Photocuring Kinetic Studies of TMPTMA Monomer by Type II Photoinitiators of Different Weight Ratios of 2-Chlorohexaaryl Biimidazole (o-Cl-HABI) and N-Phenylglycine (NPG)

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The curing behavior of the type II photoinitiator package based on different weight ratios of o-Cl-HABI (hydrogen acceptor)/NPG (hydrogen donor) systems (where o-Cl-HABI is a 2-chlorohexaaryl biimidazole, NPG is an N-phenylglycine) was investigated through FT-IR, gel-fraction, electron spin resonance (ESR) and photoluminescence (PL) methodologies. As the amount of NPG increasing, the faster curing speed occurred. However, the curvature photo-reactivity phenomenon was observed as the amount of o-Cl-HABI at 0.5, 1 and 2 wt%, respectively. In addition, the radical transfer mechanism in the presence of air and nitrogen atmospheres was also discussed in this study.

Keywords: Photoinitiator, Photoreactivity, o-Cl-HABI/NPG, Different weight ratios, Radical mechanism

1. Introduction

Photopolymerization reactions, which allow the phase or solubility transformation under a light source, has been widely encountered in many industrial applications, such as coating, adhesives, 3D printing, microlithography, optics, medicine, nanotechnology, etc [1–8]. In this photochemistry, the photo-initiators (PIs) play an important role in photocuring reactions, i.e. they absorb light radiation and produce active species such as free radicals that trigger the photo-reactions.

Generally, there are two types of initiated mechanisms for free radical polymerization process: (1) Type I PIs generate the radicals from direct homolytic cleavage process under light irradiation, and (2) Type II PIs consisting radical generation and electron transfer process between hydrogen acceptor and hydrogen donor units [9, 10]. Printed circuit board (PCB) was one of the industrial using Type II PIs. This kinds of photo-imaginable materials also named as negative photoresist or dry films, which developed by DuPont in 1960’s [11]. The general compositions for this materials, including photo-initiators (PIs), acrylate monomers (M) and binder polymers (B). For PIs components, the common hydrogen acceptor compound was hexaaryl biimidazole (HABI, or Lophine dimer, L₂) and its derivatives such as 2-chlorohexaaryl biimidazole (o-Cl-HABI). The usage of HABI compound was due to the high yield of the lophyl radical (L•) generation (equation 1) and low sensitivity in the presence of oxygen [12]. Therefore, high concentration and stable lophyl radical (L•) can abstract hydrogen atoms from hydrogen donor coinitiators (e.g., an amine, a thiol etc.) (equation 2) and consequently initiate the vinyl addition polymerization (equation 3). The mentioned above of Type II photopolymerization process shown below:

\[
L₂ \rightarrow 2L· \quad (1)
\]

\[
2L· + RH \rightarrow LH + R· \quad (2)
\]

\[
R· + \text{Monomer} \rightarrow \text{Polymerization} \quad (3)
\]

One of the amine based hydrogen donors, N-phenylglycine (NPG), adopted recently for PCB dry films was due to the faster photo-reactivity than
other components [13, 14]. Moreover, as comparing to traditional thiol based hydrogen donor materials, the sulfur units from thiol materials ascribed to the smell stinks and strong chelated onto the copper surface, which limited the widely used for industrial applications. Although, o-Cl-HABI and NPG materials had been used for lone a while, however, there was no report regarding to the curing properties at different weight ratios, and radical stability in the presence of different atmospheres. In this study, we intend to understand the kinetic process, radical stability of o-Cl-HABI/NPG photoinitiator packages at different weight ratios under the same acrylate monomer. The correlation between curing performance and photo-physical properties also conducted.

2. Experimental
2.1. Materials
2-chlorohexaaryl bisimidazole (o-Cl-HABI), N-phenylglycine (NPG) were provide by DuPont, Taiwan. Trimethylolpropane trimethacrylate (TMPTMA; Aldrich) was used as received without further purification. Solvents: hexane, dichloromethane was used as received.

2.2. Degree of conversion (DC)
2.2.1. FTIR
A small amount of formulation (TMPTMA/o-Cl-HABI/NPG = 97.95/2/0.05 wt%) was drop into KBr disk (0 s cure time) and recorded in transmittance mode of FTIR ranging from 4000 to 400 cm\(^{-1}\). Afterward, the disk was irradiated for 30, 60 and 120 sec under the same light source and exposed distance for DC testing. The DC results was determined according to the literature and calculated by the following equation 4 [15]:

\[
DC(\%) = \frac{(A_{810}\text{ to } A_{1730})_{\text{original}} - (A_{810}\text{ to } A_{1730})_{\text{final}}}{(A_{810}\text{ to } A_{1730})_{\text{original}}} \times 100\%
\]  

(4)

2.2.2. Gel fraction
The gel fraction was another approach to obtain the DC value and calculated by the following equation 5 [15]. Gel fraction is a convenient method to measure the insoluble fractions, such as the cross-linked or network polymers. In this study, different cured samples (around 0.5 g) was washed by soxhlet extraction under hexane as solvent for 6 h. After that, the sample was filtered out and dried to get the final polymerized samples.

where \(W_0\) is the original weight and \(W_t\) is the weight after drying. For make sure the results, an average of at least three individual determinations was used.

2.3. Measurements
The photopolymerization was using a Philips 16 W lamp (type Actinic BL) with a total light around 150 mJ/cm\(^2\) for 30 sec, 295 mJ/cm\(^2\) for 60 sec and 605 mJ/cm\(^2\) for 120 sec exposed time, which was test by radiometer. IR spectra were measured on a Perkin Elmer Spectrum One FT-IR spectrometer. Ultraviolet–visible (UV–vis) spectra were determined by a Perkin Elmer Lambda 35 UV/VIS Spectrometer. Fluorescence spectra (PL) were conducted by a HITACHI F-4500 Fluorescence Spectrometer. ESR spectra were recorded on a Freiberg Instrument at 9.4085 GHz without any radical capturing agent. Same UV lamp was used for irradiation at around 33 ˚C in the ESR cavity. Pure o-Cl-HABI and relative weight ratios of o-Cl-HABI and NPG was selected and dissolved into CH\(_2\)Cl\(_2\) with a concentration of 1 x 10\(^{-3}\) mol/L. The ESR peaks are displayed the radical concentration of lophyl radical (L•) that generate from o-Cl-HABI.

3. Results and discussion
The possible photopolymerization mechanism was shown in Scheme 1. First, the imidazole dimer (o-Cl-HABI; L\(_2\)) was convert into a free radical (L•) under light exposed. This kinds of radical can’t initiate photo-polymerization process. On the other hand, it need proton or electron transfer combine with hydrogen donor, such as N-phenylglycine (NPG), to produce a corresponding phenyl-amine radical. Thus, this kind of radicals can initiate the polymerization of the monomers. Different compositions between o-Cl-HABI and NPG weight ratios were evaluated under the same tri-functional methacrylate monomer (TMPTMA).

Figure 1 shows FTIR spectra of o-Cl-HABI and NPG at weight ratio of 2:0.05 as a function of exposure times. It was found that the acrylate groups (C=\(\equiv\)) of TMPTMA gave a characteristic band at 810 cm\(^{-1}\) decreased with increasing exposed time from 0 to 120 sec. This is due to the double bond consuming of the TMPTMA monomer under photo-polymerization process. Furthermore, the (C=O) shows no significant change after light irradiation. The calculated DC (%) was recorded at
0, 17, 27.5 and 34.3 %, calculated by the equation 4 mentioned previously.

Degree of conversion (DC %) was also test by gel fraction method mentioned above (equation 5).

Figure 2 exhibits gel fraction results as a function of exposure time under the weight composition of o-Cl-HABI:NPG at 2:0.05. Again, the DC values increased as the UV irradiation time increasing. The conversion rate achieved at 53.4% after 120 sec. Comparing gel fraction with FTIR results at the same exposure time, conversion rate for FTIR method exhibited relatively lower value than the gel fraction one. The photo kinetics studies at different weight ratios were test by gel fraction manner in this study at least 3 times for each package.

The radical concentration of o-Cl-HABI and o-Cl-HABI/NPG (2:0.05 wt%) was also investigated by ESR spectra shown in Fig. 3. The intensity represented the radical concentration of lophyl radical (L•). For the o-Cl-HABI only component, the intensity was increased dramatically from 0 to 30 sec. And then the intensity increased slightly from 30 sec to 120 sec. This as the exposure time increasing. This means the o-Cl-HABI component was easily to convert into a free radical under short of light exposed time. In addition, under the exposed time around 30 sec to 120 sec, the intensity showed insignificant improvement. This indicated parts of the o-Cl-HABI component was consumed within 30 sec under light exposed. The ESR spectra of the o-Cl-HABI/NPG at weight ratio of 2:0.05 under 120 sec exposed time was also conducted, and the result shows in Fig. 3. As comparing to o-Cl-HABI at the same irradiation time, the o-Cl-HABI/NPG package exhibited lower intensity than pure o-Cl-HABI because of the electron transfer from L• to NPG moiety (Scheme 1).
Figure 4 shows the DC values at different weight ratios of o-Cl-HABI or NPG. The results are also summarized in Table 1. When the NPG weight ratios of 0.05, 0.1 and 0.25 wt% were adopted, the DC values were around 53.4, 81.8 and 86.8% under 120 s exposure time. The conversion rate increased as the NPG weight ratios increasing. In addition, the DC % increased rapidly as the NPG weight ratio from 0.05 to 0.1 wt% and then became constantly from 0.1 wt% to 0.25 wt%. This indicated the optimization of NPG weight ratios should be around 0.1 wt% when o-Cl-HABE was 2 wt%. However, the curvature results were observed at different weight ratios of o-Cl-HABI. The 55.2, 64.7 and 53.4% of conversion rate at 0.5, 1 and 2 wt% of o-Cl-HABI, respectively. The higher amount of o-Cl-HABI (2 wt%) resulting higher lophyl radical concentration might lead to the re-coupling reaction from lophyl radical to o-Cl-HABI [16], hence this package showed relative lower DC value than 1 wt% of o-Cl-HABI.

The photophysics properties of various weight ratios of package were test by UV-Vis and PL instruments. The UV-Vis spectra at different PI weight ratios are presented in Fig. 5. All the spectra showed the absorption peak at around 270 nm is attributed to the π-π* transition of biimidazole [17]. In addition, the absorption intensity at 270 nm for those two compositions decreases in the order of 2 wt% > 1 wt% > 0.5 wt% of o-Cl-HABI and 0.05 wt% > 0.1 wt% > 0.25 wt% of NPG. The higher concentration of o-Cl-HABI results in considerable larger absorption intensity. However, the better light harvesting based on UV-Vis absorption does not guarantee faster photo reactivity.

The PL spectra of those compositions are measured to demonstrate the photo reactivity properties, and their results are illustrated in Fig. 6. Figure 6a shows the PL spectra of pure o-Cl-HABI and o-Cl-HABI/NPG packages at different weight ratios of o-Cl-HABI. The pure o-Cl-HABI showed the highest emission peak at around 385 nm when excited at 270 nm. When introduce NPG into o-Cl-HABI, all the emission intensity decreased. This is due to the quenching effect by NPG, which means proton transfer is underway from HABI to NPG structure. Moreover, the emission intensity decreased in the following order for o-Cl-HABI at 2 wt% > 0.5 wt% >1 wt%. This observation is consisted with the results of the DC% results mentioned above. The lower emission intensity lead
to more proportion of proton transfer. Therefore, it obtained higher concentration of phenyl-amine radical for photo-polymerization [18]. In addition, different NPG weight ratios investigation was also test in the same manner as shown in Fig. 6. The emission intensity based on 0.05 wt% of NPG exhibited the highest intensity than 0.1 and 0.25 wt% of NPG which caused to the lowest DC%. The double bond conversion closed to stable at 0.1 and 0.25 wt% of NPG, therefore, the consisted PL intensity also showed insignificantly.

![Image of PL spectra](image)

Fig. 6. PL spectra of pure o-Cl-HABI and various weight ratios of NPG.

The radical stability of the o-Cl-HABI/NPG (2:0.05 wt%) was investigated in nitrogen and air atmosphere. The formulation was purged by air or nitrogen atmosphere for 30 min, respectively, and then irradiated at the same exposure time. The nitrogen based sample (DC = 63%) exhibited a higher DC value than their air counterparts (DC = 50%). This means the exposed environment indeed play an import factor on conversion efficiency.

The proposed scheme was shown in Scheme 2. The initiate L• processed electron transfer and form the phenyl-amine radical, followed by transformation of monomer (M) into a propagating radical (Mn•) and polymerized to the polymer chain subsequently. However, the competing radical, unreactive peroxyl radical (MnOO•), would occur in the presence of oxygen. Although the NPG could generate CO₂ to lower down the oxygen concentration during photodecompose process (Scheme 1). The amount of CO₂ may not be sufficient to exclude oxygen during the photocuring process [19]. If the MnOO• still exist, the hydrogen donor could react with MnOO• to form MnOOH and a new reactive radical (R•) capable to be a circle of propagating polymerization. Therefore, more oxygen will cause higher peroxyl radical concentration. As a result, the concentration of NPG (hydrogen donor) could be diluted, hence reduce the electron transfer possibility from o-Cl-HABI to NPG.

![Scheme 2](image)

Scheme 2. Mechanism of oxygen influence on o-Cl-HABI (L₂)/NPG (RH) photoinitiator package.

4. Conclusion

In this study, the photo kinetic properties of the o-Cl-HABI/NPG photoinitiator package was studied by FTIR, gel fraction and ESR methods. In addition, the influence of weight ratios between o-Cl-HABI and NPG had been examined and explained. In this study, the optimized weight ratios of o-Cl-HABI and NPG could be 1.0 wt% and 0.1 wt%, respectively. Finally, the atmospheres effect did influence the photo-reactivity. And their photo-polymerization mechanism was proposed in this study.

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