
Thermal Measurements of the Light-Curing Reaction of Photoresist

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1. Introduction

Photoresist provides high resolution and can be used in microfabrication. Furthermore, it can be used to form etching-resistant thin-film in a short period of time. Due to these features, it is used in a wide number of areas, including printed circuit board wiring, electronic parts manufacturing and print plate-making. However, it is known that conditions during light curing, including exposure wavelength, irradiation intensity and reaction temperature, change the formation of etching-resistant thin-film. Therefore, it is necessary to consider various curing conditions when attempting to form the optimal etch-resistant thin-film.

Dry film photoresist is used in the etching of printed circuit boards. It is composed several components, including an acrylic monomer that hardens through a polymerization reaction, a binder polymer to form the film, a light-curing initiator and other additives. It is important to measure the light-curing reaction in all characteristic evaluations.

In this brief, a photochemical reaction calorimeter is used to measure the curing reaction of dry film under various conditions to evaluate its responsiveness.

2. Measurements

The measurement samples were round, extracted dry film weighing 1mg. Measurements were performed using a PDC121 photochemical reaction calorimeter connected to a SSC5200H Disk station.

To investigate the differences in calorific value due to curing, measurements were performed under different irradiating light wavelength, irradiation intensity and curing reaction temperature conditions. The light source was an Hg/Xe lamp and the irradiating light wavelength was selected from interference filters.

3. Results

Figure 1 shows the DSC measurement results for the different irradiation intensities. The irradiation wavelength was 365nm. Irradiation was started one minute after measurement was started and four irradiation intensities were used : 1, 5, 10 and 50mW/cm². Immediately after irradiation, exothermic heat was generated by the light-curing reaction and the reaction ended after about 6 minutes. In general, the higher the irradiation intensity, the higher the number of reaction calories. This shows that when the irradiation intensity is low, the curing reaction does not completely progress and the degree of polymerization is lower.

The integral curves shown in Figure 2 were created by peak area integration software for the measurement results in Figure 1. The total calorific value was set as 100% on the vertical axis and the peak percentage up to each time period is shown. The results show that higher the irradiation intensity, the greater the initial rise of the integral curve and the faster the curing reaction rate.

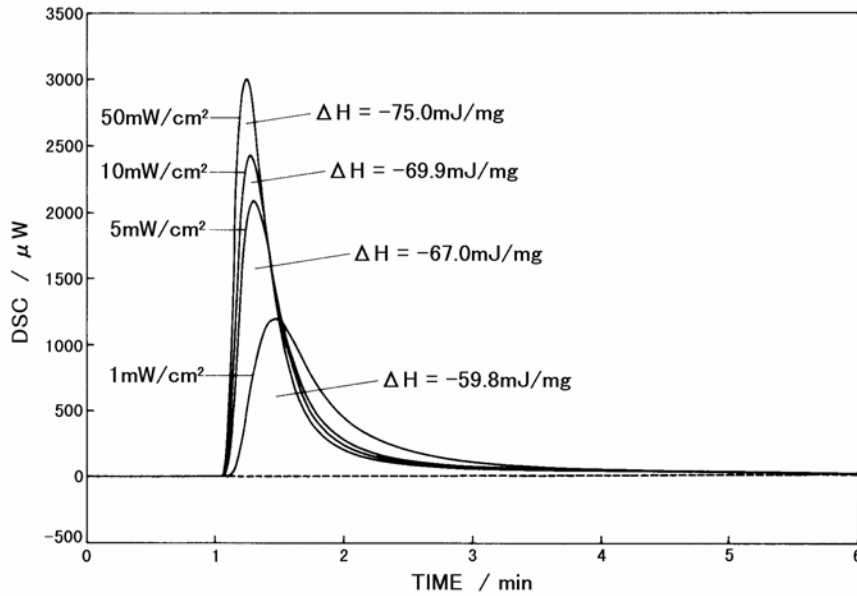


Figure 1 DSC curves for dry film at different irradiating intensities
 Irradiating wavelength : 356nm
 Measurement temperature : 25°C

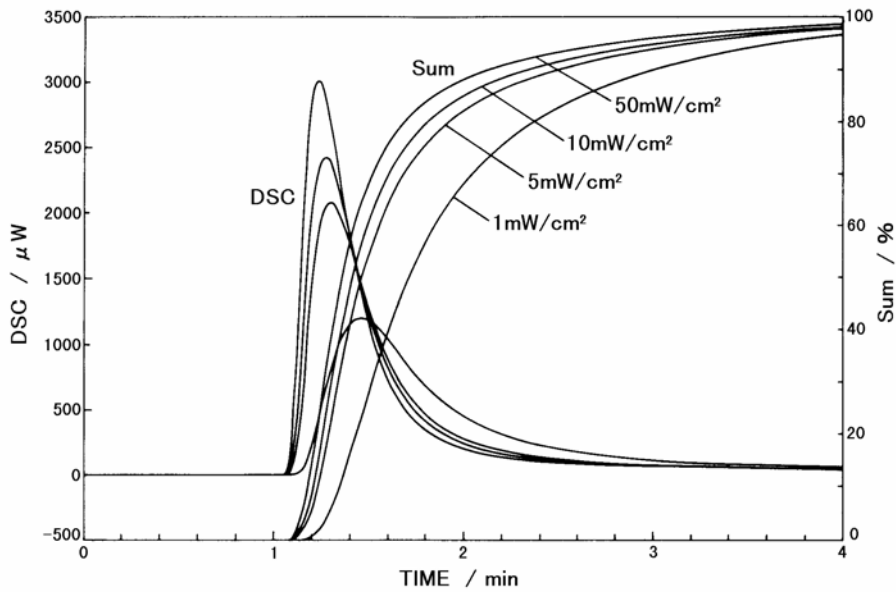


Figure 2 Integral curves of calorific values
 Irradiating wavelength : 356nm
 Measurement temperature : 25°C

Figure 3 shows the DSC measurement results for the different irradiation wavelengths. The irradiating intensity was 5mW/cm² and the irradiation wavelengths were selected from 5 interference filters. According to these results, when the wavelength was 365 or 405 nm, the peak was particularly large for this measurement sample, which indicates that wavelength has a large effect on the reaction rate. Accordingly, careful attention must be paid to irradiating wavelength when curing measurement samples such as this.

Figure 4 shows the DSC measurement results for different measurement temperatures. The results indicate that the higher the measurement temperature, the larger the calorific value and shows that the polymerization reactions advance quickly.

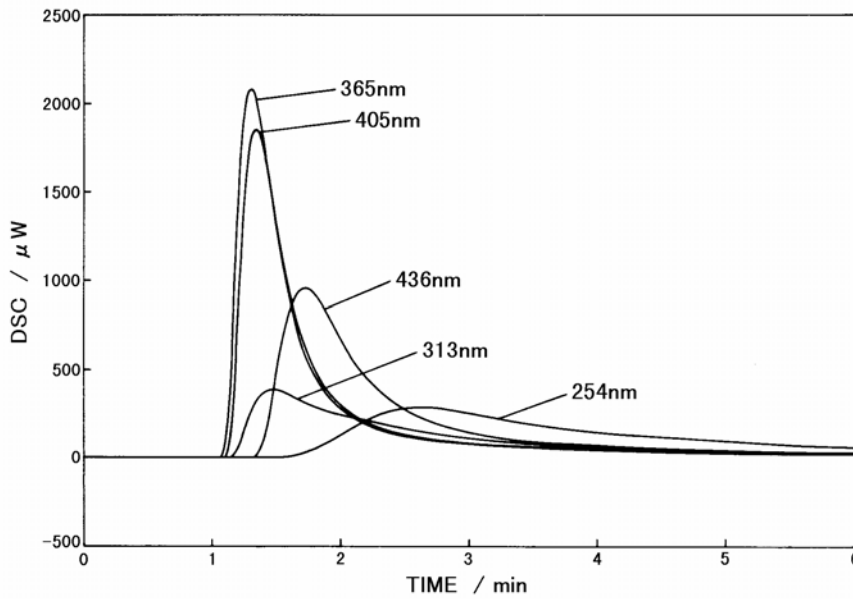


Figure 3 DSC curves for dry film at different irradiating wavelengths
 Irradiating intensity : 5mW/cm^2
 Measurement temperature : 25°C

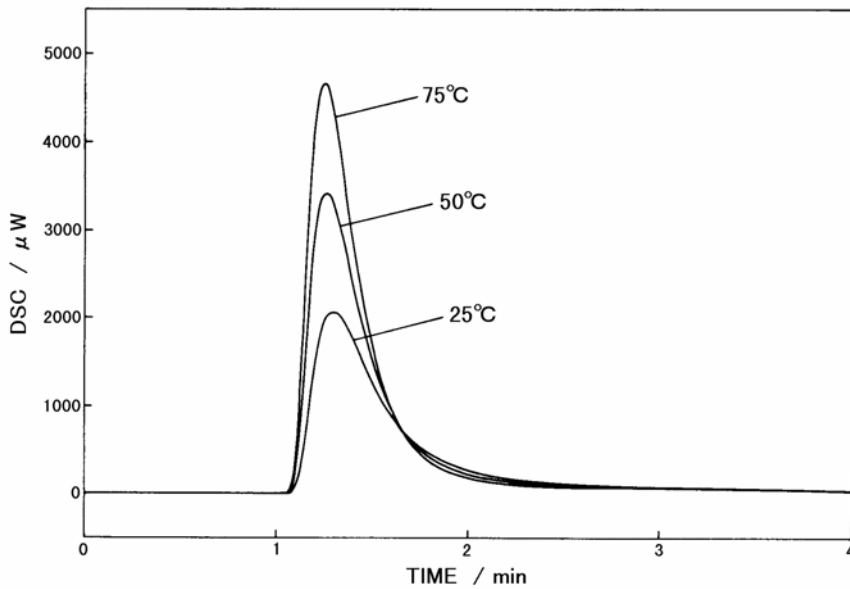


Figure 4 DSC curves for dry film at different measurement temperatures
 Irradiating intensity : 5mW/cm^2
 Irradiating wavelength : 356nm

4. Summary

In this brief, a photochemical reaction calorimeter was used to evaluate responsiveness by measuring the curing reaction of photoresist under various conditions. The various characteristics of photosensitive resin are being applied to an increasing number of fields and there are demands for increased sensitivity and resolution. When new photosensitive resins are developed, responsiveness is one of the characteristics that must be evaluated and photochemical reaction calorimeters can be a valuable part of this evaluation process.