Study on Photosensitive Imaging System and Its Performance

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Abstract

In this paper, several affinity switching copolymers had been synthesized by the copolymerization of butyl acrylate (BMA), methyl methacrylic acid (MAA) and styrene as monomers. The photosensitive imaging system was composed with the copolymers, bisvinyl ether (BPA-DEVE) and photoacid generators (PAGs). The imaging performances and dissolution property of the tercomponent system were systematically investigated, and results showed that the imaging performances and dissolution property of the tercomponent systems were strongly dependent on the specific composition of the copolymer, the photoacid generator, the baking temperature and the baking time. Meanwhile, the crosslinking degree could be deepened by increasing the amount of BVE and the pre-baking temperature as well as prolonging the pre-baking time. Ideal results would be obtained when the three factors were adjusted properly. In addition, the higher proportion of MMA unit in the copolymers, the better performance of the tercomponent system.

Keyword: Acid Sensitive Polymer, Imaging System, Imaging Performances

Introduction

Acid sensitive imaging system was first used in the photoresist imaging system. At present it was applied in the computer to plate in the printing[1-4]. gradually which was high sensitive to violet laser. The imaging system was composed with the acid sensitive copolymers, bisvinyl ether type cross-linker (BPA-DEVE) and photoacid generators (PAGs). At the condition of a given wavelength, the imaging process of acid sensitive imaging system following by decomposition reaction made use of photoacid generators (PAG) to produce proton acid. Under the action of the acid generated and heated, the side chains protected group (carboxylate, sulfonate, etc.) of acid sensitive copolymers was reduced to decompose in imaging system. The ester groups of copolymer were removed to form hydrophilic acid radical (carboxyl group, sulfonic group, etc.), which caused to cross-link and de-cross-link of the polymer matrix and changde from hydrophobic to hydrophilic[5-7], at the same time, non-exposed regions was resulted to form differences including dissolution and affinity switch, and so the development processing helped to form images. The acid generated can also catalyze the side chain groups of resin to react with bisvinyl ether type cross-linker reacted to form the negative image. In fact, it can improve the acid production efficiency, as added acid proliferation agent into the system, thereby obtaining high chemical amplification and high sensitivity imaging system. The photoresist of photochemical acid system was widely used in large scale integrated circuits, which was due to good chemical amplification effect, high imaging sensitivity and imaging resolution.

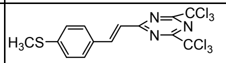
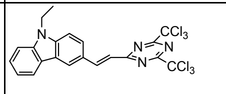
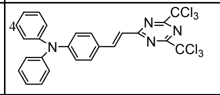
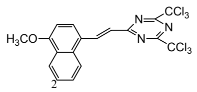
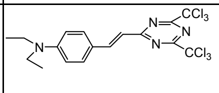
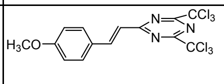
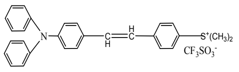
In this paper, a study was carried out on performance of the photosensitive imaging system which contains acid sensitive copolymer, bisvinyl ether type cross-linker and photoacid generators. The ideal results of the imaging system may be achieved by chose acid sensitive copolymer, photoacid generators and adjusted the concentration of bisvinyl ether, the concentration of photoacid generator, post-baking temperature and post-baking time.

Experimental

Reagents and Instrumentals

Acid sensitive copolymers, bisvinyl ether and photoacid generators were synthesized in our Lab.. Their molecule structure were determined with IR spectra were measured with SHIMADZU FTIR-8400 spectrophotometer and 1H NMR spectra were recorded with ARIA EMAN FX-300. Figure1 showed the molecule structure of acid sensitive copolymer and table 1 showed the molecule structure of photoacid generators. Other reagents were purchased and used as received. Most reagents were purified and dehydrated before used.

Table 1: The critical quantity of the divinyl ether

PAGs' NO.	PAGs' molecule structure
1#	
2#	
3#	
4#	
5#	
6#	
7#	

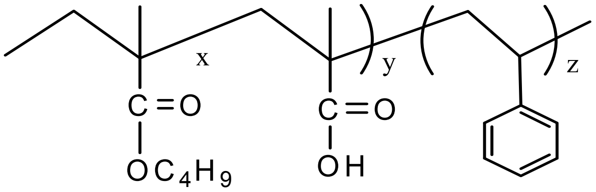


Figure1. The copolymer molecule structure and reactive process

Preparation of Imaging System

Under continuous agitation, the copolymer was completely dissolved in purified 1,4-dioxane and then divinyl ether type cross-linker and PAG were added, giving a transparent solution. The coating solution was applied to an aluminum substrate by using a modified spin-coater. The sample was dried in an open-air oven at 70 °C for 30min.

Measurement of Imaging Performance

Imaging properties were examined by using density method which was established in our Lab.. The plate density was measured by using iCPlate II of gmb Gretagmacbeth. The Blue Point4 light which made in Germany was used as the exposure light and monochromatic radiation was obtained by passing the light through a interference filter. Light intensity was measured by using Gamma Scientific's Digital Radio/Photometor DR-1600.

Results and Discussion

Determination of cross-linking agent concentration

Table 2: The critical quantity of the divinyl ether

Resin	MAA content (wt%)	the critical quantity of the divinyl ether (divinyl ether /resin)mass ration	divinyl ether content needed to build imaging system(divinyl ether /resin)mass ration
TPTB1	20.76	3%	5%
TPTB2	45.33	18%	19%

In imaging system, if the cross-linking agent content of photosensitive layer is too low, the degree of cross-linking is too small, and as a result, exposed regions of the photosensitive layer is limitedly resistant to developer, which results in swelling; Higher cross-linking agent concentration of photosensitive layer which raises the degree of cross-linking increases the acid concentration for de-cross-linking under the condition of post-baked and brings to the increase of the non-reacted divinyl ether. In the existence of acid, the divinyl ether reacting with cationic polymerization consumes part of acid, resulting in too low system sensitivity to image. Therefore, it is significance to determine the concentration of the cross-linking agent in the tercomponent system. Table 2 that is the critical quantity of the divinyl ether. divinyl ether concentration is slightly more than the critical quantity for building imaging system. As can be seen from Table 2, the more MAA unit concentration in the resin, the more divinyl ether needed to build imaging system. The reason is that the alkaline solubility of the copolymer P(TBMA-MAA-St) is better with the MAA unit concentration increased in the copolymer. Under a given baking temperature and baking time, it is necessary to increase the divinyl ether concentration to increase the degree of cross-linking and raise anti-alkaline of the imaging system.

Determination of the types of PAG

Table 3 is the shortest exposure time for the system to image clearly by adding kinds of PAG. As can be seen from table 2, it is less than 60s which is the shortest exposure time for the seven kinds of PAG to image clearly, but among the shortest exposure time which the PAG1# and PAG6# required is the shortest, that is high sensitivity. The sensitivity of the PAG1 # and PAG6 # is higher than other triazine PAG, which is due to the strong absorption in the position of 406.8nm. In that position PAG7# also has strong absorption, however, the degree of sensitivity of the PAG7# not higher than the other triazine PAG except PAG3#. The reason for this is that the quantum yield of acid production of triazine PAG is higher than the sulfonium salt PAG, that is ,with the same PAG's concentration the produced acid consistency of triazine PAG is higher than the sulfonium salt PAG, and the consistency of acid solution determine the degree of cross-linking directly. So far, as the degree of de-cross-linking, the effect of triazin PAG is better than the sulfonium salt PAG. The acidity of trifluoromethanesulfonic acid produced from sulfonium salt PAG is stronger than hydrochloric acid produced from triazine PAG. The removal of tert-butyl group of copolymer depends on the acidity, so sulfonium salt PAG is helpful for the removal of tert-butyl. Following the sample preparation and imaging conditions above, in view of the integrated effect resulted from de-cross-linking and the removal of tert-butyl, the PAG7# is inferior to PAG1#and PAG6#.

Table 3 The shortest exposure time for the system to image clearly by adding kinds of PAG

The kinds of PAG	1#	2#	3#	4#	5#	6#	7#
The shortest exposure time for the system to image clearly (s)	5	15	60	15	15	5	15

Influence of PAG concentration on sensitivity

Figure 2 that is the relationship between PAG concentration and lowest exposure energy curve. As can be seen from the curve, when PAG concentration increased from 5 wt% to 12 wt%, the lowest exposure energy decreased continuously and the lowest exposure energy decreased from 701mJ/cm^2 to 406mJ/cm^2, approximately decreasing 295mJ/cm^2. But, when the PAG concentration raised to 12 wt% from 10 wt%, the lowest exposure energy improved slow, approximately 1mJ/cm^2. When the PAG concentration up to 10wt%, with the acid action, the de-cross-linking and removal of tert-butyl could meet the requirements of affinity switch in imaging system, so the choice of PAG concentration was 10 wt%.

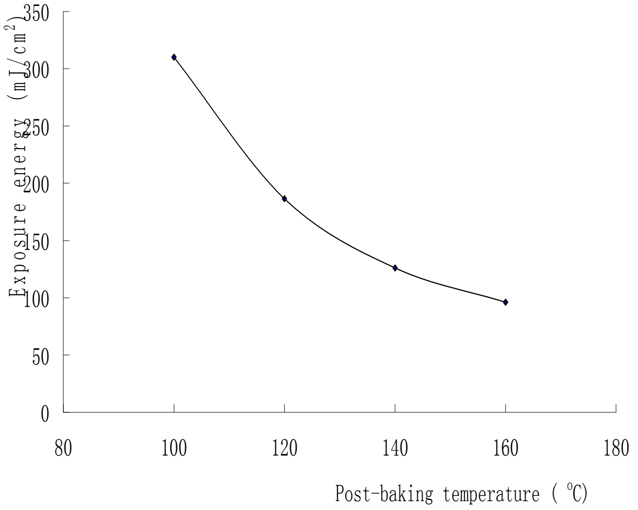


Figure2 The relationship between PAG content and sensitivity

Influence of baking temperature on sensitivity

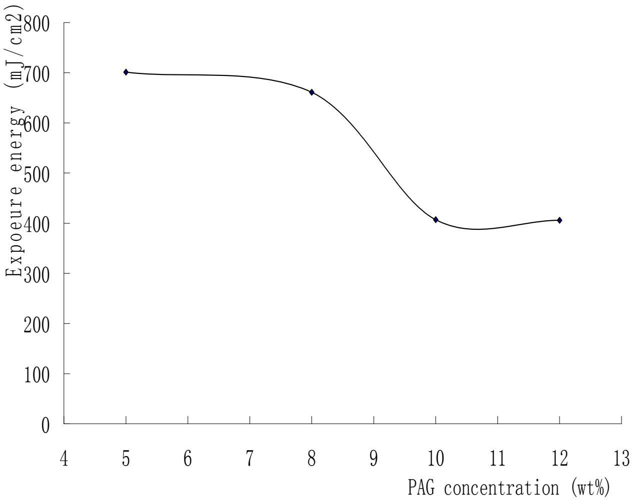


Figure 3 The relationship between baking temperature and exposure energy

Figure 3 that is the relationship between baking temperature and lowest exposure energy curve. As can be seen from the chart, with the increasing of baking temperature, the lowest exposure energy decreased continuously over a range of temperatures, under the condition of the fixed baking time which was 10min. This is because the activity of the acid and decomposition units of resin enhanced by increasing baking temperature, so that the acid decomposition of tert-butyl and de-cross-linking of the system promoted, the solubility of the system improved after exposed. When baking temperature was above 160 °C, the thermal stability of film-forming resin begun to decrease, accompanying with thermal decomposition reaction. Therefore, the baking temperature was 160 °C.

Influence of baking time on sensitivity

Figure4 is the relationship between baking time and exposure energy curve. As can be seen from the figure4, under the condition of fixed baking temperature which was 160 °C, with the increasing of baking time, the lowest exposure energy decreased continuously. When the baking time was up to 10 minute, the lowest exposure energy was basically stable, even though the exposure time was extended. The reason was that the degree of de-cross-linking and acid decomposition of tert-butyl increased gradually associating with exposure time extended. When the post-baking time was up to 10min, under the acid solution, the de-cross-linking and removal of tert-butyl could fully meet the requirements of affinity switch in imaging system. Therefore, the baking time was 10 minute.

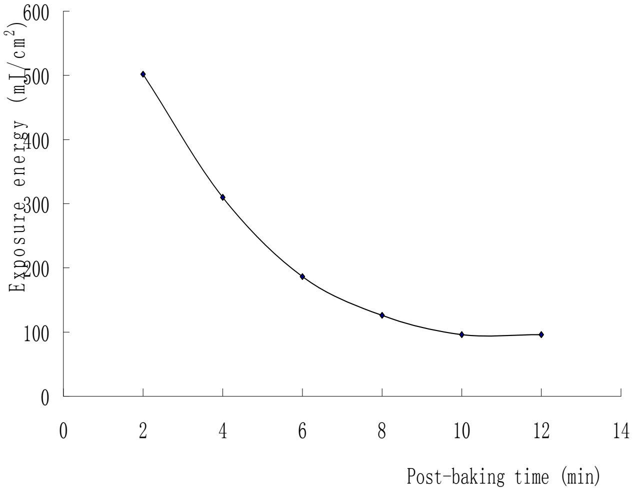


Figure 4 The relationship between baking time and the exposure energy

Conclusion

Fully studies were made on the imaging performances of photosensitive imaging system in which contained acid sensitive copolymer, bisvinyl ether type cross-linker and photoacid generators. Results showed that the imaging performances of the tercomponent systems were strongly dependent on the specific composition of the copolymer, the photoacid generator, the post-baking temperature and the post-baking time. Meanwhile, the cross-linking degree could be deepened by increasing the amount of BVE and the pre-baking temperature as well as prolonging the pre-baking time. Ideal results would be obtained when the three factors were adjusted properly. In addition, the higher proportion of MMA unit in the copolymers, the better performance of the tercomponent system. In the experiment condition, the lowest imaging exposure energy was 96mJ/cm^2 when the concentration of PAG was 10% and post-baking temperature was 160 °C and post-baking time was 10 minutes.

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