APPLICATION**NOTE**

Thermokinetics Software to Predict a Curing Reaction

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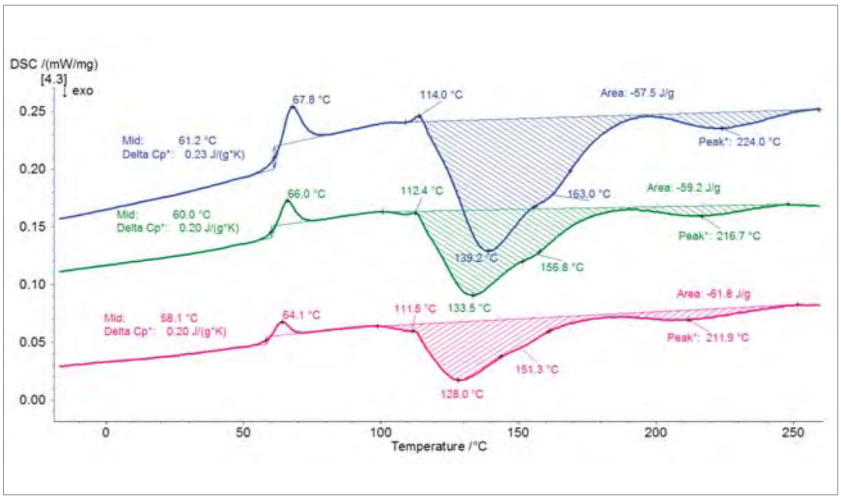
Introduction

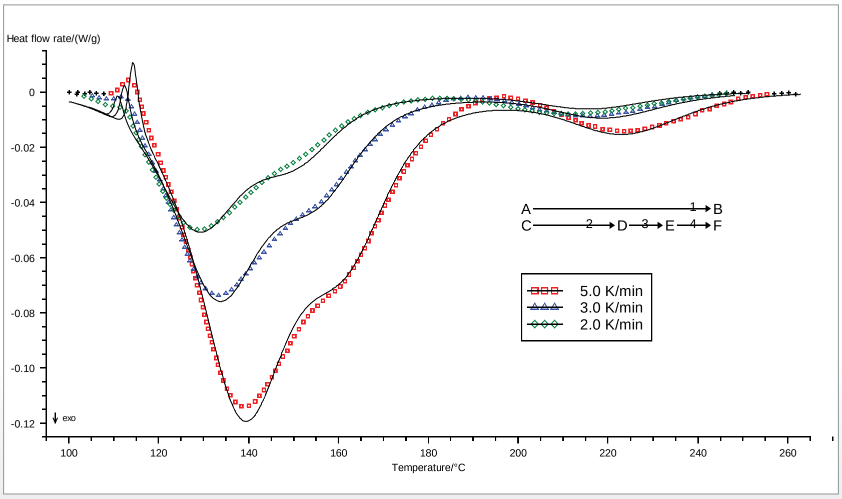
Phenol formaldehyde resins are thermosets obtained by the polycondensation of formaldehyde with phenol or substituted phenol. They are the first synthetic resins to have been developed. The most famous phenol formaldehyde resin, best known as Bakelite, got its name from Leo Baekeland who produced it commercially.



1 DSC measurement at 2, 3 and 5 K/min

Test Conditions

The curing of a phenol formaldehyde resin was measured with the DSC 214 *Polyma* using high-pressure crucibles. The curing of PF is a polycondensation reaction which is connected with a loss of water. In an open crucible, the evaporation of water would cause an endothermic effect in the DSC curve which superimposes the exothermic curing reaction.



2 Comparison of the DSC curves measured with the DSC 214 *Polyma* (dotted lines) and those calculated with *Thermokinetics* software (solid lines); coefficient of correlation >0.99.

Three samples of approx. 20 mg each were prepared and measured at 2, 3 and 5 K/min from room temperature to 260°C.

High-pressure crucibles hold 100 bar of pressure and are consequently ideal for measuring polycondensation reactions in a DSC

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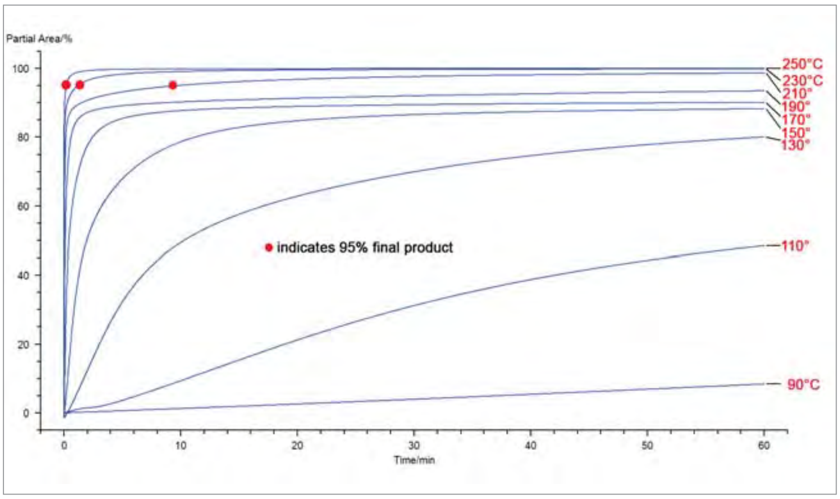
Test Results

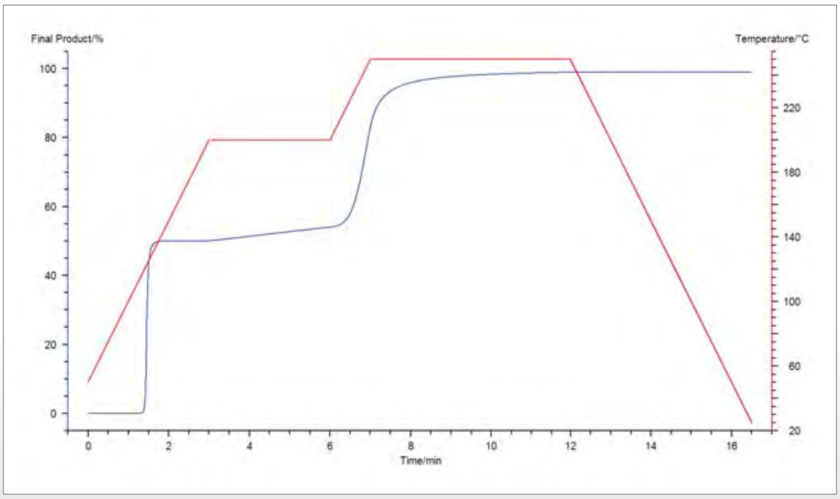
The endothermic step detected in the three DSC heating curves comes from the glass transition of the uncured polymer. As expected, it shifts to higher temperatures as heating rates increase (mid-point at 58°C and 61°C for the measurements at 2 K/min and 5 K/min, respectively). It is overlapped with a relaxation peak that comes from the release of mechanical stress within the sample. The exothermic double peak between 100°C and 250°C is due to the curing of the resin. All three curves additionally have a shoulder at temperatures ranging from 151°C (at 2 K/min) to 163°C (at 5 K/min). The curing reaction is overlapped with a small endothermic peak detected at 112°C (2 and 3 K/min) and 114°C (5 K/min) that most probably comes from the melting of an additive.

These three curves were used to determine the kinetics of the curing reaction by means of the NETZSCH Advanced Software *Thermokinetics*. Due to the complex peak structure, it is supposed that the curing is a three-step reaction. The melting peak was also taken into account for the kinetics model with an independent, one-step reaction.

The result is given in figure 2. The best model for the curing reaction is a three-step one in which each step is of the n-th order type with autocatalysis. Additionally the melting effect is taken into consideration by means of a one-step reaction of the second order. With a correlation coefficient of over 0.99, the curves calculated by the kinetics model (solid lines) are in good agreement with the measured ones (dotted lines), which confirms the initial assumption.



3 Prediction of degree of conversion for different isothermal temperatures. A degree of conversion of more than 95% (displayed by red point on the curves) can only be achieved within 60 minutes for temperatures higher than 230°C.



4 Prediction of degree of conversion for a user-defined temperature program. A degree of conversion of 98% is achieved during the second isothermal segment (250°C) after 9.5 minutes.

The kinetic model can now be used to predict the rate of reaction for a specified temperature program. As an example, figure 3 shows the curves of the final product determined by the partial area as a function of time for different temperatures between 90°C and 250°C. It is also possible to predict the percentage of final product during any temperature program defined by the user, as shown in figure 4.

Conclusion

High-pressure crucibles were used with the DSC 214 *Polyma* to investigate the curing reaction in a phenol formaldehyde resin. Three measurements at different heating rates allow for the determination of the reaction kinetics by means of the *Thermokinetics* software. The kinetics model can then be used to make predictions with regard to the behavior of the system under user-defined temperature conditions like processing conditions.

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