INTRODUCTION

During the last several years the coatings industry has met the challenges of government regulations concerning volatile organic compound emissions and the increasing costs of petroleum based solvents by developing a variety of new coatings technologies. This has led to a need for improved methods of materials characterization. Techniques for assessing degree of cure and fractional conversion based upon fundamental reaction kinetics are included in these needs.

Mathematical modeling of the cure process coupled with the automation of various thermal analytical instruments and Fourier Transform Infrared Spectroscopy (FT-IR) have made possible the determination of quantitative cure and chemical reaction kinetics from a single dynamic scan of the reaction process. This paper describes the application of FT-IR, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) in determining cure and reaction kinetics in some model organic coatings systems.

Cure Kinetics Methodology

By assuming that the chemical and physical changes occurring during a reaction are proportional to the extent of reaction, \( F(t,T) \), a general nth order rate expression can be used to characterize reaction kinetics information obtained from FT-IR, DSC and DMA. In the equation

\[
\frac{dF(t,T)}{dt} = A \exp\left(-\frac{E}{RT}\right) [1-F(t,T)]^n
\]

\( n \) is the order of reaction, \( E(\text{kcal/mole}) \) is the activation energy.

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energy and $A(\text{sec}^{-1})$ is the Arrhenius Frequency Factor. Methods for generating fractional conversion curves from DSC data and degree of cure curves from DMA data have been described previously$^{1-3}$; the methodology for DMA cure is summarized in Figure 7.

In the single dynamic temperature scan FT-IR method, absorbance bands for reactive functionalities which have decreased or increased during a reaction are compared to absorption bands corresponding to non-reactive, and therefore unchanging, functionalities. Changes in the ratio of these values during a reaction are illustrated in Figure 1a. Normalization of the curve in Figure 1a according to equation (2) leads to the conversion curve in Figure 1b.

\[
F(t, T) = \frac{A(t, T) - A_0}{A_f - A_0}
\]

(2)

where $A_0$ is the absorbance of the functionality of interest prior to the start of the reaction, $A(t, T)$ is the absorbance at a specific time and temperature, and $A_f$ is the absorbance at the end of the reaction. Evaluation of DSC data to obtain the kinetics parameters $n$, $E$ and $\ln A$ involved a multiple regression method$^{1-3}$ applied to equation (1). Evaluation of FT-IR and DMA data to obtain the kinetics parameters $n$, $E$ and $\ln A$ involved a simplex minimization method applied to fractional extent of conversion or degree of cure curves, respectively$^4$.

**MATERIALS**

The samples used in this study include a modified blocked isocyanate, isophorone diisocyanate (IPDI), (B-1370, Huls AG, Gelsenkichen-Buer, W. Ger.) and both catalyzed and uncatalyzed polyester gel coat resins. Gel coat cure reactions were initiated with the addition of 1.0 wt. percent of methyl ethyl ketone peroxide (MEKP, Lucidol Div., Pennwalt Corp., Buffalo, N.Y.) and catalyzed with the addition of 0.15 wt. percent cobalt octoate solution (12% cobalt in mineral spirits, Mooney Chemicals, Cleveland, OH.).

**EXPERIMENTAL**

**FT-IR**

Spectra were obtained at a resolution of 4 cm$^{-1}$ with a Digilab FTS-15E Fourier Transform spectrophotometer. Thirty scans were co-added to produce one spectrum. A reference spectrum of the NaCl salt crystal was collected before the material to be analyzed.