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NOTE

Refractometric Determination of the Stoichiometry of Reacting Polymer Systems

INTRODUCTION

The measurement of refractive index is an analytic technique frequently applied to the study of polymers and polymer systems. This method has found useful application in the determination of the density and birefringence of polymer films,[1-3] evaluation of the partial specific volume of macromolecules,[4,5] and analysis of monomer–polymer solutions.[6]

Another application in which the refractometric technique can conveniently be used is to monitor the stoichiometry of reacting two component streams, which are dispensed from metering-mixing equipment during the fabrication of cast polymer systems. Although the technique is a classical use of refractometry, i.e., measurement of the refractive index of a two-component solution and determination of component concentration from a calibration curve, the significance of the method lies in the rapidity of the measurement. Because the stream components begin reacting when mixed, the changing concentration of the reactants makes it difficult to use standard wet method analysis for determining component stoichiometry. Since the refractive index can be measured rapidly (15–20 sec), this method can be used to determine the concentrations of components before they are significantly changed by the reaction. In some cases the reaction of the components may be very rapid, thus eliminating refractometry as a useful technique. Using equipment such as an in-line infrared analyzer for direct analysis of the stream components, one could determine component concentrations at even shorter reaction times. The increased expense of in-line analysis frequently eliminates this technique from being used. The rapidity of the refractometric method and relatively low instrument cost makes this an ideal way to measure reacting component concentrations.

In this work, the application of the refractometric method to check the stoichiometry of urethane streams containing polyurethane prepolymers and amine curatives is described. Although the method was applied to polyurethane systems, it can also be used to monitor other types of reacting two-component streams.

EXPERIMENTAL

For this study, the refractive index of polyurethane prepolymer–amine curative mixtures having curative concentrations between 0 and 12% was measured. The prepolymer was Cyanaprene A-8 urethane elastomer (American Cyanamid Co.), and the amine curative was methylenebisorthochloraniline (Cyanaset M urethane elastomer curative, American Cyanamid Co.). The two components were weighed, melted, and mixed at approximately 100°C. The refractive index of the mixture was measured with an Abbe refractometer within 30 sec after adding the curative to the prepolymers. It should be noted that the refractive index values were measured at room temperature, since the hot component mix cooled when smeared on the refractometer prism. Although both the prepolymer and curative are solids at room temperature, the refractive index measurement could be made because both the pure polymer and prepolymer—curative mix supercool and remain as clear viscous liquids. If this technique is applied to a system which solidifies, it may be difficult to obtain a good separation of the dark and light fields of the refractometer. If solidification becomes a problem, the measurements should be attempted at elevated temperatures.

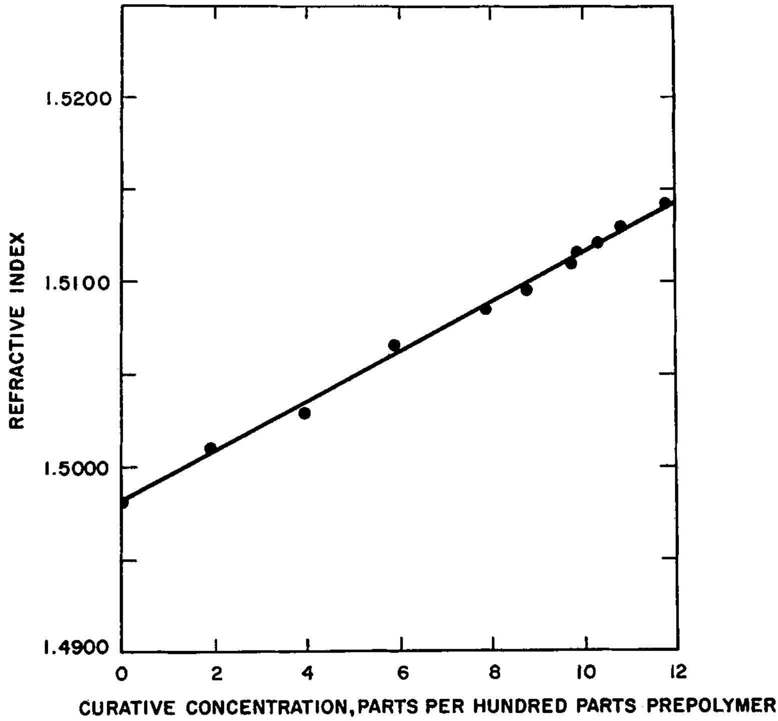

Fig. 1. Refractive index of prepolymer curative mix vs. curative concentration.

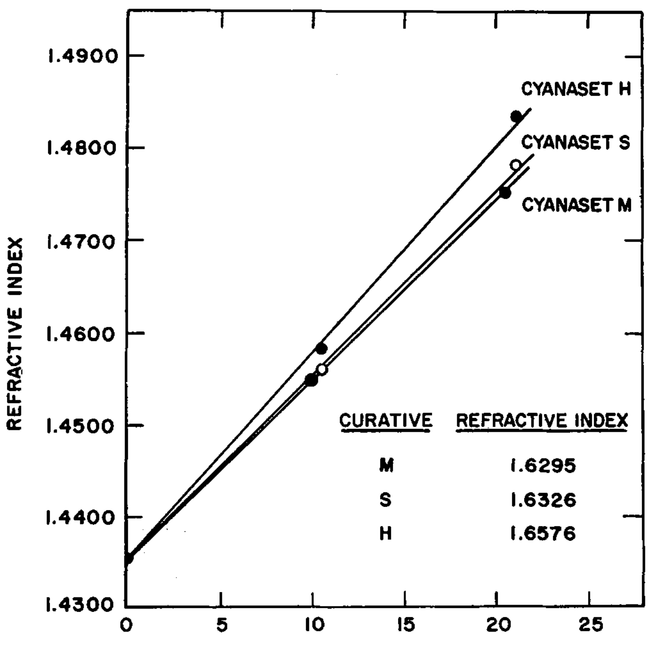

Fig. 2. Refractive index vs. concentration of curative dissolved in dimethylacetamide.

DISCUSSION

The refractive index of a two-component mixture depends primarily on the refractive indices and concentrations of the components and on the association or intermolecular forces existing between the components. In many cases, the refractive index of the mix can be expressed in terms of an empirical linear or nonlinear mathematical expression which allows one to predict the mixture refractive index from the concentrations and refractive indices of the components. Such expressions are established by measuring the refractive index of mixtures of the two components of interest, plotting an experimental calibration curve, and determining an empirical equation which relates the refractive index to component concentration. This technique was used in this work.

In Figure 1 is shown a plot of refractive index as a function of the amount of Cyanaset M curative added to a Cyanaprene A-8 prepolymer. It can be seen that, for the system tested, the refractive index of the mixture was a linear function of curative concentration described by the equation

$$\eta_m = (\eta_2 - \eta_1)C_2 + \eta_1 \tag{1}$$

where η_m, η_1, and η_2 are the refractive indices of the mix, prepolymer, and curative, respectively, and C_2 is the curative in the mix, in parts per hundred. From the slope of the line and measured refractive index of the prepolymer, $\eta_1 = 1.4980$, the effective refractive index, $\eta_2 = 1.6293$, of the amine curative was determined.

Because the melted curative solidifies when placed on the refractometer prism at room temperature, the refractive index of this material could not be measured directly as was done with the prepolymer. An alternate method of determining the curative refractive index used in the laboratory involved dissolving known amounts of the curative in dimethylacetamide and determining the curative refractive index from a plot of solution refractive index versus curative concentration. This method requires fewer data points, is easier to set up experimentally, and is done in a system in which the curative is unreactive. Figure 2 is a plot of refractive index as a function of curative concentration for three amine curatives, which include Cyanaset S and H (methylenebisorthochloraniline + dichlorobenzidine) and Cyanaset M (methylenebisorthochloraniline).

It can be seen that for these systems, as for the prepolymer–curative system, the refractive index was a linear function of the curative concentration. The value of $\eta_2 = 1.6295$ calculated for Cyanaset M agrees well with the index of 1.6293 determined from the data in Figure 1. From the slopes of the lines for Cyanaset S and H (Fig. 2), respective refractive index values of 1.6326 and 1.6576 were determined. Utilizing the curative and prepolymer refractive indices and eq. (1), relations describing prepolymer–curative concentrations could be established for various component systems.

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