Nonradiative Fraction in Photopolymerization Analysis of Thick Negative Photoresist Film Using Photocalorimetry

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Photopolymerization kinetics of thick aqueous-developable negative photoresist film was studied using photo-DSC in order to correct the background properly. We compared the heat fraction from ingredients in photopolymer. Thus, we confirmed that the typically used second scan method will derive overestimation of photochemical conversion, using the photobleachable aminobenzophenone photosensitizer. In the case of benzilidimethylketal formulation, the second scan method will derive underestimation due to photocoloring. In order to solve this problem, we devised a background correction method using a dummy formulation and demonstrated that this method will improve the quantitative analyses using photo-DSC.

Keywords: photopolymerization, photo-DSC, negative resist, bleach, background

1. Introduction

Since photo-DSC started in late 1970s\(^1\), it has been conveniently used to study kinetics of photopolymer, together with a relatively new tool of real-time FTIR(RT-FTIR) method\(^2\). It looks that RT-FTIR seems to have two advantages over photo-DSC: (i) versatile detectable chemistry, and (ii) ATR option, while other approaches are still being sought\(^3\), \(^4\), \(^5\). However when detecting absorption change of double bonds in acrylates by RT-FTIR method, there would sometime be inconsistency between two characteristic peaks of 1635\(\text{cm}^{-1}\) and 810\(\text{cm}^{-1}\) from unknown reason. Because of its simplicity, photo-DSC is currently a very popular kinetic tool for photopolymers, especially for thicker one. Unfortunately its background correction has not been focused so far in spite of its importance. According to the typical second scan method\(^6\), samples are thoroughly exposed to light after the 1\(^{st}\) scan so that crosslinkers in the samples would be consumed. The method runs the following procedure: for instance, samples are exposed to light after 1\(^{st}\) scan in order to complete whole polymerization, and then we measure the 2\(^{nd}\) scan to obtain the background. We would encounter the following problems:\(^1\) incompletion of acrylic polymerization by the 1\(^{st}\) scan, \(^2\) baseline fluctuation, and \(^3\) inconsistency of quantitative results. In this paper, a thick aqueous-developable negative photoresist which contains a three component photoinitiating system of N,N,N',N'-tetraethyl-4,4'-diaminobenzophenone (EAB) / o-chloro hexaarylbiimidazole (o-CIHABI) / mercaptobenzozazole (MBO), as well as a self-degradative type; benzilidimethylketal (BDK)\(^6\), were subjected to photo-DSC kinetic study. The results were compared with the results from RT-FTIR and discussed. An alternative background correction method using a dummy sample was also shown considering the absorption change during irradiation.

2. Experimental

2.1 Photopolymerizable film preparation

The compounds studied and their source are shown in Chart 1. Each photopolymer solution was prepared by mixing up alkaline-soluble methacrylic polymer(56 wt parts), difunctional methacrylic crosslinker(14G, 44 wt parts), photoinitiator, and solvent. Each photopolymer solution was coated on a 16-\(\mu\)m-thick polyethylene terephthalate film using a bar coater so that gave 40-\(\mu\)m-thick photoresist film is formed after evaporating the
solvent.

\[
\begin{align*}
\text{o-Cl-HABI} \\
\text{MBO} \\
\text{BDK} \\
\text{14G} \\
\text{HO-} & \text{(CH}_2\text{CH}_2\text{O)}_n\text{-H} \\
\text{PEG-600} \\
\end{align*}
\]

Chart 1. Molecules studied
EAB (Hodogaya Chemical Co., Ltd.)
o-ClHABI (Hodogaya Chemical Co., Ltd.)
MBO (Tokyo Kasei Kougo Co., Ltd.)
14G (Shin-Nakamura Chemical Industrial Co., Ltd.)
PEG-600 (Wako Chemical Co., Ltd.)
BDK (I-651, Ciba Specialty Chemicals Co., Ltd.)

2.2. Photo-DSC

Photopolymerization was conducted using a differential scanning photocalorimetry (SEIKO Instruments, PDC121) equipped with a 200 W mercury-xenon lamp and light transfer optics. Monochromatic light (365 nm) was used with a bandpass filter. The film sample was punched with a document puncher to obtain 7.5 mm diameter circular samples. Then a stamped film was placed on an aluminum sample pan, followed by pressing with a finger to give it better contact. Each sample weighed approximately 1 mg.

A dummy film was also prepared in which polyethylene glycol-600 was used in place of the methacrylic crosslinker but with the same photoinitiator as the sample.

Method A (conventional)

The sample pan was placed on the sample holder and an empty aluminum pan was placed on the reference holder. The measurement was done in N₂ at 25°C.

After stabilization of the isothermal system for 5 min, the sample and the reference were exposed to light for 10 min. After 3 min holding in the dark, they were exposed to light again keeping the same sample setting to obtain 2nd scan. The corrected p-DSC chart and observed heat were obtained by subtracting the 2nd scan from the 1st scan.

Method B (dummy method)

The sample and the dummy film were measured independently by the same procedure as the 1st scan of Method A. The corrected p-DSC chart and observed heat were then obtained by subtracting the dummy film scan from the sample scan.

Theoretical heat

Theoretical heat in this study was derived based on the concentration [mol/mg] of acryl functionality in the crosslinker used and reported polymerization heat, 54.8 kJ/mg, determined from the thermal polymerization of lauryl methacrylate(7).

Conversion

Conversion was obtained from the theoretical heat [ΔH₀] and the heat observed [ΔH₁] through the 10 min exposure using eq.1.

\[
C = \frac{ΔH₁}{ΔH₀} \quad [1]
\]

Rate of polymerization (Rp)

A slope was obtained from the first six plots after induction period in the time-conversion curve. The rate of polymerization (Rp) (mol · kg⁻¹ · s⁻¹) defined eq.2 was obtained.

\[
Rp = - \frac{d[M]}{dt} = k(s⁻¹) [M]₀(mol/kg) \quad [2]
\]

Fig.1 Time-conversion curve by photo-DSC (conceptual)
2.3 Absorption spectra

Absorption spectra were measured using a U-3310 Spectrophotometer (Hitachi).

2.4 RT-FTIR

The photopolymerization kinetic was also obtained with an RT-FTIR spectrometer (Excalibur FTS 3000MX, DIGILAB). Each sample film with PET film was laminated on a 625 μm-thick silicon wafer(100). The sample was placed on the holder with the angle of 45° for measurement under horizontal monitoring IR and vertical UV light (SP-7, USHIO, guided through fiber optics). Light energy irradiated to the sample was corrected by cosine 45°. The progress of polymerization was observed every 0.134 second by detecting of the disappearance of C=C stretching band at 1637 cm⁻¹. The conversion and the rate of polymerization of the acrylate crosslinker were determined by the same procedure as photo-DSC.

3. Results and Discussion

Thirty micron-thick photopolymerizable films containing an acrylic binder polymer, difunctional crosslinker and photoinitiator system were prepared and measured by photo-DSC. The photoinitiator system was the three-component (Film 1), or the self-degradative type: benzildimethylketal (BDK) (Film 3). Two kind of dummy films (Film 2 and Film 4) containing polyethylene glycol in place of the difunctional acrylate were also prepared and tested.

Fig. 2 (a) shows the original photo-DSC chart (1st scan) and the 2nd scan for Film1, and the dummy chart (for Film2) for background correction. Fig. 2 (b) shows the same three charts for BDK. The rate of polymerization for the first 15 s and the conversion through the 10 min photoreaction were corrected and summarized in Table 1. In EAB/o-CI-HABI/MBO experiment, the exothermic curve of the dummy film showed a peak and decayed in first 3 min, while the 2nd scan was mostly flat. 2nd scan correction gave excessive conversion to the theoretical polymerization heat. On the other hand, dummy correction gave a reasonable conversion result (73.1%) which was consistent with RT-FTIR result (79.0%).

Fig. 3 shows three time-conversion curves obtained by the two methods of photo-DSC, and the RT-FTIR method for the EAB/o-CI-HABI/MBO photoinitiator system. It seems that the photo-DSC method with 2nd scan correction will clearly result in overestimated time-conversion compared with the other two methods. Even though the dummy background corrected photo-DSC will give kinetics similar curve to that of RT-FTIR, the latter will give faster photospeed in the early stage than the former. In photo-DSC measurement, the sample temperature, more or less, is kept at room the sample is subjected to heat in the RT-FTIR measurement condition.

Since significant photobleaching in this system was shown in the dummy film as shown in Fig. 4 (a), it is expected that the sample (Film1) after the 1st scan was already photobleached. The overestimation in the conversion by the 2nd scan correction method was probably due to this photobleaching. Effect of the absorption change on photo-DSC analysis is discussed in the latter part of this paper.
Table 1 Photopolymerization kinetics data
(a) \( R_p [10^2 \text{mol kg}^{-1} \text{s}^{-1}] \)

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<tr>
<th></th>
<th>Photo DSC</th>
<th>RT-FTIR</th>
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<tbody>
<tr>
<td>EAB/(o)-Cl-HAB/MBMO (Film 1 and 2)</td>
<td>2.8 (2nd scan method)</td>
<td>17.4</td>
</tr>
<tr>
<td>EAB/(o)-Cl-HAB/MBMO (Film 3 and 4)</td>
<td>2.6 (dummy method)</td>
<td>3.0</td>
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<tr>
<td>BDK (Film 3 and 4)</td>
<td>-</td>
<td>78.5</td>
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Light intensity: 10 mW/cm²

(b) Conversion [%]

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<th>RT-FTIR</th>
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<tr>
<td>EAB/(o)-Cl-HAB/MBMO (Film 1 and 2)</td>
<td>123.1 (2nd scan method)</td>
<td>79.0</td>
</tr>
<tr>
<td>EAB/(o)-Cl-HAB/MBMO (Film 3 and 4)</td>
<td>73.1 (dummy method)</td>
<td></td>
</tr>
<tr>
<td>BDK (Film 3 and 4)</td>
<td>-</td>
<td>78.5</td>
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Light intensity: 10 mW/cm², 10 min

In Fig. 2 (b), besides the initial peak for photopolymerization heat, the three photo-DSC curves gradually increase. Since the 2nd scan intersects the 1st scan at about 60 s, this 2nd scan can not be used as the background for correction. The dummy scan also intersects after another 60 s. We gave up deriving any kinetic data from this experiment. Absorption change for the BDK dummy film, in Fig. 4 (b), reveals showed significant photocoloring by the action of light. The absorption spectra for BDK film before and after light exposure are shown in Fig. 5. According to the known BDK photoreaction, excited BDK unimolecularly decomposes via \( \alpha \) scission as shown in Scheme 1. Both radical species or benzil generated by recombination of two benzoyl radicals may account for this emerging absorption.

![Absorbance vs Exposure](image)

**Fig. 3 Conversion curve**

**Fig. 4 Absorption change during light exposure**
(a) EAB/\(o\)-Cl-HAB/MBMO (Film 2), (b) BDK (Film 4)
Light intensity: 10 mW/cm² at 365 nm, Absorption at 365 nm, Film thickness: 30 \( \mu \)m

![Absorbance vs Wavelength](image)

**Fig. 5 Absorption spectra of BDK film before and after exposure**
Film 4 (BDK), Film thickness: 30 \( \mu \)m, Exposure: 365 nm
We demonstrated that the dummy photo-DSC background correction, which considers absorption change during light exposure, will give reasonable kinetics for the photoinitiator system of EAB/o-CIHAB/MBO.

In order to find the ingredient which affects the consistency in photo-DSC analysis, we collected photo-DSC scan charts from several blank films which contained the ingredients differently. These blank films had no polymerizable compound. Results are shown in Fig. 6 (a) and (b) for two photoinitiator systems. Fig. 6 (a) clearly shows that light will change to heat in the blank films with containing o-CIHAB and EAB together. Considering that these blank films have no acrylic compounds, o-CIHAB and EAB will be good physical converters of light to heat, as is shown by Jablonsky diagram, in Fig. 7. And also, while the blank o-CIHAB film (Fig. 6) was stable, the blank film containing EAB and o-CIHAB together (Fig. 7) gave a significant decay in the photo-DSC chart, as was already shown in the dummy chart of Fig. 2 (a).
It may be concluded that, when EAB is used as a photosensitizer, it will undergo photobleaching and give a reduced background for the 2nd scan correction, resulting in quantitative inconsistency in photo-DSC analysis. We also showed same chart for BDK in Fig. 6(b).

4. Conclusion

We have demonstrated that in photo-DSC analysis (1) the light absorption property of the photoinitiator (system) used will affect the kinetic analysis, (2) kinetics corrected by second scan method will give over- or under-estimation depending on the absorption change in the photoinitiator (system), (3) the dummy background correction is effective in the photochemical change will similarly occur in both photopolymerizable system and inert matrix. Using dummy correction, photo-DSC analysis will give a slower kinetic in the early period than the RT-FTIR analysis. This is probably caused by the isothermal condition in photo-DSC.

5. Acknowledgement

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References
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