Chemorheology

Reaction kinetics of an Epoxy Resin under Isothermal Conditions – the Time-Temperature-Transformation (TTT) Diagram

Giorgia Scetta

Introduction

Crosslinking or "cure" of a thermoset polymer is the transformation of a liquid thermoset resin formed by small functional molecules (monomers) into a polymeric solid made up of a three-dimensional macromolecular network. The crosslinking reaction is of fundamental importance for the manufacture of a wide range of structural composites, coatings, adhesives, etc.. During the reaction, the material may pass through some or all of several different physical states:

1. Liquid
2. Rubbery sol/gel (rubbery network diluted by free monomers and oligomers)
3. Elastomer (rubbery network incorporating all the molecules initially present in the mixture)
4. Glassy state (vitrified liquid, sol/gel or elastomer)
5. Carbonization (charring)

The transitions between these states are characterized by a corresponding transition time, which is in turn linked to the reaction kinetics. The fundamental parameter that defines the transition from the liquid to the gel state is the chemical conversion. If the temperature dependence of the reaction kinetics is known, it is possible to predict the chemical conversion and hence the gelation time, $t_{gelation}$, as a function of time and temperature, based on isothermal experiments at different reaction temperatures, T_{cure}. Most thermoset resins react at temperatures well below $T_{g\infty}$, defined as the glass transition temperature, T_g, of the fully reacted thermoset polymer, provided they are liquid, i.e., that $T_{cure} > T_{g0}$, where T_{g0} is the initial T_g of the reaction mixture. However, the T_g of the system will generally increase with conversion, and therefore with time, until $T_g = T_{cure}$, which defines a vitrification time, $t_{vitrification}$. After vitrification, the reaction rate decreases very sharply, because it is strongly dependent on the mobility of the reacting species, and mobility is suppressed when the system enters the glassy state. If we want the reaction to go to completion and hence optimize T_g in a reasonable time, it is therefore important that T_{cure} be close to or above $T_{g\infty}$. However, if T_{cure} is too high, chemical degradation may result in carbonization or "charring" after long times. A convenient way to represent these events as a function of time and T_{cure} is to construct a time-transformation-temperature (TTT) diagram for a given resin, as described in the attached article. Such diagrams are an important tool for optimizing processing conditions for a given resin.

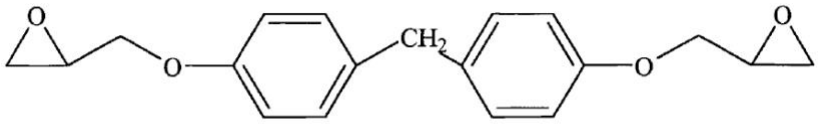
The purpose of this practical is to use rheology to monitor the rheological properties of an epoxy resin during cure and hence to identify the gelation time at different T_{cure}. The activation energy of the reaction will then be estimated from the gelation time, $t_{gelation}$, at different T_{cure}, assuming gelation to occur at constant conversion. Finally, a TTT diagram will

be sketched semi-quantitatively for this system. The practical lasts a total of four hours (2 hours in the laboratory and 2 hours to write the report).

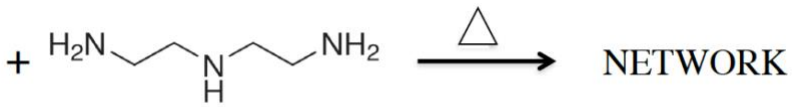
Theory

Crosslinking (Curing) of an Epoxy resin

The starting thermoset resin is a liquid epoxy precursor, consisting of bisphenol F diglycidyl ether (DGEBF)-based bifunctional oligomers, mixed with a liquid cross-linking agent (hardener), diethylenetriamine (DETA). All the molecules in this liquid have a low molecular weight compared with the final thermoset polymer, whose molecular weight becomes effectively infinite as the reaction goes to completion. They are hence referred to as monomers. Crosslinking initially involves reactions between the epoxy groups of the DGEBF -based precursor with primary and secondary amine groups of the DETA crosslinking agent to form dimers. The dimers can then react with each other or with other monomers to form trimers, and so on, resulting ultimately in a single macromolecule (polymer) incorporating all the monomers initially present in the system, assuming the reaction mixture to be stochiometric, so that there are no unreacted functional groups left over at the end. In the present system, reaction of an epoxy group with a primary amine will result in a secondary amine, which may react with another epoxy group. The effective functionality, f, of the DETA is therefore theoretically 5, which means that if we have enough DGEBF molecules in the mixture for all of these functional groups to react, each DETA molecule will be linked, via DGEBF molecules, to 5 other DETA molecules. We therefore obtain a three-dimensional crosslinked network rather than linear macromolecules as the reaction progresses.



Bisphenol F Diglycidyl Ether



DETA

The time, $t_{gelation}$, often referred to as the gelation time or *gel point*, at which a continuous three-dimensional network is first established (the gel point) corresponds to the transformation from a viscous liquid to a viscoelastic sol/gel, i.e., a mixture of a continuous elastic network and unattached monomers and oligomers. Beyond this time, the remaining sol molecules gradually attach to the network, and, if the temperature, T_{cure}, is high enough, and the reaction mixture is stochiometric, the final result is a fully crosslinked network. However, as the degree of crosslinking increases, the molecular mobility decreases, implying an increase in the glass transition temperature, T_g, of the system. Hence, as discussed previously, if T_{cure} is too low, vitrification will take place well before the reaction is complete. The molecular mobility will then decrease to very low levels, making it difficult to achieve a high degree of conversion and a high T_g within a reasonable reaction time. On the other hand, too high a T_{cure} may result in chemical degradation and carbonization (charring) after long times.

Experimental part

Tests

The crosslinking reaction of an epoxy/hardener mixture is monitored by measuring the time-dependent rheological properties of a few drops of the mixture placed between the parallel plates of an Anton Paar shear rheometer. The real and imaginary parts of the complex shear modulus, G' and $G"$, are determined as a function of time at different temperatures.

Materials

The material is a bifunctional Epon™ 862 epoxy resin based on DGEBF mixed with a diethylenetriamine hardener (DETA, Aldrich) in a 100/12 ratio by weight.

Analysis

The dependence of the reaction rate of a given system on temperature may be expressed using an Arrhenius-type equation. If the reaction rate is independent of time and $t_{gelation}$ corresponds to a certain constant degree of conversion, this implies that

$$t_{gelation} = A \exp \frac{E_A}{RT_{cure}} \quad (1),$$

where:

A is a constant
E_A is the activation energy f the reaction
R is the universal gas constant (8.3144 J/mol/K)
T_{cure} is the temperature of reaction

By assuming $t_{gelation}$ under isothermal conditions at different T_{cure} to correspond to the time at which G' and $G"$ cross over, it should hence possible to determine the constant A and the activation energy E_A. Depending on the available time, at least two isothermal experiments will be carried out during the practical.

- To analyze the reaction kinetics, you may make use of the results of these experiments together with results for the same resin obtained previously at other temperatures, to be provided during the TP.
- Plot $\ln t_{gelation}$ as a function of $1/T$ and hence determine A and E_A.
- Sketch a TTT diagram for the resin in question indicating not only the gel point according to your results, but also (qualitatively!) the regimes where you would expect full cure, vitrification and degradation to occur.

Discussion

1. Based on the constitutive equations for a Newtonian liquid and a linear elastic solid, explain the difference between purely viscous and purely elastic behavior. Describe *briefly* the behavior of a viscoelastic polymer.
2. How do G' and $G"$ change during cure of a thermoset resin? How do these changes relate to the corresponding changes in its chemical structure?
3. Describe the utility of the TTT diagram and explain the meaning of T_{g0} and $T_{g\infty}$ (see attached article).

4. Why is T_g generally expected to depend on the degree of crosslinking?

References

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