

Thermally-stable Photosensitive Polymer System Using Fullerene as a Sensitizer

Etsu Takeuchi[†], Yusuke Tajima^{††}, Yasuo Shigemitsu^{††}
and Kazuo Takeuchi^{†, ††}

[†]; Graduate School of Science and Engineering, Saitama University,
255 Shimo-Ohkubo, Urawa-shi, Saitama, 338-8570, JAPAN.

^{††}; Applied Laser Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research),
2-1 Hirosawa, Wako-shi, Saitama, 351-0198, JAPAN

Fax: 81-48-462-4702, e-mail: etakeuti@postman.riken.go.jp

A new thermally stable photosensitive epoxy resin system using the photo-oxidation induced polycondensation (POP) reaction was developed, which consists of furan-substituted novolac, an epoxy resin and a curing agent of epoxy resin with fullerene as the sensitizer. The addition reaction of furfuryl glycidyl ether to novolac produced the furan-substituted novolac, whose degree of furan-substitution well reproduced the feed molar ratio of the starting materials. UV irradiation of the resin led to the crosslinking of the polymers to afford fine patterns with good quality. The polymer system had a high thermal stability with curing up to 180°C.

Key words: Photosensitive, Epoxy Resin, Thermal Stability, Fullerene, Photo-oxidation

1. Introduction

Epoxy resin has unique properties for use in electronics devices, such as thermal stability by curing at a moderate temperature and high adhesive strength. In addition, epoxy resin is much cheaper than the other thermally stable polymers such as polyimide. In recent years, a photosensitive epoxy resin, which has the processibility to make fine through-holes by photolithography, has been used as interlayer dielectrics or cover resists in semiconductor devices and printed circuits such as chip size package (CSP), ball grid array (BGA), multi chip module (MCM), built-up printed circuit boards and so on¹. In general, however, photoreactive groups and sensitizers used for these photosensitive resins are thermally unstable, causing a reduction in the heat resistance of the entire polymer system.

We have found that the UV-VIS irradiation of methyl 2-furoate in the presence of fullerene C₆₀ and oxygen molecules yielded a polycondensation resin precipitate, which was formed by the intermolecular dehydration induced by abstraction of the active hydrogen by the peroxy radical formed by the photo-oxidation of the furan ring (Photo-oxidation induced polycondensation; POP)². Based on this mechanism, a polymer having a 2-substituted furan in its side chains can be crosslinked by UV-VIS irradiation in the presence of C₆₀ in air. If this photocuring mechanism can be applied to a thermally stable polymer, it is expected that the polycondensation crosslinking will contribute to an increase in their thermostability after the UV-VIS irradiation. Moreover, the high thermal stability of C₆₀ as a photosensitizer provides a tolerance for use at high temperature. Consequently, the POP mechanism is expected to afford a new photosensitive resin having a highly thermal stability.

In the present paper, we report the development of a new photosensitive epoxy resin system based on the POP mechanism, consisting of furan-substituted novolac, epoxy resin, a curing agent and the fullerene. We evaluated its properties in terms of photosensitivity and thermal stability.

2. Experimental

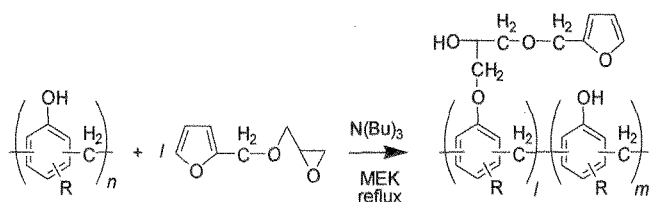
2.1 Preparation of furan-substituted novolac

The typical procedure for the reaction is as follows. A mixture of 9.361g of furfuryl glycidyl ether (FGE, Aldrich Chemicals Inc.) and 19.97g of 67.3% methyl ethyl ketone (MEK) solution of novolac (LF-4871, Dainippon Ink and Chemicals Inc.) was heated to its reflux temperature (110°C) and 0.05g of tri-*n*-butylamine was dropwise added. After 15 hours of heating, the reaction mixture was dropwise added into 1L of water and the precipitated resin was collected and dried *in vacuo* at 50°C to produce the furan-substituted novolac resin as a dark-brownish brittle solid in 85% yield. The spectroscopic data (IR and ¹H-NMR) were consistent with the given structure.

The methacryloyl-substituted novolac resin was also prepared by a similar procedure except using 8.63g of glycidyl methacrylate (Blenmer GMR, NOF Corp.) instead of FGE.

2.2. The formulation of photosensitive epoxy resin film

A typical preparation of the POP epoxy resin film is as follows. To a 0.4ml MEK solution of the furan-substituted novolac (degree of furan-substitution: 50%, 0.36g) were added the novolac type epoxy resin (N870, Dainippon Ink and Chemicals Inc., 0.25g), 0.083% (w/w) toluene solution of the fullerene C₆₀ (purity; >99.98%, Term Co., 4.2g), tri-*n*-butylamine (0.05g) and MEK (1.4g). A glass substrate was coated



Scheme 1.

with this solution using a spin coater. The substrate was prebaked for 10 minutes at 50°C in a forced convection oven. A 1.8 μm film thickness was determined using Alpha-Step500 surface profiler (KLA. Tencor Inc.).

The preparation of the epoxy resin film having methacryloyl moiety is as follows. To a 0.4ml MEK solution of methacryloyl-substituted novolac (0.36g) were added the novolac type epoxy resin (N870, 0.25g), the photoradical generator (Irgacure 651, Ciba Spezialitätenchemie AG, 0.034g), tri-*n*-butylamine (0.05g) and MEK (1.4g). The film preparation was performed in a similar manner as in the case of the epoxy resin film with furan moiety.

2.3. Photosensitivity and imaging

The epoxy resin film prepared by the above method was exposed to ultraviolet light using a 500W high-pressure mercury lamp for 5 minutes at room temperature. The intensity of the exposed surface was measured with an USHIO UTI-150 UV light meter, and adjusted to 20mW/cm² at 365nm. An imagewise exposure was carried out in the contact mode using masks made of quartz. The film was developed by dipping in a solution of tetramethylammonium hydroxide in water/MEK (85/15, v/v) for 15 seconds, and then rinsed in water for 1 minute.

2.4. Thermal stability

A polyethylene terephthalate film substrate (MRX-100, Diafoil Hoechst Co., Ltd.) was coated with the polymer solutions prepared in section 2.2. The coating was cured at up to 180°C for 1 hour. The thickness of the coating was determined to be 12 μm . The substrate was peeled off to obtain the cured epoxy resin film. A thermogravimetric analysis (TGA) of the film was performed using a TGA 2950 (TA Instruments Inc.) under nitrogen with 10°C/minute temperature ramps.

3. Results and Discussion

3.1 Synthesis of furan-substituted novolac

In order to utilize the photo-oxidation induced polycondensation (POP) reaction for a photosensitive

epoxy resin system, furan-substituted novolac was prepared by the ring-opening addition reaction of furfuryl glycidyl ether (FGE) to the phenolic hydroxyl group of novolac as shown in Scheme 1. The hydroxyl group of novolac is suitable to introduce the furan moiety by the addition reaction. Moreover, the remaining phenolic hydroxylic units not only can afford solubility to the aqueous alkaline developer, but also have reactivity with epoxy groups during thermal curing to produce a crosslinked structure after the photolithographic procedures. The ring-opening addition reaction was carried out at various feed molar ratios of FGE to the hydroxyl group in novolac. The degree of furan-substitution of the obtained polymer was calculated by the relative integral areas of the peaks at 6.4ppm (furan ring) and 6.5~7.5ppm (benzene ring) in the ¹H-NMR spectra. The relationship between the degree of furan-substitution and the feed molar ratio of FGE and novolac is summarized in Table 1. Table 1 shows that the degree of furan-substitution is in good agreement with the feed molar ratio. These results indicate that the ring-opening addition reaction of FGE to novolac stoichiometrically occurs. Therefore, the ratio of the furan moiety and phenolic hydroxyl group can be controlled readily by the feed molar ratio of the two starting reagents.

3.2 Lithographic evaluation

A film of photosensitive thermosetting resin consisting of the furan-substituted novolac, epoxy resin, fullerene C₆₀ and tri-*n*-butylamine was prepared to evaluate the pattern processibility. Figure 1 shows the imaged patterns of the film. The pattern had excellent quality with a resolution of better than 10 μm . The radiation-curing of the POP system is considered to proceed by the following process. The

Table 1. Degree of furan-substitution in the reaction of furfuryl glycidyl ether and novolac

| feed molar ratio | degree of substitution |
|------------------|------------------------|
| 0.35 | 0.33 |
| 0.55 | 0.50 |
| 0.73 | 0.71 |
| 1.02 | 1.00 |

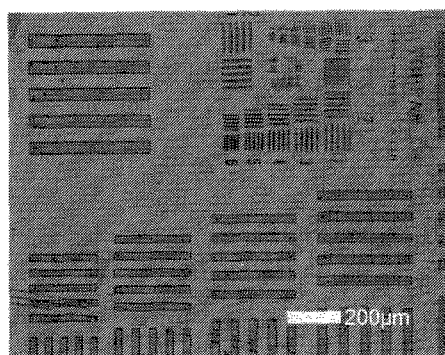


Figure 1. Photograph of the POP epoxy resin pattern (Film Thickness: 1.8 μm).

photosensitization of oxygen by the triplet state of C_{60} generates singlet oxygen, which adds to the furan units to form an endoperoxide. The peroxide then undergoes condensation by intermolecular dehydration to give a crosslinked polymer^{2,4}. The photocrosslinking procedure of the present photosensitive epoxy resin is summarized in Scheme 2

3.3 Thermal stability of the resin film

Thermal curing of the resin at a temperature up to 180°C was carried out to produce the crosslinked structure. Figure 2 shows the infrared spectra of the resin before and after the thermal curing. Disappearance of the absorption of the epoxy ring at 915cm^{-1} indicates that the thermal curing forces the reaction of epoxy resin to completion to give the crosslinked polymer network as shown in Scheme 2. The thermal stability of the photosensitive resin films was evaluated using a thermogravimetric analysis (TGA). Figure 3 shows the

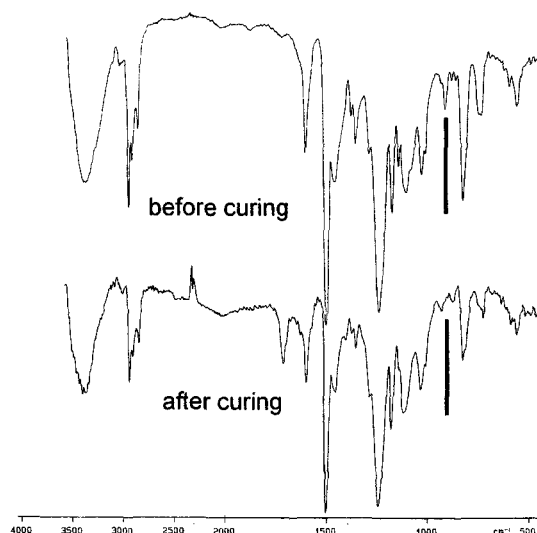


Figure 2. Infrared spectra of the POP epoxy resin mixture before and after thermal curing.

TGA curve of the resin after the thermal curing together with that of the epoxy resin having the methacryloyl moiety. The epoxy resin with the furan moiety showed a high thermal stability whose thermal degradation scarcely occurred below 300°C. On the other hand, the weight loss of the photosensitive epoxy resin using the methacryloyl moiety occurred at as low as 200°C. This result indicates that the POP epoxy resin system has a good thermal stability over 300°C.

Conventional photosensitive polymer systems using thermally weak photoreactive groups and sensitizers suffer from a lack of thermal stability unless they were annealed at high temperature to remove them. In contrast, our POP epoxy resin system does not need any annealing at high temperature to obtain a high heat resistance. The structures of both the photoreactive furanyl group in polymer and the photosensitizer, i.e., fullerene, contribute to its stability. Both the unreacted furan moiety and the final network structure shown in Scheme 2 may have a high thermal stability. Fullerene neither vaporizes nor decomposes below 300°C. Therefore, fullerene has no detrimental influence on the heat resistance of the resin.

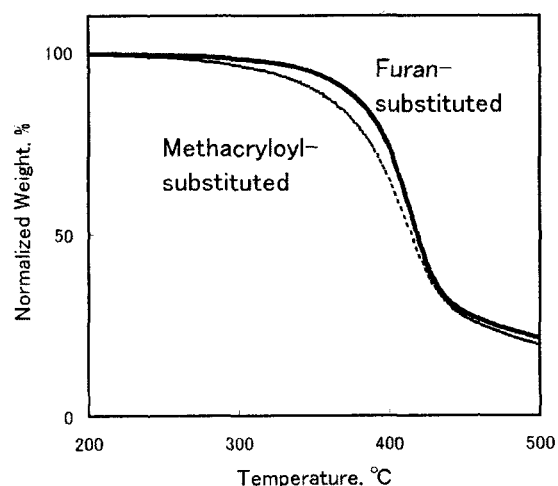
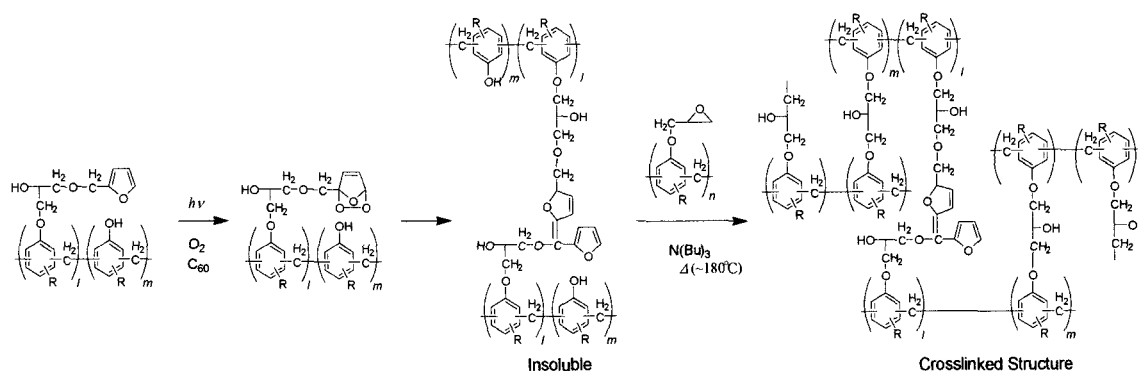


Figure 3. Thermogravimetric curve of photosensitive epoxy resin after curing (Heating rate = 10°C/min. in nitrogen).



Scheme 2.

4. Conclusion

We have developed a new thermally stable photosensitive epoxy resin system using fullerene as a photosensitizer. The photosensitive resin film can produce a fine pattern using the photolithographic process. The resin film showed good thermal stability, which was achieved after the curing process at moderate temperature. It will be suitable for use as semiconductor or printed circuit materials due to its unique properties in terms of high heat resistance, photolithographic capability and low temperature processibility. More detailed studies on the photosensitivity and thermal

properties of the POP epoxy resin system are now in progress.

References

- (1) T. Takahashi, *Journal of Japan Institute of Electronics Package*, **2**, 430(1999).
- (2) Y. Tajima, Y. Tezuka, T. Ishii and K. Takeuchi, *Polym. J.*, **29**, 1016(1997).
- (3) Y. Tajima, E. Takeuchi, Y. Shigemitsu and K. Takeuchi, manuscript in preparation.
- (4) Y. Tajima, H. Arai, Y. Tezuka, T. Ishii and K. Takeuchi, *Fullerene Sci. Technol.*, **5**, 1530(1997).

(Received December 7, 2000; Accepted January 31, 2001)