



Synergy of the combined application of thermal analysis and rheology in monitoring and characterizing changing processes in materials

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SCOPE

Rheology and Thermal Analysis are important technologies used in material characterization and applied to performance and processing problem solving issues. Both techniques are extensively used in product formulation and development of new or modified products, and in the past these techniques were applied independently most of the time.

However for many applications and especially for monitoring and characterizing physical or chemical structure changes in materials, as shown in the following, the combined and targeted use of the two methods provides also synergy advantages.

INTRODUCTION

Chemical and physical processes in materials often go along with quite significant changes of the materials' microscopic and/or molecular structure. Typical examples of chemical processes are the cross-linking of thermosets or the gelification of starch. Examples of physical processes, usually reversible, are the gelation of gelatin or the structure build-up in complex fluid systems including cosmetics, paints, slurries, etc..

Product quality and performance during processing or in the final application are not only dependent on the actual or final structure of the material, but also on the time dependent changes and the external conditions. Thermal Analysis and Rheology have become the most important characterization techniques because of their sensitivity to small changes in structure and the ease to monitor these structure changes. Recent developments of TA also have advanced considerably the frontiers in speed and accuracy of these techniques. [1]

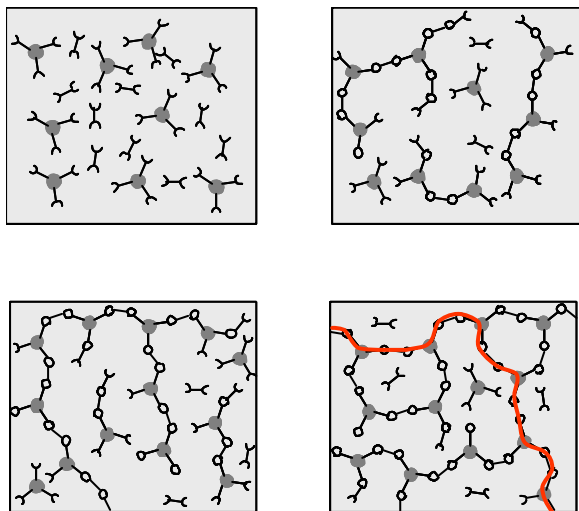


Figure. 1 Schematical representation of the formation of a cross-linked network

APPLICATION EXAMPLE: THERMOSETS

Thermosets are solid materials, which result from cross-linking of multifunctional monomer units. The typical example are the Epoxy, Phenolic and Urethane based resins. The functionality of the monomers defines to a large extent the structure of the network. For a cross-linked system to form not just linear polymer chains, at least one of the educts

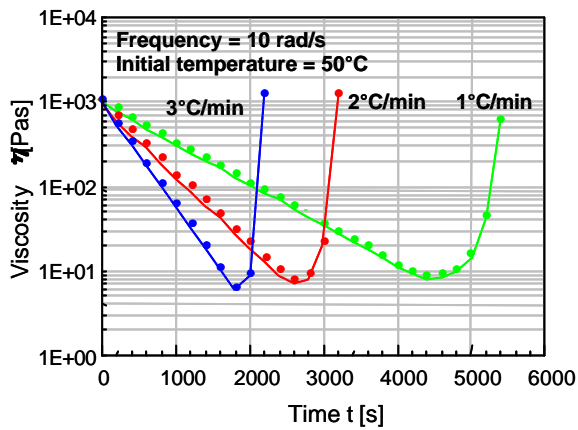


Figure. 2 Viscosity profile during curing at different heating rates

has to be tri-functional. For example, cross-linked poly-urethane grows from a di-isocyanat and a triol.

In figure 1, the crosslinking reaction of a dimer and a trimer are shown schematically. An important physical quantity is the time, when a closed path over covalent bonds throughout the sample exists. At this point the steady viscosity becomes infinite – this point is referred to as gel point and depends predominantly from the chemical network structure.

A cross-linking reaction is typically monitored at constant temperature (isothermal) or at increasing temperature from a starting to a final value while recording the thermal and/or rheological parameters. As such, the viscosity decreases first with increasing temperature, then goes through a minimum as time and temperature advance to increase again, due to the extend of the cross-linking reaction. The viscosity of the resin during the reaction is an important parameter during manufacturing of carbon fiber reinforced composites for example. At the minimum, the viscosity has to be low enough to allow good wetting of the fibers and consequently

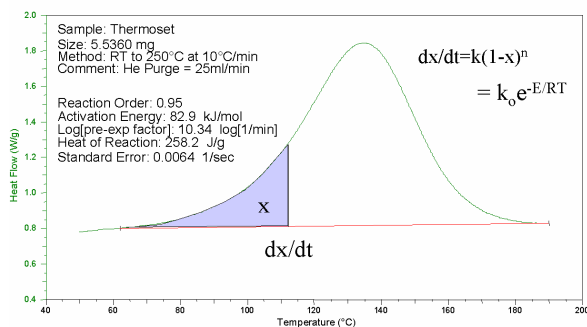


Figure 3 DSC trace used to determine the kinetics of the reaction.

provide a good adhesion of the fibres in the final product.

The location of the viscosity minimum in time is important and controls manufacturing parameters such as processing equipment settings. The heat flow, measured in a differential scanning calorimeter DSC under the same thermal conditions represents mainly the reaction heat of the cross-linking process. The reaction heat is a thermodynamic parameter and correlates to the conversion of the educts. Therefore, the measured heat flow represents the extend of reaction, or - how many monomer units have reacted under the given temperature conditions. (Figure 3)

A direct result of the cross-linking reaction for thermosets such as Epoxy- and Phenolic- resins, is a strong increase of the glass transition temperature. While the glass transition temperature of the educts

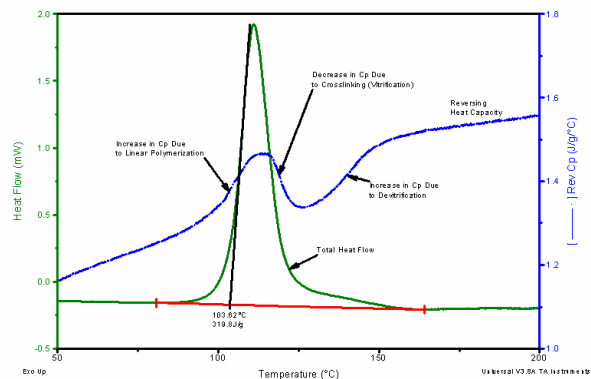


Figure 4 MDSC trace obtained during the reaction of an epoxy resin

is below the reaction i.e. test temperature, the glass transition, depending on the imposed temperature profile, may increase faster than the test temperature. As the glass transition temperature approaches the test temperature, the mobility of the growing network is significantly reduced. The reaction is now controlled by the diffusion of the reactive end groups and comes to a stop. The classic DSC measurement however cannot determine the change in the heat capacity, because the test signal is dominated by the heat of reaction. The modulated DSC (MDSC) however can detect the small change in the heat capacity. The MDSC modulates the temperature ramp with a small amplitude sinusoidal oscillation. These small variations in the temperature induce also small periodic variation of the measured

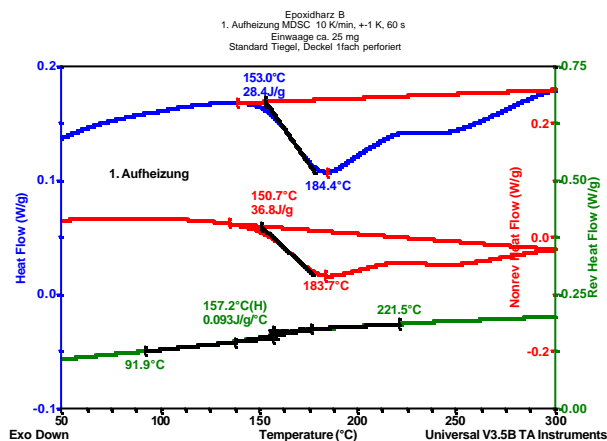


Figure 5 Postcuring of an epoxy resin (heating rate: 10 K/min, Amplitude: 1 K, Periode: 60 s)

heat flow. The correlation of temperature and heat flow generates two heat flow signals, the reversing heat flow, which represents the heat capacity changes during the reaction and the non-reversing heat flow, which is a measure of all kinetic effects, as shown in figure 4. The glass transition is a reversible quantity and therefore shows up as a change of the heat capacity. The heat of reaction is non reversible and therefore has no influence on the heat capacity.

With increasing temperature, the heat capacity signal increases as a result of the advancing cross-linking reaction. After reaching a maximum in the heat flow, the heat capacity signal decreases, due to the glass transition temperature approaching the test temperature - the sample changes from a rubbery to a glassy state - the reaction is now diffusion controlled. Since the test temperature increases continuously, the sample devitrifies and the heat capacity increases again, the reaction continues. The prove is the slow asymptotic fall of the reaction heat.

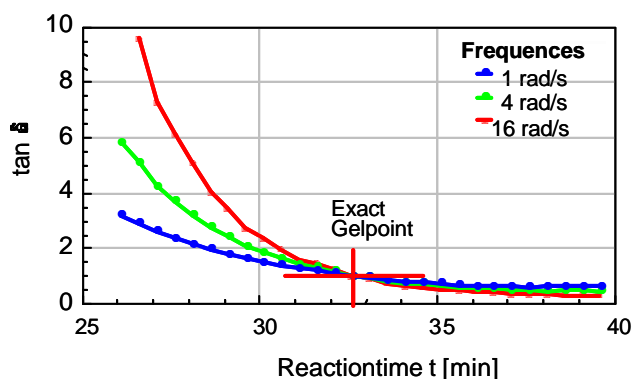


Figure. 6 Determination of the gel point

High performance composites, have to follow a well defined temperature profile in order to be able to reach the desired conversion level and the required strength. In order to determine the extend of reaction, the cured sample is subjected to a new DSC run. The post cure reaction hides the effect of the glass transition. (Figure 5). Again, only the MDSC is able to provide the desired glass transition temperature and the extend of the post curing.

The measurement of the heat flow or the heat capacity provides important information on the reaction, the reaction kinetics and the conversion. However, the thermal analysis does not provide any information about the structural changes at the molecular level. When probing the sample during the reaction with a small sinusoidal deformation, then the measured torque, after correlation with the input deformation, provides two quantities, the storage modulus G' or the stored (recoverable) mechanical energy and the loss modulus G'' or dissipated (non-recoverable) mechanical energy. The storage modulus and the mechanical loss $\tan \delta$ (the ratio of G''/G') are characteristic for the

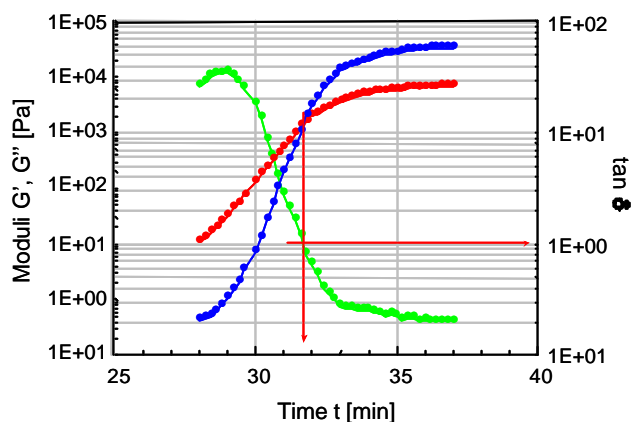


Figure 7 Determination of the gel point from the cross over of G' and G''

changes of the material's structure during cure [2]. According to Winter et al [3], G' and G'' as a function of frequency, follow a power law behavior at the gel point, in other words, the $\tan \delta$ curves cross at the same time for all frequencies (Figure 6).

At the gel point, G' and G'' are proportional to the frequency to the power n

$$G' \propto G'' \propto a\omega^n \quad [6].$$

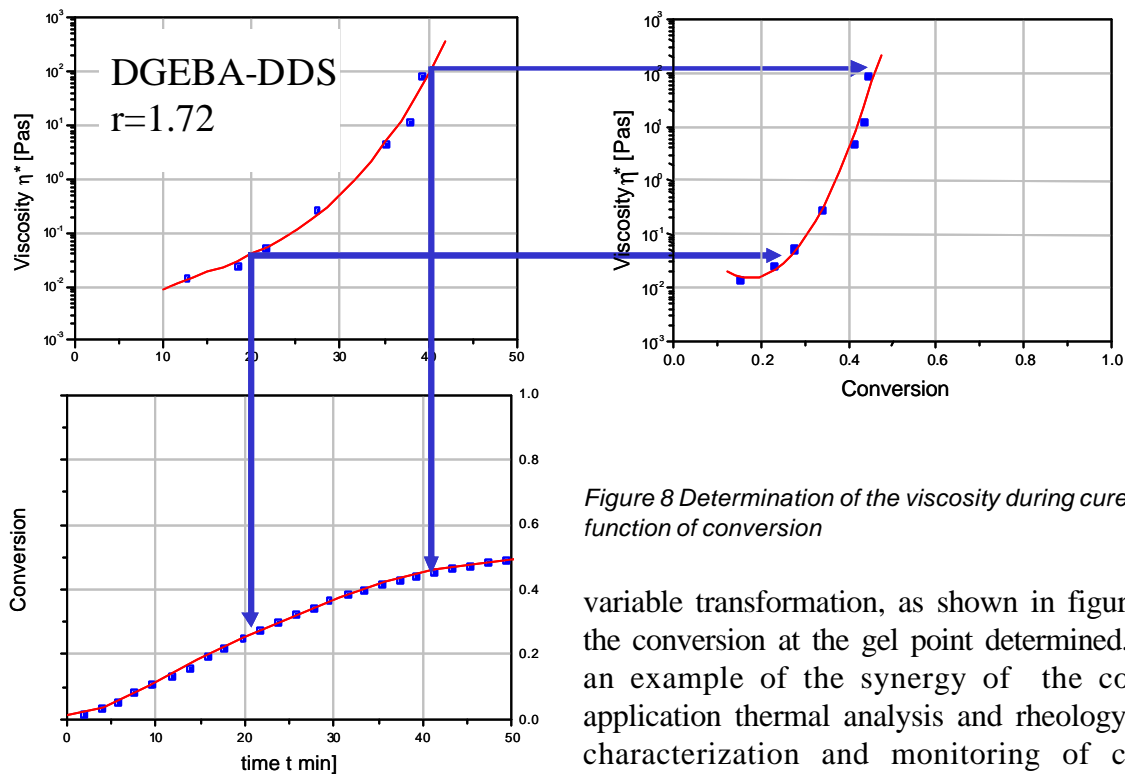


Figure 8 Determination of the viscosity during cure as a function of conversion

variable transformation, as shown in figure 8 and the conversion at the gel point determined. This is an example of the synergy of the combined application thermal analysis and rheology for the characterization and monitoring of chemical processes in materials

The value of the exponent is approximately 0.5, if the stoichiometry is equilibrated. In this case $\tan \delta$ is approximately 1 at the gel point. This is the reason, why the cross over of G' and G'' can be used to determine the gel point according to figure 7.

Rheology and thermal analyses complement each other extremely well for measuring chemical changes in materials, such as the curing of thermosets. The DSC provides information on the extend of reaction and the conversion as a function of time, the rheology provides information about the structural changes, the gel point and also processing parameters in terms of the viscosity as a function of time. If the thermal and mechanical analysis have been performed with the same thermal history (temperature profile), the viscosity as a function of conversion can be easily calculated by

CONCLUSION

Thermal Analysis and Rheology are complementary analytical techniques for the characterization of chemical processes in materials, as shown for the crosslinking of thermosets. The combination of the two techniques is synergetic and - thus provides additional information in regards to the structural changes and conversion during the crosslinking reaction.

LITERATUR

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