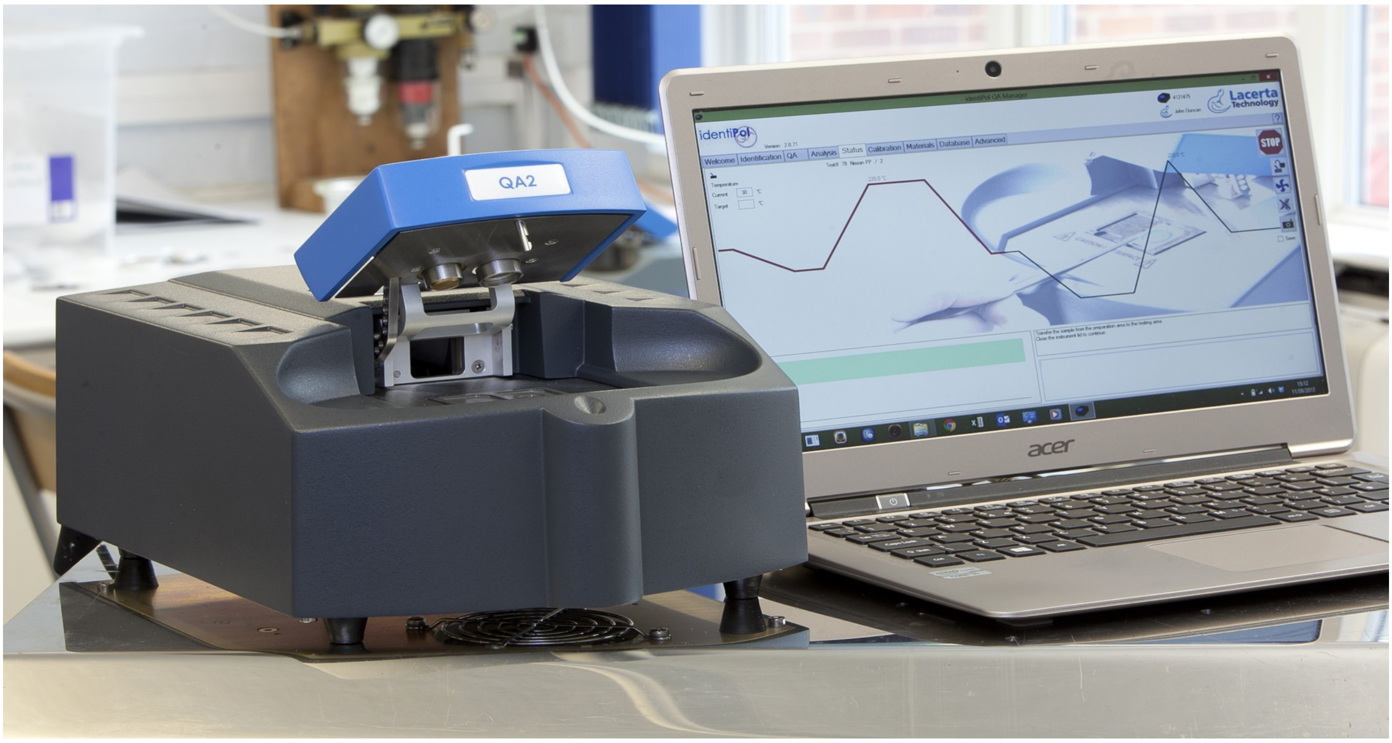
1. “Principles of Thermal Anaylsis and Calorimetry” Haines (Editor), RSC Paperbacks, 2002.

2. “Thermal Analysis of Polymers: Fundamentals and Applications” Menczel & Prime (Editors) Wiley Online, 2008.

3. “Pattern recognition and feature selection for the discrimination between grades of commercial plastics. Lukasiak, Zomer, Brereton, Faira & Duncan. Chemometrics and Intelligent Laboratory Systems. **87** (2007) 18-25

4. “Pattern recognition for the analysis of polymeric materials”. Lukasiak, Faria, Zomer, Brereton & Duncan. The Analyst, **131** (2006) 73-80

5. “Dynamic mechanical analysis and chemometrics for polymer identification”. Faria, Duncan, Brereton. Polymer Testing, **26** (2007) 402-412



The identiPol QA2 at work