Real time resin analysis

Headquartered in Greece, ACM Wood Chemicals specialises in formaldehyde based resin systems. The company recently developed a non-destructive testing system for resins and impregnated papers which provides information previously not available without destructive processes. We look at how the system works and its applications

Formaldehyde based resins have been produced and used industrially for several years. However, there are still difficulties associated with the accurate analysis of their intermediate and final products, even when applying the most advanced analytical methods and the most elaborate equipment. This is due to the 'living' nature of these systems, and the destructive nature of the sample preparation (dilution, drying, etc), necessary for most analyses.

Furthermore, these analyses are labour intensive, time consuming and, therefore, rather expensive.

There are difficulties in characterising the intermediates of resin synthesis. These, combined with several factors such as pH, temperature and raw material quality which affect, in subtle ways, the synthetic pathways, result in inevitable variations during resin production.

The impact of these variations on the final quality of the resin is not always easy to assess. However, it is easy to argue that improvement in the reproducibility will result in overall quality improvement as well as minimisation of the risks associated with resin production.

For this purpose, new methodologies have been developed by ACM Wood Chemicals to allow the fast and reliable analysis of raw materials, monitoring and control of the pathway(s) followed during resin production, and the assessment of the quality of the products.

The methodologies are based on FT-NIR chemometrics. No sample manipulation is necessary and the complete evaluation can be performed on- or off-line in less than one minute.

To explain the background to this, the use of NIR spectroscopy to monitor various processes has been developed systematically during recent years and, in the Fourier transform mode, is known to yield high signal-to-noise spectra in a matter of seconds. The use of optical fibres has allowed remote and non-destructive operation.

Parallel advances in computing hardware have enabled the coupling of NIR with chemometrics, the discipline concerned with the application of statistical and mathematical logical methods to large sets of data.

ACM research and development has developed the technique for use in resin manufacturing and laminating paper production and application. The work concerns the development of software packages that translate the values of the NIR measurement to usable graphics that permit monitoring of processes, characterisation of materials and quality evaluation of the final products. Data can be obtained on line and real time measurements allow for interventions in the processes.

Application of the methodologies leads, says Dr Eugenia Dessipri of ACM, to production optimisation, increase in reproducibility, reduction of errors, reduction of the time needed for analysis and therefore overall cost savings. The methodologies are protected by patent applications and under the trademark 'GNOSSI'.

Reaction mixtures during resin synthesis are multi-component systems where the concentration of reactants, intermediates, products (and by-products) are time-dependent. At the same time, pH and temperature may also vary. The methodologies developed cover all the steps of resin production, from the analysis of the raw materials used to the control of the pathway followed during synthesis and the assessment of the quality of the final product.

The instrumentation used consists of an FT-NIR spectrometer designed to be connected via optical fibres to process probes. The process probe enters directly into the reactor or storage tank which is being monitored. The optical fibres can be up to 200m long and each spectrometer can monitor up to six reactors.

Spectra acquisition and data manipulation is performed via a computer connected to the spectrometer.

For the analysis of raw materials, software has been developed that allows measurement and automatic transformation of the data to the required values. For example, this application has been found to be most useful for the analysis of UFC (urea-formaldehyde concentrate). The method allows (after calibration) the calculation of the percentage urea and percentage formaldehyde in a UFC sample in less than two minutes, says ACM.

In order to describe a synthetic pathway, the strategy employed allows the construction of an algorithm to monitor the kinetics of spectral changes during the process. The algorithm gives the reaction progress by interpolating between two or more reference states.

These reference states now define a phenomenological reaction pathway that accurately describes the synthesis. NIR can be used to check whether this is followed by an unknown reaction and to establish how fast the reaction moves from one reference state to the next.

As an example, the green line in Figure

Fig 1: Monitoring resin synthesis

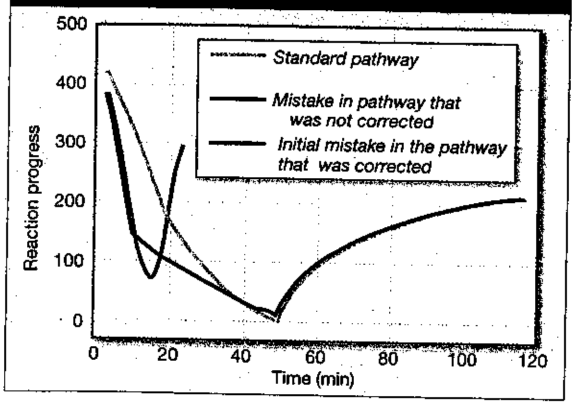
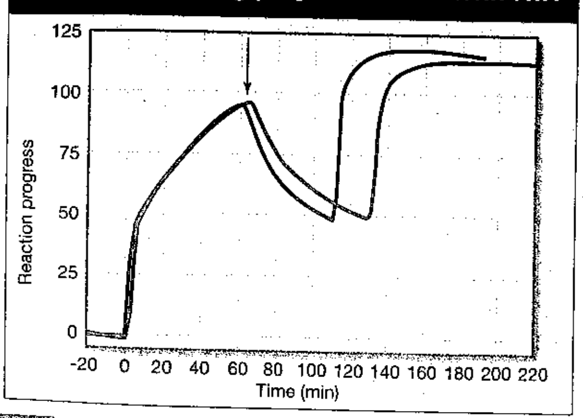


Fig 2: monitoring polymerisation with NIR



1 represents the standard pathway for synthesis steps in a known resin reaction. The score, (calculated automatically from the NIR spectra as the reaction proceeds) monitors the approach to a state (where score = 0, observed at t = 50 min) when the synthesis requires an external change of reaction conditions.

The red line demonstrates the reaction pathway after an incorrect application of the same synthesis. In this latter case, the reaction is seen to start much faster and deviates from the desired reference state. NIR can be used to provide an early warning of this deviation, and, in this case, allows the operator to apply corrective action to save the reaction (blue line).

A subtler situation is shown in Figure 2. Here, the indicator is chosen to magnify the spectral changes occurring during the polycondensation stage of production of a UF resin.

The onset of this stage, (score = 100 at t = 70 min), is marked by the arrow on the standard pathway (red line). Polycondensation rate is strongly dependent on pH. A difference in pH of less than 0.1 is difficult to measure reliably in real conditions and yet results in a considerably faster polycondensation (blue line).

NIR monitoring provides a clear warning of this situation and prompts the operator to initiate viscosity measurements much earlier.

While reaction monitoring by NIR chemometrics is a valuable laboratory and industrial tool, the evaluation of finished products is, per se, an interesting and useful application.

It can be used to provide a quick and reliable conformity test, especially when ageing and storage conditions affect the quality of the product.

The following example concerns the usability of laminating papers and is of paramount importance because alternative non-destructive techniques are not widely available.

Spectra from melamine paper samples can easily be obtained in the diffuse reflectance mode. Comparison of such spectra taken from fresh samples with spectra taken from samples that had been subjected to accelerated ageing suggests that ageing induces major spectral changes.

Chemometrics have been employed to translate these changes into an empirical usability index, varying between the values of 100 (fresh paper) and 0 (representing the spectrum of the 'worst' sample observed).

Figure 3 demonstrates the variation of this usability index as a function of time upon ageing at 55ºC and 65% relative humidity.

The spectroscopically defined usability index is found to decrease monotonically with time in a manner that can be fitted quite successfully by a single exponential decay function. Deterioration of fresh samples can be quite rapid under improper storage conditions, but aged samples deteriorate more slowly. Independent laboratory evaluations of paper usability indicated that the paper became unusable after the first day of treatment.

The spectral differences observed among fresh and aged paper are similar to the differences observed among paper from good or problematic pallets.

The spectroscopic usability index has been employed in order to evaluate a large number of industrial samples of varying quality. The distribution of NIR usability indexes is depicted in the upper histogram of Figure 4. The cluster with index values ranging between 15 and 50 had been classified as unusable.

After two weeks of ageing at ambient laboratory conditions, the usability index of the same samples was re-evaluated (lower histogram in Figure 4). The usability of the fresh sample was found to be reduced by some 20 units, while the aged specimens suffered less severe deterioration and the centre of distribution had fallen by around 10 units. This trend is in agreement with the previously deduced exponential law of ageing.

In Figure 4 the useable and unusable ranges are clearly defined and separated by 50 usability units. On-line calibration would be necessary in order to accurately define the zone where the melamine papers may safely be used for production and to dictate appropriate pressing conditions.

The deterioration of the quality of laminating paper is associated with inappropriate storage conditions. Board manufacturers often assume that the papers coming from one pallet are all of the same quality. However, the possibility of differential deterioration of melamine paper within a pallet is demonstrated in Figure 5, where the usability of samples from different positions on the same pallet is shown.

It is apparent that sample deterioration commences at the bottom of the pallet. This may be attributed to factors such as moisture absorption, and clearly indicates that local environmental changes may affect paper quality. In addition, deterioration of paper at the top left side is apparent throughout the height of the pallet.

The data collected from the top left side exhibits a wide spread. This may be explained by the fact that there is damage nucleation extending radially on the surface of the paper.

The above-mentioned data have been obtained off-line. Application of the methodologies on-line for assessing the quality of the laminating paper just before pressing has shown that the method can be used to avoid the use of low quality paper and therefore help to reduce second quality products or rejects in the laminating process.

To sum up, GNOSSI is a new method developed by ACM to allow the on-line, continuous, non-destructive monitoring of aminoplastic resin production and application.

The data obtained relate to the chemical composition of the system monitored and are directly translated to useful information for the operators.

The company says GNOSSI (the word in Greek means knowledge) is a unique tool to increase knowledge about the resin production process, the sources of lack of reproducibility and their effects on the final products.

Moreover, says ACM, it is a tool to evaluate, non-destructively and on-line, products such as impregnated paper.

The company claims the following as the benefits of this new technology: production optimisation; increase in reproducibility; reduction of errors; reduction of the time needed for analysis; and overall cost savings. ■

Fig 3: Usability index of paper

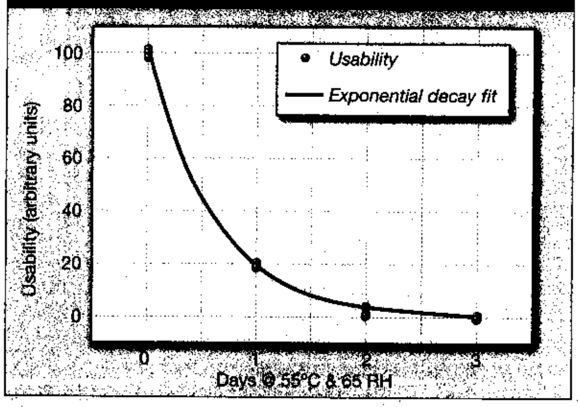


Fig 4: Usability distribution

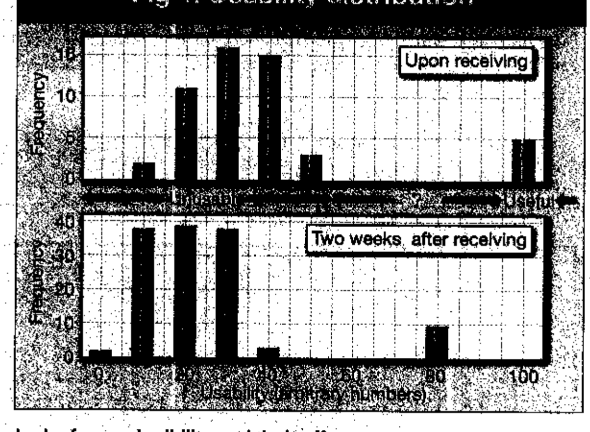


Fig 5: Sample from problematic pallet