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Characteristic of Photocurable Organic/Inorganic Hybrids Utilizing Acid Proliferation Reactions

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ABSTRACT

UV-cured hybrids characteristics were investigated by evaluating FTIR spectrum and pencil hardness test. Acid amplifier increased pencil hardness level of cured films by generating more acids to harden the coatings. A broad IR spectrum of cured film showed that siloxane oligomers generated by hydrolysis during exposure to UV. The acid proliferation had higher curing efficiency on PMAS, showed characteristic concentration, temperature and time dependency relationships for pencil hardness level.

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INTRODUCTION

Photoacid generator are cationic photoinitiators (Shirai, M., Tsunooka, M., 1996). A photoinitiator is a compound especially added to a formulation to convert absorbed light energy, UV or visible light, into chemical energy in the form of initiating species, free radicals or cations.

To improve photosensitivity of chemically amplified photoresist, Ichimura (Ichimura, K., 2002) proposed an idea of autocatalytic formation of acid from acid-sensitive compounds referred to as "acid amplifiers". An acid amplifier is decomposed by a photogenerated acid to give new acid so that the rates of acid based reactions may be significantly enhanced. A chemically amplified photoresist was prepared from an acid-sensitized polymer and a photoacid generator. In order to improve the sensitivity of this material, a proposal to put an acid proliferation reaction into the system to generate more acid by acid autocatalytic decomposition, was successfully demonstrated.

Acid amplifiers should fulfill at least the following requirements for achieving nonlinear catalytic reactions and for developing novel photopolymer systems. First, an acid amplifier should be readily subjected to an acid-catalyzed decomposition to liberate a strong acid that is capable of catalyzing the decomposition itself to display autocatalytic generation of an acidic species. Second, an acid amplifier should be thermally stable in the absence of an acid at least under the reaction to carry out the autocatalytic decomposition and subsequent acid-catalyzed reaction. Third, the liberated acid should be strong enough to catalyze a subsequent chemical reaction to display a nonlinear chemical transformation (Ichimura, K., 2002). However, when acid amplifiers tested with cationic UV-curing materials containing epoxy resins and a photoacid generator, no effect was detected. Therefore, there are only a few researches about acid proliferations in UV-curing materials.

As base for curing reaction, sol-gel reaction was selected because the acid does not inhibit the reaction. Metal alkoxides are members of the family of organometallic compounds, which are organic compounds which have one or more metal atoms in the molecule. Metal alkoxides (R-O-M) are like alcohols (R-OH) with a metal atom, M, replacing the hydrogen H in the hydroxyl group (Helmut, D., 1971). This study was carried out to create high sensitivity UV-curing materials utilizing acid proliferation reactions.

Materials:

3-Methacryloxypropyltrimethoxysilane (MAS) was purchased from Chisso Corp.

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UV Curing Process:

UV-curable hybrid solution were prepared by dissolving **PMAS** (0.1g), photoacid generator **1a** (5 wt% relative to **PMAS**), acid amplifier **2a** (0~20 wt% relative to **PMAS**) in tetrahydrofuran (THF), bar-coated on a glass plates and prebake at 60 °C for 1 min to remove residual solvent. Films were exposed to 254 nm light from a handheld lamp UVP-11, followed by post-exposure baking (PEB) at 60~100 °C for 10~40 min on a hot plate and FT-IR measurements at intervals. After the PEB, pencil hardness tests were performed. The pencil-hardness was evaluated by scratching UV-cured coatings with pencils, the hardness of which is arranged as follows: 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, and 9H (hardest).

Instruments and Measurements:

FT-IR spectra were obtained by using JASCO FT/IR-410 spectrometer. Pencil hardness was obtained by No. 553-M Film Hardness Tester from Yasuda Seiki Seisaku, Ltd. Irradiation was provided by handheld lamp UVG-11 from Funakoshi, Ltd. Exposure dose was obtained by UV Power Meter model C8026 from Hamamatsu Photonics, Ltd.

RESULTS AND DISCUSSION**Effects of Acid Amplifier on Curing Efficiency of PMAS:**

Figure 1 shows the effect of **2a** on **PMAS** curing efficiency. From this figure, cured film without **2a** showed level of 4B after 10000 mJ/cm^2 exposure. However, cured film doped with 10 wt% of **2a** showed a level of F after only 100 mJ/cm^2 exposure. This result indicates that the enhancement of the UV-curing arises from the acid proliferation reaction of **2a** to generate more acid involved in the sol-gel reaction of **PMAS** side chains to lead to the sufficient hard coating. In conclusion, the addition of the **2a** to UV-curable organic-inorganic hybrids resulted in the marked improvement of curing efficiency.

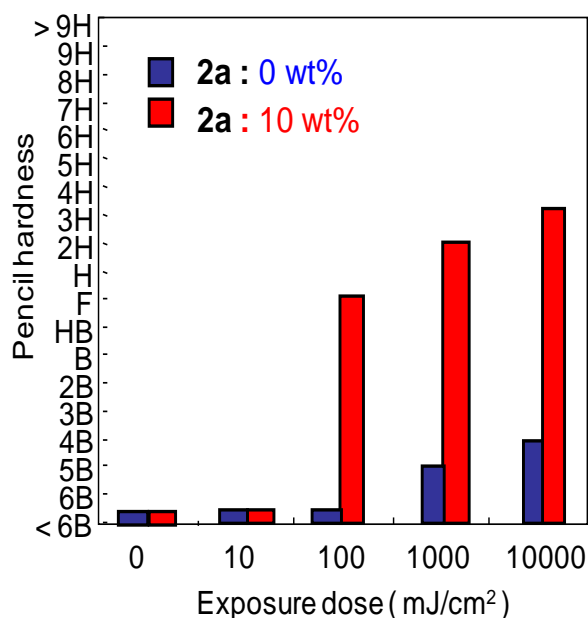


Fig. 1: Effect of **2a** on **PMAS** curing efficiency. (**1a** : 5 wt%, **PMAS** : 0.1 g, THF : 1 ml, PEB: 100 °C, 40 min)

The acid-catalyzed cleavage of the **PMAS** side chains was followed by FT-IR spectral measurements of a film of **PMAS** containing 5 wt% of **1a** and 10 wt% of **2a**. The film was exposed to 254 nm and baked subsequently at 100 °C for 40 min. As shown in Figure 2, before the exposure, the absorption band at 1082 cm^{-1} due to siloxane (Si-OC) peak of **PMAS** were observable. After the exposure, Si-OC peak were slightly decreased. IR spectrum showed a broad peak around $3,300\text{ cm}^{-1}$ which corresponds with the hydroxyl groups, indicating that the siloxane oligomers include silanol groups (Si-OH) generated by hydrolysis of alkoxy groups. It is supposed that silanol group condensation proceeds under the acid generated with exposure. After PEB, there were greatly decreased on Si-OC peak and sulfonate ester peak.

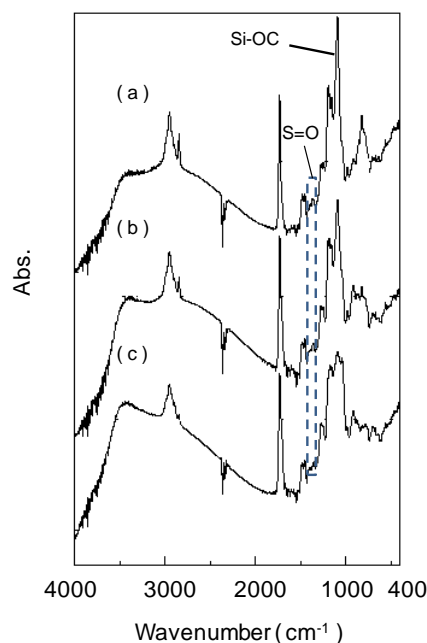


Fig. 2: FT-IR spectral changes of a film of **PMAS** containing 5 wt% of **1a**, 10 wt% of **2a** (a) before and (b) after 1000 mJ/cm² exposure and (c) after PEB at 100 °C for 40 min.

Figure 3 shows the changes in band intensities of the sulfonate peak at 1362cm⁻¹ as a function after PEB periods. Because of the declination, it is considered that acid proliferation reaction occurred in film. The film was heated until the peak disappeared to examine the relation between acidity and film hardness. When the peak disappeared, considering same acid concentration, each film doped with **2a** and **2c** has the same result of hardness level, over than 9H. However, for film doped with **2b** showed a level of 7H. These results indicate that stronger acidity affects the curing efficiency.

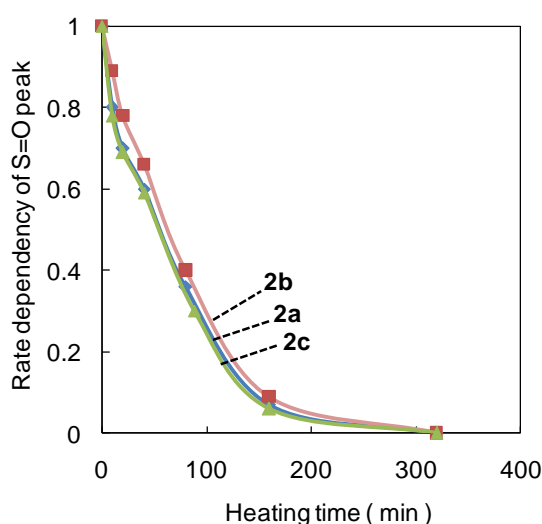


Fig. 3: Time courses of the decomposition of acid amplifier. (1 : 5 wt%, 2 : 10 wt%, Heating Temperature: 100 °C)

Effects of Acid Proliferation Reactions on Curing Efficiency of PMAS:

Figure 3 shows the effects of **2a** concentration on curing efficiency of **PMAS**. This result indicates that when concentration of **2a** increased, film hardness level also increased. This is because generated acid from acid amplifier increased when more acid amplifier added.

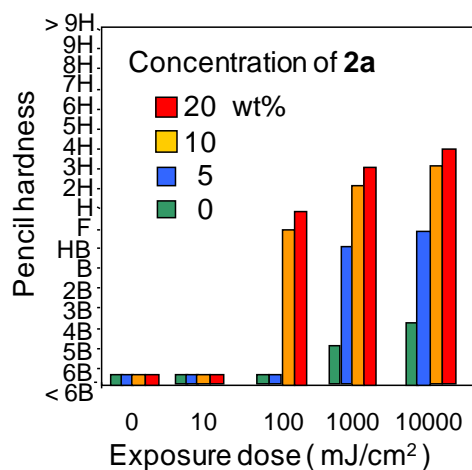


Fig. 4: Effects of **2a** concentration on curing efficiency of **PMAS** (**1a** : 5 wt%, **PMAS** : 0.1 g, THF: 1 ml, Heating : 100 °C, 40 min)

Figure 5 showed that when heating time was extended, film hardness level also increased. This is because the acceleration of acid proliferation reaction is accomplished by heat. Furthermore, as shown in Figure 6, when heating temperature increased, film hardness level also increased. The result shows that heating temperature also affect acid proliferation reaction rate.

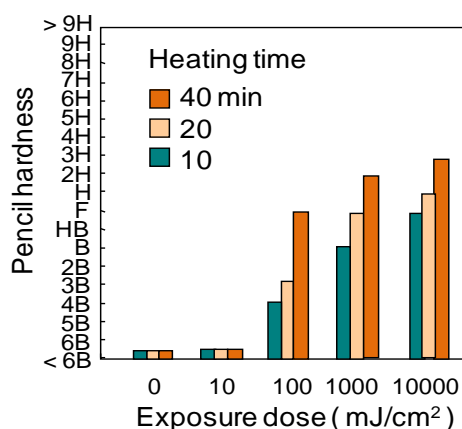


Fig. 5: Effects of **2a** PEB heating time on curing efficiency of **PMAS** (**1a** : 5 wt%, **2a** : 10 wt%, **PMAS** : 0.1 g, THF: 1 ml, Heating Temperature : 100 °C)

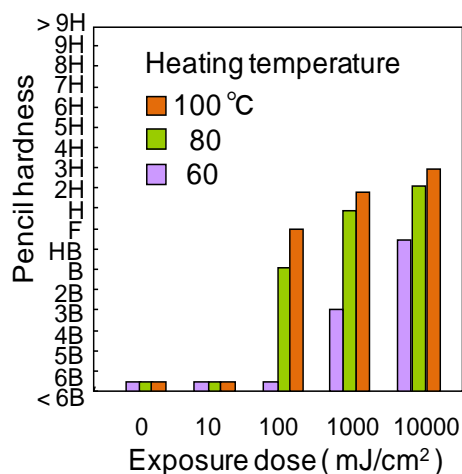


Fig. 6: Effects of **2a** PEB heating temperature on curing efficiency of **PMAS** (**1a** : 5 wt%, **2a** : 10 wt%, **PMAS** : 0.1 g, THF: 1 ml, Heating Time: 40 min)

REFERENCES

Helmut, D., 1971. "New routes to multicomponent oxide glasses", *Angew. Chem. Internat. Edit.*, 10(6): 363-434.

Ichimura, K., 2002. "Nonlinear organic reactions to proliferate acidic and basic molecules and their applications", *Chem. Rec.*, 2: 46-55.

Shirai, M., M. Tsunooka, 1996. "Photoacid and photobase generators: chemistry and applications to polymeric materials", *Prog. Polym. Sci.*, 21: 1-45.