

Measurement Methods Relating to the Processing of Plastics: The measurement of reactive polymer systems

Introduction

For many years computer simulation packages have been used to assist designers in their work. Modelling software has enabled improved mould design and as a result more complex mouldings can be produced reliably and consistently, being formed with less wastage and enhanced productivity. These packages have enabled the designer to see into the mould. Software packages like Moldflow and C-Mold require reliable data from which to perform the necessary calculations and thereby furnish the user with the required quantitative predictions. Historically this data has been available for thermoplastic materials. The challenge now is to transfer this modelling principle to reactive polymer systems such as thermosetting materials. Compared with conventional thermoplastics, thermosetting materials require more involved characterisation due to their properties which are dependant on time and temperature.

NPL has demonstrated that such reactive polymer systems may be characterised for use in commercial modelling software packages. Several material properties require characterisation for complete modelling, e.g. the cure kinetics, the viscosity, the gel time, the specific heat, the thermal conductivity and the density of the material. Such measurements have been carried out on four different materials; these being a polyester dough moulding compound, a nitrile rubber, a cross-linking polyolefin and a fluoroelastomer.

This document summarises the key features of such measurements and provides an example of the initial results for a completely characterised material.

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July 1999

Methods

Cure kinetics

The cure kinetics of a reactive polymer system defines the relationship between the cure level, temperature and time, here they are modelled using the Kamal equation:

$$\frac{dc}{dt} = (k_1 + k_2 c^m)(1 - c)^n \quad (1)$$

where c is the conversion level, t is time and m , n , k_1 and k_2 are model coefficients. Using a standard differential scanning calorimeter (DSC) uncured samples of the material were heated over a specified temperature range with a range of heating rates, thus generating a data set which allowed for the effect of heating rate to be observed. The Kamal equation was then fitted to the experimental results using a curve fitting routine ([Fig. 1](#)), thereby supplying the necessary parameters needed for the modelling software.

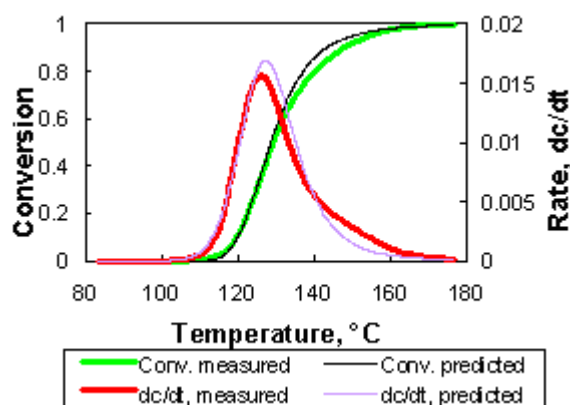


Figure 1. The cure behaviour of a polyester dough moulding compound measured using a DSC at a heating rate of $20^{\circ}\text{C min}^{-1}$

Viscosity

The viscosity of the polymer as it cures is a very important parameter which requires accurate predictions. Experimental data were obtained from multi-wave oscillatory rheometry tests conducted over a specific temperature range with heating at a constant rate. Depending on the rheological-cure behaviour, an appropriate model was chosen from those supported by the software package. The input parameters required by the model were then determined by fitting the experimental data to the model. The accuracy of the parameters was checked with the experimental data and adjusted so as to improve the fit (Fig. 2).

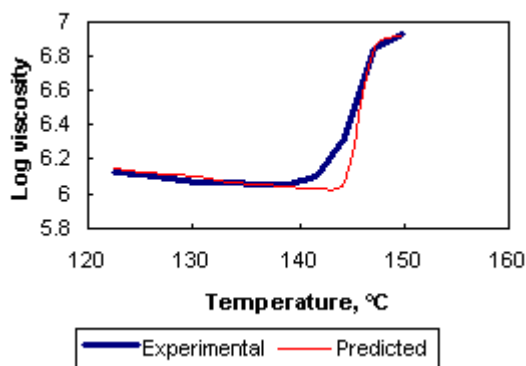


Figure 2. The fitting achieved for the viscosity of the nitrile rubber tested at a oscillatory frequency of 0.3Hz

Gel Point

In flow simulation modelling a 'gel point' is used to set a point where the viscosity tends to infinity, and thus the termination of flow. However this does not occur in practice and an alternative approach is required. One approach is to define the gel point as the point at which the material changes from having viscous behaviour to elastic behaviour as it cures. The multiple oscillation test used to determine the viscosity measures the elastic and viscous modulus under the same conditions, so no extra testing is necessary to apply this approach. It is however also possible that some materials will not show a gel point as defined above, in these cases an arbitrary gel point may need to be defined, such as a 20-fold increase in the viscosity.

Thermal Conductivity, Specific Heat and Density

There are three more material properties that need to be characterised in order to carry out flow simulations. These measurements are normally carried out on cured samples of the material.

The thermal conductivity used by the modelling software is taken as the average value of thermal conductivity measured at room temperature and at the processing temperature. These measurements were conducted on a

guarded hot plate thermal conductivity rig.

The specific heat is also needed. An average value is obtained from the total enthalpy from a DSC scan, from 30°C up to the maximum processing temperature of the material, at a heating rate of 10°C min⁻¹.

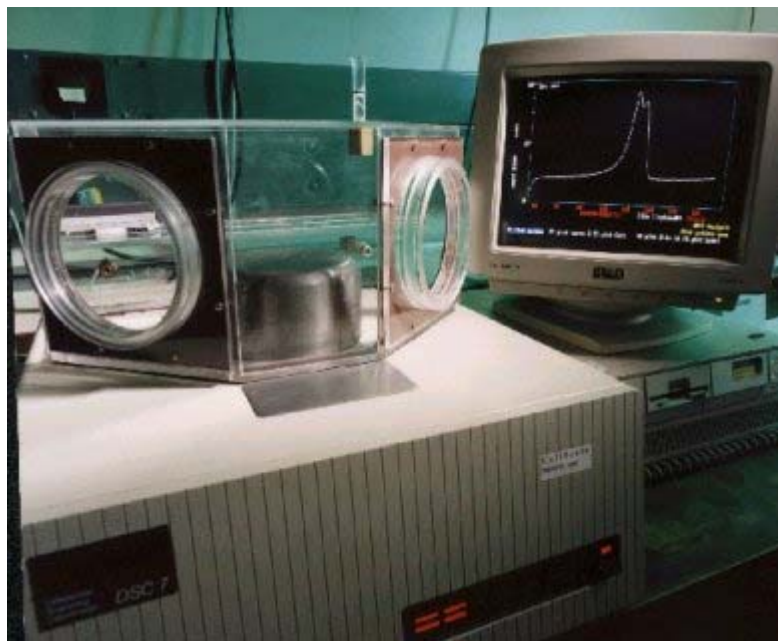


Figure 3. DSC 7 used to measure the specific heat of reactive polymer systems.

The density was calculated from measurements taken using a buoyancy balance, and by the application of Archimedes' principle.

Discussion

Figures 1 and 2 show that good fits can be obtained between the experimental data and the behaviour achieved from the fitting of specific models. For cure kinetics the data were grouped for different heating rates, and for viscosity at different oscillatory frequencies. This then enables a model to be fitted to the experimental data sets and a single set of parameters given to describe the behaviours. The accuracy of such fitting is not as good, mathematically, as is the case when fitting to just a single experimental curve, due to the range in the data set, but it is thought that this procedure is more representative of the normal behaviour of the material. The sensitivity of models to such uncertainties in the data is to be investigated within the next stage of the project.

It has been shown that the technology and expertise exist to measure and characterise the properties of reactive polymer systems. Within this project four materials have been characterised. The thermal conductivity, specific heat and density measurements on cured material were straight forward to conduct. The cure kinetics and viscosity measurements however tended to be more involved as was expected because of the complex nature of the thermo-rheological behaviour of reactive polymers.

Conclusions

- It has been demonstrated that the properties of reactive polymer systems required by commercial modelling software can be measured satisfactorily.
- For the cure kinetics and viscosity appropriate fitting routines need to be applied to obtain the desired parameters.

Further Information

A full report on this work is available. It covers the five measurement methods in more detail and presents full results on the four materials studied including details of the data fitting procedures. Please ask for an order form

from the contact below.

Further information is also available on other aspects of polymer processing including:

- Industrial Assessment of Techniques to Measure Rheological Properties of Polymers During Processing.
- Heat Transfer Relating To Polymer Processing.
- Viscoelastic Measurement Techniques for Polymer Melts (improved MFI and extensional viscosity testing).
- Improved Pressure/Volume/Temperature Measurements for Polymer Processing.

Acknowledgements

This research was supported by the DTI *Materials Measurement Which Affect Processability* programme.

Additional Information

NPL also runs a Polymer Processing Measurement Club. For further information on this club, the other research projects or to order a copy of the full report on the measurement of reactive polymer systems please contact:

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CMMT(MN)047

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