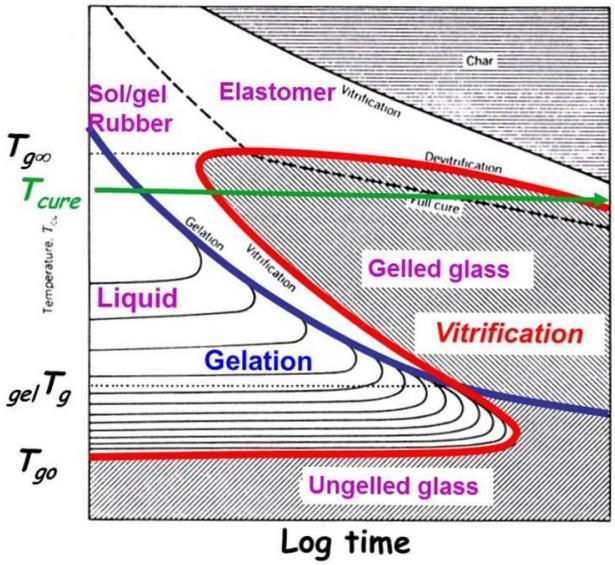
Thermoset Characterization

by:

R. Bruce Prime, Ph.D.

and

Jeffrey Gotro, Ph.D.



InnoCentrix, LLC
22431 Antonio Parkway, Suite B160-515
Rancho Santa Margarita, CA 92688
1-877-887-6596 (toll free)
Jgotro@innocentrix.com

InnoCentrix
WHERE SCIENCE IMPACTS BUSINESS™

Table of Contents

Introduction

This ebook on Thermoset Characterization is ,he first in a series on Thermosets. Others will include Thermoset Rheology, Cure Kinetics, Curing Chemistry and more titles under development. Ultimately these ebooks will be merged into a comprehensive book on thermoset characterization and practical applications of thermosetting polymers.

Thermosets are network-forming polymers. They include epoxy, phenolic, unsaturated polyester, polyurethane, dicyanate, bismaleimide, acrylate and many others. Unlike thermoplastics, chemical reactions are involved in processing by the end user. As a result of these reactions the materials first increase in viscosity and eventually crosslink and gel, and as a result they can no longer flow or dissolve. Under certain conditions the thermoset will vitrify or become glassy due to its increasing T_g. Cure is most often thermally activated, which gives rise to the term *thermoset*, but network-forming materials where cure is light activated are also considered to be thermosets.

In the uncured state thermosets are mixtures of small reactive molecules, often monomers. Catalysts are often added to accelerate cure. Most thermosets incorporate particulate fillers, fiber reinforcement or other additives to modify properties, e.g. to reduce cost, to modify physical properties such as thermal expansion or toughness, or to reduce shrinkage during cure. Thermosets generally possess good dimensional stability, thermal stability, chemical resistance and electrical properties. Because of these attributes, they find widespread use in several applications such as adhesives; primary and secondary structural members in aerospace; countertops and floors for manufacturing facilities and homes; printed circuit boards, conductive polymer elements, and encapsulation materials for electronic applications; dental materials, especially adhesives; and recreational products such as tennis racquets, bicycle frames, golf clubs and fishing rods.

Two distinguishing characteristics of thermosets are gelation and vitrification. Cure begins by the growth and branching of chains. As the reaction proceeds, the increase in molecular weight accelerates, causing an increase in viscosity and reduction in the total number of molecules. Eventually several chains become linked together into a network of infinite molecular weight. The abrupt and irreversible transformation from a viscous liquid to an elastic gel or rubber is called the gel point. In the early stages of cure the thermoset can be characterized by an increase in its viscosity. The gel point coincides with the first appearance of an equilibrium (or time-independent) modulus. Reaction continues beyond the gel point to complete the network formation, where physical properties such as modulus build to levels characteristic of a fully developed network.

Gelation is the incipient formation of a cross-linked network, and it is the most distinguishing characteristic of a thermoset. A thermoset loses its ability to flow and is no longer processable above the gel point, and therefore gelation defines the upper limit of the work life. As an example, for a *Five Minute Epoxy*, which can be found in any hardware store, the five minutes refers to the gel point. After the two parts are mixed the user must form an adhesive joint within five minutes while the material is still liquid and can flow, before it becomes rubbery, and then keep the repaired part fixtured, usually for several hours until cure is sufficiently complete. Gelation does not usually inhibit cure (e.g., the reaction rate remains unchanged), and it cannot be detected by techniques sensitive only to the chemical reaction, such as differential scanning calorimetry (DSC). Beyond the gel point, reaction proceeds toward the formation of an infinite network with substantial increases in crosslink density, glass transition temperature and ultimate physical properties.

Vitrification, a completely distinct phenomenon from gelation, may or may not occur during cure depending on the cure temperature relative to the T_g for full cure. Vitrification is glass formation due to T_g increasing from below T_{cure} to above T_{cure} as a result of the cure reaction, and is defined as the point where $T_g = T_{cure}$ (1). Vitrification can occur at any stage during the reaction to form either an ungelled glass or a gelled glass. It can be avoided by curing at or above $T_{g\infty}$, the

glass transition temperature for the fully cured network. In the glassy state, the rate of reaction will usually undergo a significant decrease and fall below the chemical reaction rate as the reaction becomes controlled by the diffusion of reactants. It is common for complete vitrification to result in a decrease in the rate of reaction by 2 – 3 orders of magnitude. Unlike gelation, vitrification is reversible by heating, and chemical control of cure may be reestablished by heating to devitrify the partially cured thermoset.

We begin with three chapters on gelation, the defining characteristic unique to thermosets. We cannot emphasize too strongly the importance of understanding this phenomenon, and also vitrification, when one wishes to design, characterize and/or control cure processes. A key aspect of understanding thermosets and their applications is to have a basic knowledge of some of the key testing methods used to characterize both the curing and final properties. These are all thermal methods where properties may be measured either while the material is being heated or at a series of constant temperatures. Because cure reactions are exothermic, i.e. heat is generated as a part of cure, differential scanning calorimetry (DSC) which measures heat flow is especially important. DSC measures conversion or degree of cure, the rate of cure and the glass transition temperature or T_g. As we will see vitrification can play a very important role in cure. While it is often to be avoided in order to reach full cure without interruption, we will see that in certain applications vitrification during cure can provide significant benefits. Thermomechanical analysis (TMA) measures linear expansion or contraction. Key properties measured by TMA are the coefficient of linear expansion or CTE, T_g, and dimensional changes associated with the relaxation of stress. Dynamic mechanical analysis (DMA) measures stress or strain under oscillatory conditions. Modulus, T_g, creep and stress relaxation may be measured. Thermogravimetric analysis (TGA) measures the mass of a material in a controlled environment. Key measurements include filler content, solvent content, moisture sorption, thermal stability, and cure that involves mass loss such as phenolics. In the following chapters we describe these techniques and illustrate the major applications to thermosets.