Influence of Viscosity on Photopolymerization in Film as Studied by Real Time FTIR

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1. Introduction

Photopolymerization is widely used in negative polyimide for buffer coating, photosensitive films for printed circuit board fabrication etc. The requirements for photosensitive systems are high sensitivity and high resolution. It is important to understand the reaction mechanism in the system for better performance. To trace the photopolymerization processes in film, Photo DSC (differential scanning calorimetry) has been extensively used [1]. Since FT-IR can detect the chemical bond concentration, we have tried to apply real time FT-IR to the study the photopolymerization processes. In the course of our study, we have found interesting behavior in photopolymerization processes, especially of the effect of monomer concentration on photopolymerization degree.

2. Experiment

2.1. Sample

The photopolymerization system tested was composed of an ethyl oxide- modified bisphenol-A dimethacrylate (FA-321M, Hitachi Chemicals) as a monomer, α , α -dimethoxy- α -phenylacetophenone (Irgacure 651 Ciba Specialty Chemical) as a photoinitiator and an acrylate polymer. Polyethylene glycol (Mw=600g/mol, PEG-600 Wako Chemical Co., Ltd.) was also used without purification.

The solution was bar coated on a 16 μ m polyethylene terephthalate film (PET), and dried in an air oven for ten minutes at 95°C to give a thin film whose thickness was adjusted to 30 μ m. The sample was then applied on a silicone wafer,

where the PET film would prevent O₂ diffusion from air.

2.2. Measurements

Real time FTIR spectra were recorded using a Digilab Excalibur Series infrared spectrometer. UV irradiation was performed with an USHIO spot cure SP-7 fitted with an i-line interference filter ASAHI spectra $\lambda=365$ nm. An electronic shutter Digilab Trigger interface K001 controlled by the spectrometer computer enabled the synchronization between the UV exposure and the IR spectra recording. Spectra of film absorbance were recorded for 300 s. Five seconds after the beginning of the measurement, the sample was irradiated for 10s and then the shutter was closed until the end of the measurement.

The variation of methacrylate content was observed thanks to the characteristic absorption peak at 1637 cm⁻¹ [2], which corresponds to the stretching vibration of the C=C methacrylate bond.

3. Results and Discussion

3.1. Real time FTIR

We studied the influence of monomer weight ratio in the film on the photopolymerization degree. Fig. 1 illustrates the results representing the decrease in methacrylate concentration detected by the absorbance at 1637 cm⁻¹ for the monomer ratio between 7 and 47%

Fig. 1 shows that the conversion of methacrylate groups depends on the monomer content in the film: for example, when it was lower than 27% we could not see significant decrease of the absorbance.

Fig. 1. Decrease of absorbance at 1637cm⁻¹ due to UV irradiation for several initial monomer weight ratios.

However the most interesting behavior in the Fig. 1 is the cross-over between the different absorbance curves. This means that the conversion depends not only on the monomer content in the film but also on the initial ratio of polymer to monomer: For instance, the sample loaded with 47% monomer shows an absorbance drop off lower than the absorbance corresponding to 27% initial monomer, whereas the sample loaded with 27% monomer did not show significant absorbance variation.

There are several hypotheses which can explain the phenomena: (1) temperature rise during polymerization enhances the polymerization, (2) higher monomer contents give low viscosity leading to the enhancement of polymerization.

3.2. Calibration

Fig.2. Linear dependence between methacrylate content and absorbance at 1637cm⁻¹

To discuss the polymerization process in detail, we need to confirm the linear relationship between

absorbance and the methacrylate concentration. We prepared the films with known-amount of monomers. We then measured the absorbance at 1637cm⁻¹ in the same condition as described in the experimental section except for UV irradiation. The results are shown in Fig. 2

The results clearly show a linear dependence in the range of our study

3.3. Influence of viscosity

To observe the effect of viscosity on photopolymerization, PEG-600 was added to the photopolymerization system to decrease the viscosity of the film.

Fig. 3. Absorbance at 1637 cm⁻¹ for several initial monomer weight ratios, with PEG addition

Fig. 3 clearly shows that lower viscosity in the film no longer leads to cross over. Moreover, the absorbance of film seems to reach a common asymptote. This means that initial viscosity plays an important role in photopolymerization.

4. Conclusion

We have found interesting behavior of the effect of monomer content on photopolymerization. On the basis of the viscosity effect study, we can conclude that the lower viscosity enhances photopolymerization.

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