Is it done yet? Comparison of Methods to Monitor Degree of UV Cure

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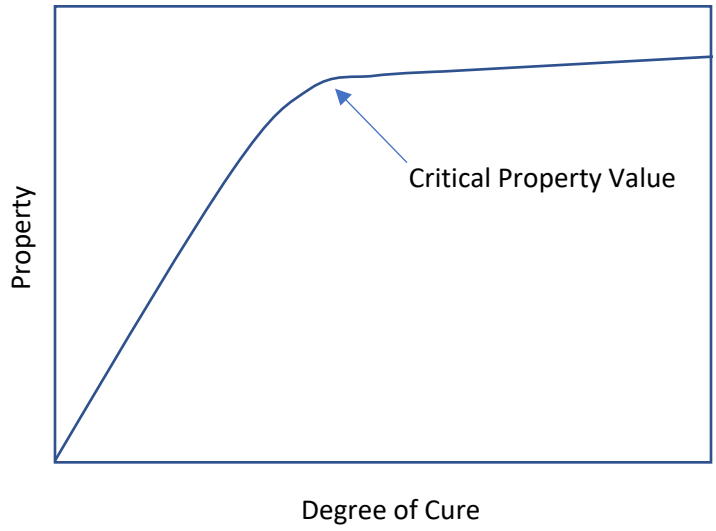
Introduction

One of the challenges with photocuring systems is understanding the development of the degree of cure and the associated physical properties. Not only do the normally measured properties like glass transitions, hardness, and strength vary with degree of cure, but important and less tested values like solvent resistance, wear, oxygen permeability, etc. also follow a similar pattern (1). The so-called dog's leg curve shows this effect; how a monomer develop polymeric properties.



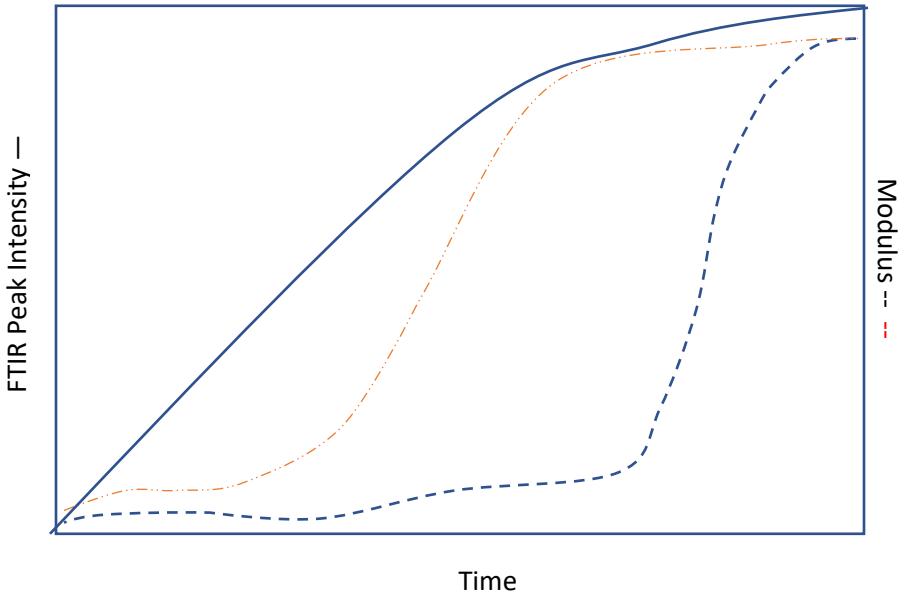
Relation physical properties to degree of cure or molecular weight. In the case where physical property is Tg, the critical Tg is where the material acts like a high polymer.

The Problem of Chemo-Rheology Agreement

One of the continuing problems with understanding the curing process is that the chemistry – the change in the components – does not always track linearly with the development of physical properties. When working in thermally cured resin systems, this was true but the development of high molecular weight species, which have implications for viscosity and other rheological properties, is dependent of the mechanism of curing. Because of this, it is possible that different methods give different answers. A classic case in thermally cured systems is certain epoxy resins, where full mechanical properties develop

at approximately 88% cure when measured by Differential Scanning Calorimeter (DSC) or Infrared Spectroscopy (FTIR).

Probably the best example of this is work done by Stansbury (2) where the cure of dental type materials by UV is followed by both Near Infrared Spectroscopy (NIR) and Dynamic Mechanical Analysis (DMA). In many cases, the chemical cure, as measured by the NIR, and the development of the viscosity and modulus, as measured by the DMA, do not track perfectly but show differences particularly in the midranges. Below we show two examples, depending on when the chains crosslink. Note in both cases, the FTIR does not track with the modulus.



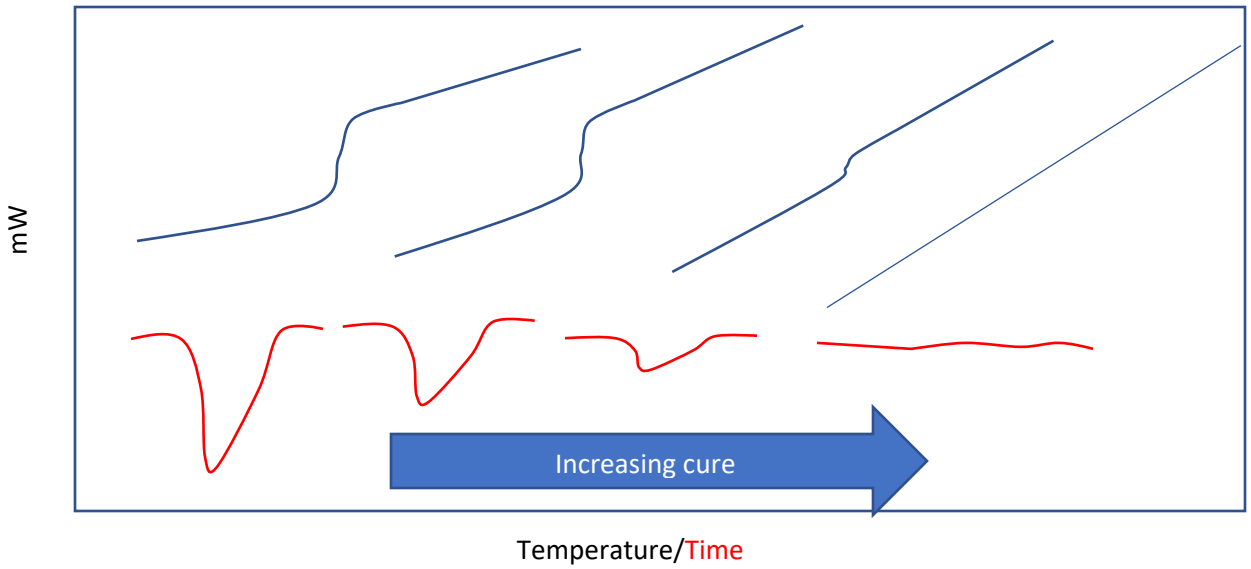
Example of relationships of FTIR and DMA tracking of UV-Cure over time.

Because of these differences, it is of importance to understand the material and what the testing method measures to obtain degree of cure. We looked at common methods to evaluate what information they give about the changes in the material and relate it to curving.

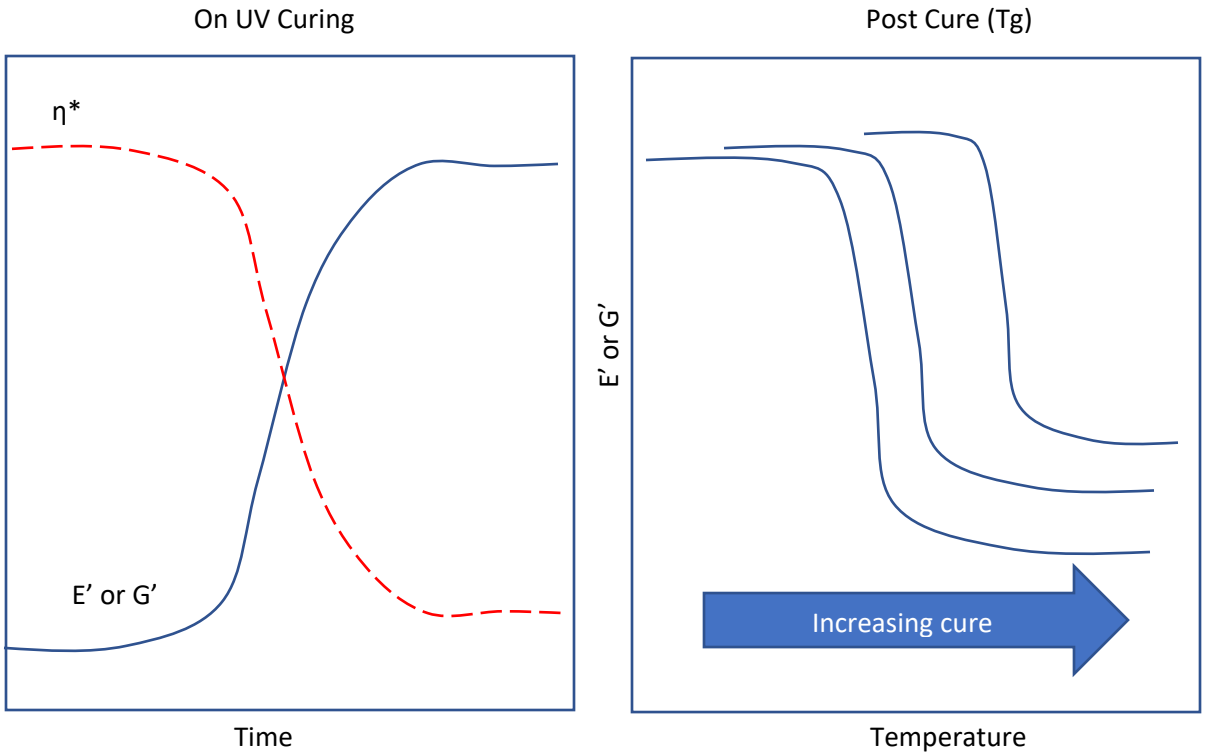
Methods: Pro and Con

Several samples of UV-curable material were tested on a variety of instrumentation. The following instruments were used with associated photo-curing attachments: PerkinElmer Spectrum 2 FTIR with ATR, PerkinElmer DSC6000 with our photo-curing attachment, Anton Paar MCR302 Rheometer, and Hitachi DMA7100. The rheometer performed testing in shear mode, with the light was applied to the sample resting on the quartz plate. The DMA test was performed in extension mode with corresponding fixtures.

Data is shown below for each method. Starting with DSC, where the flow of heat in and out of a sample is measured allowing us to determine the Tg (as a shift in the baseline heat flow signal) and the enthalpy of curing (from the peak area).



DMA and Rheology both look at the development of modulus and the increase in viscosity. As Menard (op cit.) discusses, the difference between this instrument is mostly a marketing decision as the approach is the same. An sinusoidal strain is applied to a sample and resulting stress and phase lag used to calculate modulus and viscosity.



FTIR is a special case of spectroscopic methods used for this. Depending on the chemistry, one may use FTIR, NIR, or Raman to follow the cure. The latter two allow online monitoring (for NIR, see Stansbury, op. cit.) but require considerably more investment that FTIR.

With FTIR, we track either decreasing intensity of the starting material peaks or increasing intensity of the product peaks. In an ideal system, two distinct peaks that were representative only of the uncured and cured material would be seen. As the cure progressed in said system, one peak would grow in strength, and the other shrink, until only the cured peak remains. Unfortunately, many times this is not the case and only one peak is drastically being altered during the curing process. Comparing a ratio is often used in this case.

Conclusions

Out of the variety of different test methods, no one single method of analysis is not enough to fully characterize the material, much less determine the accurate degree of cure. In many cases, there are differences in between a full compositional c Time pared to a what is mechanically full cure. Several methods are often needed to develop an understanding of the cure, which then allows use of a simpler method for production.

Method	Measures	Reports	Get degree of cure from	Pros	Cons
FTIR	Absorbance of key peaks	Peak height and cm-1	Formation/disappearance of peaks or ratios	• Rapid • Inexpensive	• Not as sensitive, may be distorted depending on if similar bonds are naturally present • No physical or thermal info
DSC	Shift in baseline	Tg	Temperature, Delta cp	• Relatively fast, • high temperature accuracy	• Have to know specific temperatures to compare to for DSC • One result per run • No mechanical data
	Energy changes	Delta H	Resulting peak/lack thereof	• Relatively fast, high accuracy	• Need comparative values • No mechanical info
DMA	Stiffness	Modulus	Modulus value, Tg location	• Effective mechanical cure	• Slow • Requires skilled tech
	Damping	Tan Delta	Peak location		
Rheology	Viscosity	Viscosity	Viscosity increase	• Apply to real world	• Very slow • Requires skilled tech

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Notes:

1) Menard, K. and Menard, N. *Dynamic Mechanical Analysis: 3rd Edition*, Taylor and Francis, 2020.

2) Stansbury, J et al. Measurement and management of stress development in Photopolymer Networks, *Radtech Reports*, Spring 2011.