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Intrinsic Fluorescence Cure Sensor for Reaction Monitoring in Polyurethane

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13. ABSTRACT *(Maximum 200 words)*

Fluorescence spectroscopy and UV absorption were used as main tools to monitor the reaction of methylene diphenyl-4,4'-diisocyanate (MDI) with 1-butanol, poly(propylene oxide) (PPO) and diethyl toluene diamine (DETDA) using the curing agent MDI as a chemical and spectroscopic sensor. The MDI virtually has no fluorescence, but shows strong fluorescence emission at about 310 nm after changing into urethane. The emission of DETDA appears at 343 nm which is about the same wavelength as that of the urea formed. However, the urea shows higher fluorescence quantum yield. The fluorescence intensity changes were applied to monitor the polymerization process. FTIR was used to obtain the extent of reaction by following the disappearance of the isocyanate group. Correlation curves between the fluorescence intensity changes and IR results were derived making the fluorescence changes applicable in the estimation of the extent of reaction.

14. SUBJECT TERMS
Intrinsic fluorescence, methylene diphenyl diisocyanate (MDI), polyurea, polyurethane, butane diol, diethyl toluene diamine

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Intrinsic Fluorescence Cure Sensor for Reaction Monitoring in Polyurethane

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INTRODUCTION

Polyurethane reaction process has been studied by many techniques such as titration [1], dilatometry [2], IR [3], thermal analysis [4] and adiabatic temperature rise [5]. However, to follow the detailed concentration change of the reaction species with these techniques is still hard to persuade. In our group, we have applied UV-VIS and fluorescence techniques in the kinetic study of urethane production, in which the reactive molecular sensor has been used to mimic the isocyanate reaction [6]. They showed an advantage in the capability of providing information on the composition of a reaction mixture beside the extent of reaction. This advantage makes it possible to follow the composition changes through the cure process and to analyze the kinetics and the mechanisms of several consecutive polymerization steps. The molecular sensor which has also diisocyanate structure showed spectral changes in UV and fluorescence due to the substituent effect on the chromophore. However, extrinsic sensor may not always be desirable and is inconvenient sometimes during the processing.

In this paper, we report on an intrinsic spectroscopic technique for in-situ characterization of polyurethane which could be used in the reaction injection molding. The commonly used diisocyanate curing agent, methylene diphenylene diisocyanate (MDI) is not fluorescent. However, it becomes highly fluorescent after it reacts with alcohol or amine to form urethane or urea links. Therefore, we applied this property to monitor the kinetics of polyurethane formation without addition of any chromophore.

The UV-visible and fluorescence behavior was studied *in model urethane reaction before the urethane* polymerization. The polymerization of urethane was carried out in solution to avoid the fluorescence intensity increase due to the viscosity change. FTIR results were used to calibrate the extent of reaction.

EXPERIMENTAL

The methylene diphenyl diisocyanate (MDI) was dissolved in cyclohexane with the concentration of 2.3×10^{-4}M. Excessive amount of dry 1-butanol was added and the reaction was carried out under dry nitrogen at two different temperatures, 50°C, and 70°C. For polymerization reaction, stoichiometric amounts of MDI and poly(propylene oxide) (PPO, Mn=2000) which was predried in vacuum oven at 50°C for 24 hours, were dissolved in anhydrous DMAc. The concentration of MDI was 3% by weight. The reaction was carried out at 50°C, and 70°C in sealed bottles. The polymerization reaction of stoichiometric amounts of MDI with diethyltoluene diamine(DETDA) which is commonly used as a chain extender, was also carried out in DMAc. Both the model compound reactions and the solution reactions were monitored by UV and fluorescence techniques, and the spectra were taken at room temperature. FTIR was used to acquire the extent of reaction.

RESULTS AND DISCUSSION

1. Model Urethane Reaction

The longest absorption peak of the UV spectrum of MDI appeared at 283 nm in cyclohexane which is red-shifted to 288 nm with the reaction process. This is due to the electron-donating nature of the urethane substituent compared to that of the isocyanate substitute. MDI virtually has no fluorescence as can be seen in Figure 1. However, with the reaction of MDI with 1-butanol, strong fluorescence emission was observed at about 305 nm with the excitation wavelength at 290 nm. The intensity of this emission peak increases with the progress of urethane reaction indicating that the fluorescence quantum yield of urethane is much higher than that of the isocyanate. Figure 2. shows the fluorescence intensity increases with reaction time at 50°C, and 70°C. The intensity change stopped at about 50 minutes for 50°C reaction, and 15 minutes for 70°C reaction. The level-off in the intensity indicates the completion of reaction based on the diurethane model compound study at the same concentration.

2. Urethane Polymerization in Solution

The fluorescence emission from the reaction of MDI with PPO was observed at 315 nm, while the emission from the reaction of MDI with DETDA was found at 344 nm (Fig.3). These two peaks are well separated. Since DETDA is a commonly used chain extender for polyurethane, it possible to monitor both urethane and urea formation at the same time during the polymerization process. The intensity of the urethane emission at 315 nm increased with the reaction time and leveled off at about 60 minutes at 50°C. In the urea reaction, it took only about 20 minutes to finish (Fig.4). DETDA shows the strong fluorescence emission at 343 nm. With the progress of polymerization, the intensity of this peak increased with reaction time. However, there is no obvious spectral shift observed. This indicates that the fluorescence emission of the forming urea has similar emission wavelength as DETDA but higher fluorescence quantum yield. The extent of reaction was obtained from FTIR study following the disappearance of NCO group (Fig.5). The data is comparable with the fluorescence results. The correlation curves were derived by plotting the fluorescence intensity changes versus the extent of reaction from IR (Fig.6). These curves can be used to estimate the extent of reaction by fluorescence measurement.

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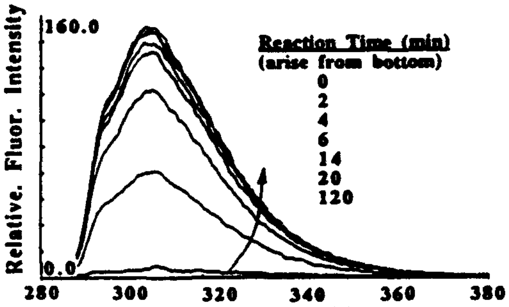

Fig.1 Fluorescence emission spectra for the reaction of MDI with excess 1-butanol in cyclohexane. Ex at 290 nm

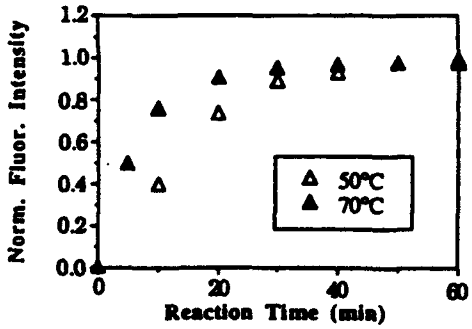

Fig.2 Relative fluorescence emission intensity at 305 nm for the reaction MDI with excess 1-butanol as a function of time at 50 and 70°C

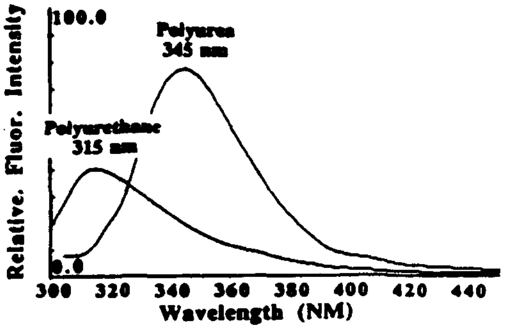

Fig.3 Fluorescence emission spectra of the polyurethane and polyurea obtained by reacting *MDI* with *PPO* and DETDA respectively in DMAc. Ex at 290 nm

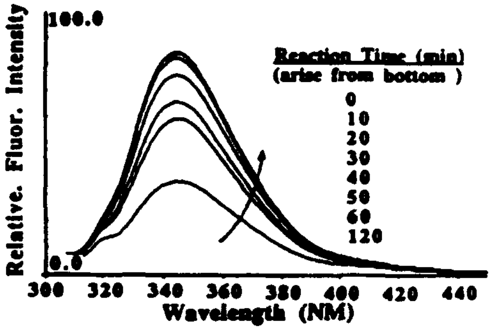

Fig.4 Fluorescence emission spectra for the reaction of MDI with DETDA in DMAc at 50°C. Ex at 290 nm

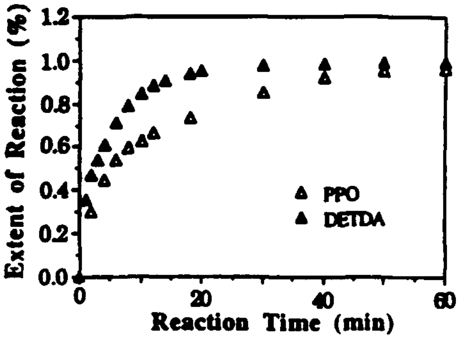

Fig.5 Extent of reaction measured via IR by following the disappearance of NCO group as a function of time for MDI/PPO reaction and MDI/DETDA reaction at 50°C

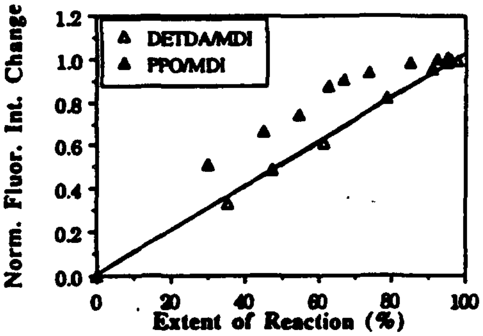

Fig.6 Correlation curve of relative fluorescence intensity change and extent of reaction for MDI/PPO and MDI/DETDA reaction