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SYNTHESIS AND PHOTOSENSITIVE PROPERTIES OF UV-CURABLE/ALKALI-SOLUBLE RESIN AS NEGATIVE PHOTORESIST

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Abstract

Novel UV-curable/alkali-soluble resins, named as PA/HEA, BA/HEA, MA/HEA, and HHPA/HEA, were prepared by esterification between 2-hydroxyethylacrylate (HEA) and different acid anhydrides respectively, e.g., phthalic anhydride (PA), succinic anhydride (BA), maleic anhydride (MA), and hexahydrophthalic anhydride (HHPA). The esterification conditions were calculated using the titration of the acid value and the FT-IR. Negative photoresists were prepared by blending AHEA with composite photoinitiators, while the optimal ratio of composite photoinitiators was determined by ultraviolet absorption spectra. The UV-curing process was investigated by FT-IR. It was found that the conversion

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of double bonds can reach 94.47% after exposure for 24s. The effect of photoinitiator on oxygen inhibition (OI) was investigated by ATR-FTIR. The results demonstrated that increasing photoinitiator concentration can produce higher OI resistance. The cured (AHEA) films showed good thermal stability under 150ºC. The PA/HEA and HHPA/HEA films could resist 10wt% hydrochloric acid for at least 30 min but could be stripped in 1wt% NaOH aqueous solution.

1. Introduction

Over the past few decades, UV lithography, as one of the most promising technologies available for fabricating micropatterns, has been widely applied in areas such as microelectronics, printed circuit boards, optoelectronics, printing plates, and photo-fabrications [1, 2]. In order to meet growing demand, the development of specific functional photoresists is highly desirable, especially for the fabrication of semiconductor devices. Compared with positive photoresist, negative photoresist has the advantages of a lower price and higher resistance to chemical agents, which are beneficial in industrial production. However, conventional negative photoresist will form a cross-linked structure after exposure to irradiation sources, making exposed parts more insoluble during development. Swelling is also a common side-effect of this process, leading to a loss of resolution [3]. On the other hand, cured negative photoresist must be stripped in organic solvents, which can be environmentally damaging.

Hence, the development of new types of negative photoresist has attracted considerable interest. Novolac resins containing pendant carboxyl groups have been prepared by the esterification of 4-hydroxyphenylacetic acid with various alcohols and ethylene glycol monobutyl ether. These novolac resins were then blended with photoacid generator (PAG) to form a negative tone photoresist [4]. Copolymers comprised of glycidyl methacrylate and acrylic acids have been synthesized in methyl ethyl ketone as a solvent via free-radical solution polymerization. In the presence of photogenerated acid, cationic crosslinking of the epoxide

rings was initiated after exposure to UV radiation. This kind of negative photoresist can also be applied in lithographic printing plates [5]. Functional monomers and monofunctional acrylic rosin derivatives have been synthesized from gum rosin and esterification of maleopimaric acid anhydride and various acrylates, respectively. With the use of trifunctional acrylates or photocrosslinkers, negative patterns can be obtained from rosin derivatives [6].

In this work, a new type of negative photoresist containing monofunctional acrylate with pendant carboxyl groups was prepared by blending with photoinitiators. Compared with other synthesis methods mentioned above, alkali-soluble resin can easily be synthesized by esterification of 2-hydroxyethylacrylate and anhydrides. After exposure to UV light, a linear polymer with functional group can be obtained. With the absence of swelling during development, UV-cured films can easily be stripped in alkali aqueous solution.

2. Experimental

2.1. Materials

2-Hydroxyethylacrylate (HEA) was kindly supplied by Aladin, Shanghai. Phthalic anhydride (PA), succinic anhydride (BA), maleic anhydride (MA), hexahydrophthalic anhydride (HHPA), and 4-methoxyphenol (MEHQ) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. They were processed to be analytically pure with the use of a polymerization inhibitor. Triphenylphosphine (TPP), a high activity catalyst, was also chemically pure and purchased from Shanghai Guanghua Technology Co. Ltd., China. Three kinds of photoinitiators in photoresist were obtained from Tianjin JiuRi Chemical Co. Ltd. China: 2-methyl-1-[4-(metylthio) phenyl]-2-(4-morpholino)-propan-2-one (907), isopropylthioanthraquinone (ITX), and α-hydroxy isobutyryl benzene (1173). All were industrial products. The reagents were all used as received. The structures of the four kinds of anhydrides used in the experiment are shown in Figure 1.

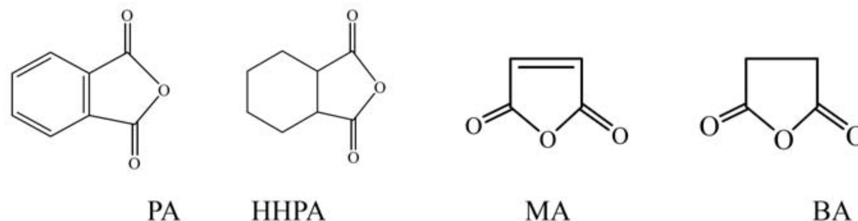

Figure 1. Structures of four kinds of anhydrides used in experiment.

2.2. Synthesis of UV-curable/alkali-soluble resin

HEA (0.2mol，23.23g), a small amount of TPP as catalyst (1%) and MEHQ as inhibitor (0.1wt%) were added into a 250mL three-necked round bottom flask, which was equipped with a thermometer, condenser and mechanical stirrer. Anhydrides (0.2mol) was dropped into the solution gradually and stirred at 80ºC under a nitrogen atmosphere. It was then heated to 90ºC and kept warm for 2~3h; the reaction formula is shown in Figure 2.

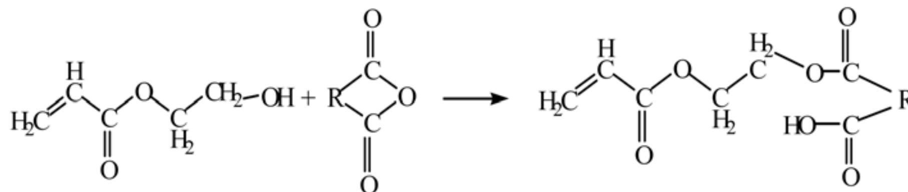

Figure 2. Synthesis of UV-curable/alkali-soluble resin.

2.3. Study of photosensitive properties

Negative photoresists were prepared by mixing UV-curable/alkali-soluble resin with photoinitiators and then stirred until complete dissolution. The blade was subsequently coated on a clean glass slide to about 30µm thickness. UV-curing of photoresist was carried out at room temperature with UV apparatus equipped with a high-pressure mercury lamp (1kw, $\lambda_{max} = 365nm$) and a speed-controllable moving belt. Exposure time was controlled by the speed of the moving belt. The

distance from the lamp to the samples was 15cm. After irradiation, the cured films were developed in acid solution (hydrochloric acid, 10wt%) and stripped in alkali solution (NaOH, 3wt%).

2.4. Analytical methods and characterization

2.4.1. Degree of esterification reaction

The progress of the esterification reaction was monitored by titration with 0.1N KOH alcoholic solution until the acid value was invariant.

Acid value (mgKOH/g) was determined by titration with 0.1N KOH alcoholic solution, using thymol blue as the indicator. Samples were taken and dissolved in mixed solution of toluene and absolute alcohol with a volume ratio of 2:1. They were then reacted with KOH. Where, A_0 is the theoretical acid value, M is the total mass at the beginning, N is the number of moles of anhydrides, A is the acid value in the reaction, C and V are the concentration and volume of standard solution in titration respectively. Where, m is mass of sample taken during reaction and P represents the degree of reaction.

$$A_0 = \frac{N \times 2 \times 56.11 \times 1000}{M}, \tag{1}$$

$$A = \frac{C \times V \times 56.11}{m}, \tag{2}$$

$$P = \frac{A_0 - A}{1/2A_0}. \tag{3}$$

2.4.2. Characterization of infrared spectra

IR spectra of four kinds of AHEA system were recorded via a Nicolet-170 SX FTIR spectroscopy (Perkin Elmer Co., USA) in the wave number range of $4000\text{-}400\text{cm}^{-1}$.

To evaluate the UV-curing process, AHEA resins were coated on KBr plates and cured with different UV dosages. By monitoring the disappearance of the specific IR absorption band at $1637 cm^{-1}$ for the stretching vibration of the $C=C$, the chemical conversion of the AHEA systems could be determined.

FTIR spectroscopy (Thermo Nicolet Co., USA) with an attenuated total reflectance (ATR) unit was employed in studying oxygen inhibition (OI) phenomenon appearing in radical polymerization [7]. Cured resins with different concentrations of photoinitiator were pressed against the germanium crystal and the surface was scanned 10 times at a $4 cm^{-1}$ resolution to generate FTIR-ATR spectra. The height of the $C-H$ absorption peak in double-bond ($810 cm^{-1}$) was measured for both the uncured ($H_{uncured}$) and cured (H_{cured}) resins. The degree of conversion (DC) was calculated from the ratio

$$DC(\%) = \left(1 - \frac{H_{cured}}{H_{uncured}}\right) \times 100. \quad (4)$$

2.4.3. Viscosity

Viscosities of different AHEA were performed at 35°C on a NDJ-8S digital brookfield rotational viscometer.

2.4.4. UV absorption spectra

The absorption spectra of photoinitiators were recorded with an UV/visible spectrophotometer (UV-2550, SHIMADZU, Japan) in the wavelength range of 200~450nm. The photoinitiator system 907/ITX with different ratios was dissolved in methyl alcohol with a concentration of 0.01mg/mL and then filled by quartz cells with a path length of 1cm.

2.4.5. Thermal analysis

Thermal gravimetric analysis (TGA) was carried out via a thermogravimetric analyzer (STA449C, NETZSCH, Germany) under N_2 atmosphere and heated from room temperature to 500°C with a heating rate of 10°C/min.

3. Results and Discussion

3.1. Synthesis of UV-curable/alkali-soluble resins

In this work, novel UV-curable/alkali-soluble resins were prepared by esterification between OH groups of HEA and different anhydride groups at a certain synthesis conditions. Table 1 lists four kinds of resin prepared by different anhydrides with HEA and the degree of reaction system as calculated. The reaction process was also monitored by acid value. The results demonstrated that different anhydrides under the same synthesis conditions can exhibit different activities when reacting with HEA. The activity diminished as follows: MA > HHPA > BA > PA. Moreover, viscosities of production varied from each other greatly, which can be attributed mainly to the different melting points of anhydrides. Take PA, for example, it is hard to dissolve in the reaction system due to its higher melting point, which makes anhydride group difficult to react with OH of HEA molecules, subsequently resulting in lower conversion and higher viscosity in all resin.

Table 1. Product of HEA modified by different anhydrides

Sample of resin	Component	Reaction time/h	Terminal acid value/mgKOH $\cdot g^{-1}$	Conversion/ %	Viscosity (35ºC) /CP
1	PA/HEA	3	316.83	49.16	21000
2	MA/HEA	3	276.12	93.42	375
3	BA/HEA	3	301.05	82.64	2600
4	HHPA/HEA	3	233.79	86.13	3710

*Reaction temperature is 90ºC; every resin is cured in the same conditions mentioned above.

The structures were confirmed by FTIR (Figure 3). As seen in the spectra, the absorption peak of hydroxyl group of HEA between $3600\sim3200cm^{-1}$ largely decreased due to the reaction with the anhydride groups. This resulted in the formation of a carboxylic acid group in different resins, which exhibited a broad absorbance range between $2500cm^{-1}$ and $3300cm^{-1}$. The absorption peak of double bonds can be

observed at $1640cm^{-1}$ and $810cm^{-1}$ in all spectra but is seen to slightly weaken from (a) to others. This can be attributed to the partial polymerization of double bonds during the reaction. While small peaks were observed at $1860cm^{-1}$ and $1280cm^{-1}$, indicating the existence of some unreacted anhydride groups in products.

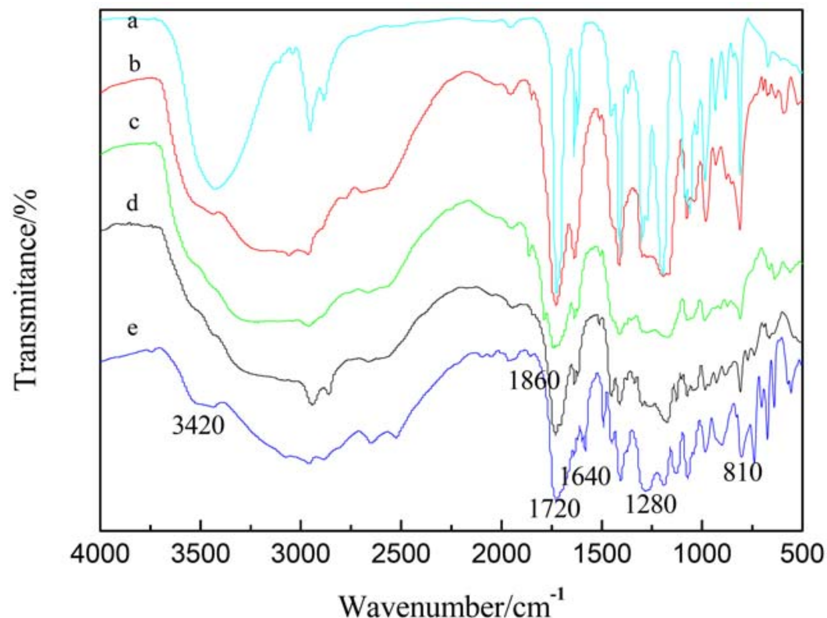

Figure 3. IR spectra of (a) HEA, (b) MA/HEA, (c) BA/HEA, (d) HHPA/HEA, and (e) PA/HEA.

3.2. Composite 907/ITX photoinitiators

Activities of photoinitiators have been widely studied in the open literature [8]. In this paper, 907/ITX composite photoinitiators were selected due to their excellent photo initiating performance and good compatibility with resin, especially in colored photosensitive systems. To determine the ratio of 907 to ITX in our experiment, composites photoinitiators were prepared by using different weight ratios of 907/ITX: 2/1, 3/1, 4/1. They were then characterized on a UV/visible spectrophotometer. The absorption spectra are shown in Figure 4.

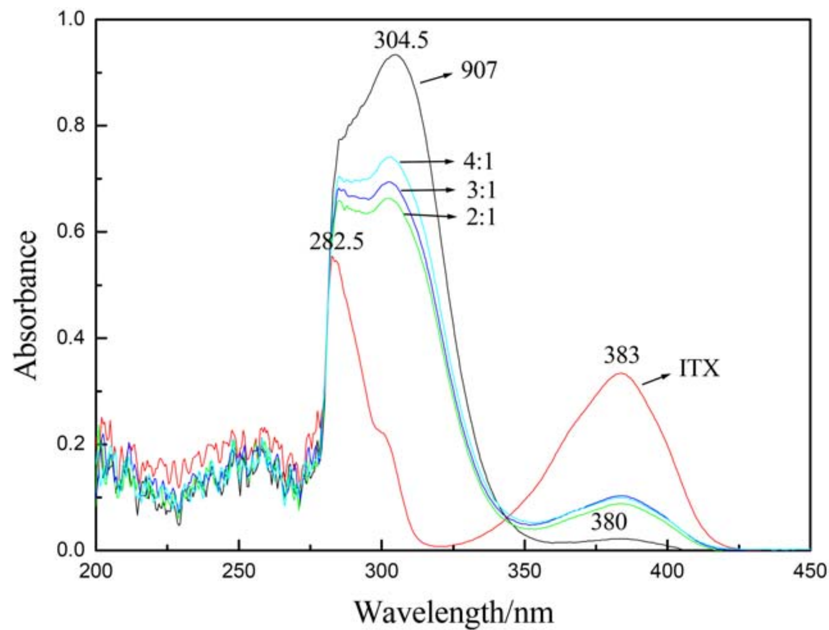

Figure 4. Ultraviolet absorption spectra of 907/ITX composite photoinitiators.

As we can see from Figure 4, absorption peaks of 907 appeared at 304.5nm and 380nm, while ITX owned maximum absorption at 282.5nm and 383nm. Composite 907/ITX demonstrated wide absorption between 280~400nm. Although the intensity of absorption decreased slightly compared with 907 or ITX, it is still beneficial for the curing of photosensitive prepolymers. In addition, composite 907/ITX showed the highest absorbance when the ratio of 907 to ITX was 4:1; this can be attributed to the synergistic effect between photoinitiator 907 and photosensitizer ITX [9]. Therefore, composite 907/ITX with a 4/1 ratio was selected as the photoinitiator system in our experiment.

Furthermore, HHPA/HEA resin with different contents of composite 907/ITX were prepared and irradiated in the UV apparatus mentioned above, and the energy of complete curing was subsequently captured by the UV energy meter (ORC UV-351, Japan). The results are shown in Table 2. Resin has proven difficult to cure without photoinitiators. With increasing amounts of photoinitiators, more free radicals were produced

and the photopolymerization of prepolymers was accelerated with relatively low energy. The energy therefore decreased dramatically. When the content was over 3wt% of resin, the change of energy was tiny, which was due to the saturation in the concentration of free radicals in prepolymers. Hence, 3wt% of the composite photoinitiators did meet demand in the curing process.

Table 2. Effect of the content of photoinitiator on curing behaviour

Mass fraction of photoinitiator/%	4	3	2	1	0.5	0
Curing energy/mJ · cm^{-2}	206	395	620	1000	> 1740	Difficult to cure

*The ratio of 907 to ITX is 4/1.

3.3. Study of photosensitive properties

Four kinds of AHEA containing 3wt% composite photoinitiators exhibited different photosensitive properties as a consequence of different structures and viscosities. As shown in Table 1, MA/HEA had bad UV-curing behaviour. This can be attributed to the very low viscosity of MA/HEA, which resulted in large gaps between double bonds and made polymerization difficult. Otherwise, BA/HEA was much better than HHPA/HEA and PA/HEA, as there was no bulky phenyl and cyclohexyl to hinder the reaction of double bonds. Figure 5 shows the IR spectra of cured films: (a) HHPA/HEA, (b) PA/HEA, and (c) BA/HEA. Noticeably, the characteristic peaks of double bonds disappeared at $1640cm^{-1}$ and $810cm^{-1}$, indicating the complete curing of these prepolymers. The bond at about $3400cm^{-1}$ can be credited to the stretching vibration of the hydroxyl group. This could be the result of the unreacted HEA participating in polymerization or a small amount of water that absorbed onto cured AHEA in storage because of the presence of polar carboxylic acid groups. Therefore, cured AHEA films should be stored in dry conditions.

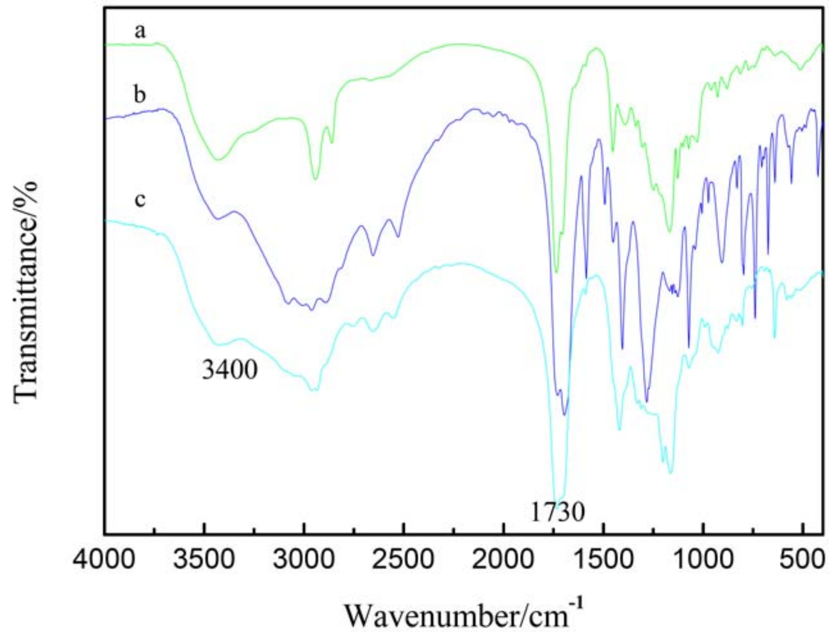

Figure 5. IR spectra of cured film, (a) HHPA/HEA, (b) PA/HEA, and (c) BA/HEA.

3.4. UV-curing process investigated by the FT-IR spectrum

HHPA/HEA containing 3wt% 907/ITX of 4/1 ratio was prepared and UV-cured with varying exposure times controlled by adjusting the speed of moving belt. Five of the selected FT-IR spectra are shown in Figure 6. It can be seen that the intensity of $C = C$ in stretching vibration absorption at 1637cm^{-1} diminished as acrylic ester prepolymer was converted to polymer. Several invariant peaks also were also displayed in the spectra. The experimental procedures for spectrometric measurements were strictly controlled to keep the absorption of the peaks stable. The absorption of cyclohexyl in HHPA/HEA at 1030cm^{-1} (A_{1030}) could serve as an internal standard to normalize the polymer spectra. As a result, the area of peak at $1637\text{cm}^{-1}(A_{1637})$ could be converted into relative values, and the conversion of double bonds (DC)

was calculated from the following equation by relative values with various exposure times (t):

$$DC\% = \frac{(A_{1637}/A_{1030})_0 - (A_{1637}/A_{1030})_t}{(A_{1637}/A_{1030})_0} \times 100\%. \quad (5)$$

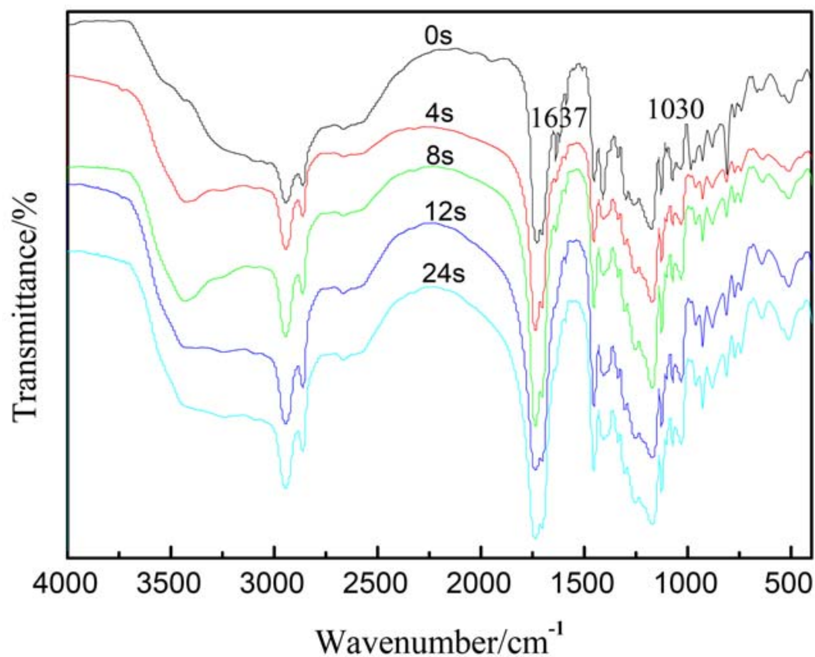

Figure 6. IR spectra of HHPA/HEA cured film in different exposure times.

Table 3 lists areas of peaks at $1637 cm^{-1}$ and $1030 cm^{-1}$. Upon increasing the exposure time from 0s to 4s, the conversion of double bonds increased by about 50%, which indicated that the photosensitive system was highly reactive in UV light. After exposure for 24s, conversion could reach 94.47%. This clearly demonstrated correlation between the rapidly increasing conversion rate in the early stage of exposure and the slow growth after exposure for 12s. This can be mainly attributed to the concentrations of double bonds dropping off while undergoing polymerization; this increases the probability of coupling

termination of radicals. Thus, it is evidently undesirable to promote the photocuring degree by extending exposure time merely with a certain concentration of photoinitiators.

Table 3. Conversion of carbonate double bond in different exposure time

Exposure time t/s	A_{1637}	A_{1030}	$(A_{1637} / A_{1030})_t$	DC(%)
0	86.003	206.675	41.61%	0
4	52.637	256.189	20.55%	50.61
8	44.867	375.814	11.94%	71.30
12	29.310	439.105	6.67%	83.97
24	10.527	456.671	2.31%	94.47

3.5. Effect of photoinitiator on oxygen inhibition

It is well known that OI is a common phenomenon in polymerization triggered by free radicals [10], which can result in a tacky surface with poor mechanical properties. In this work, resins HHPA/HEA with different concentrations of photoinitiator 1173 were cured in atmosphere and the effect of photoinitiator on OI was investigated by ATR-TTIR. The results are shown in Figure 7. Peak at $810cm^{-1}$ is the characteristic absorbance of C − H of double bonds, which showed weakening intensity with increasing concentration of photointiator 1173.

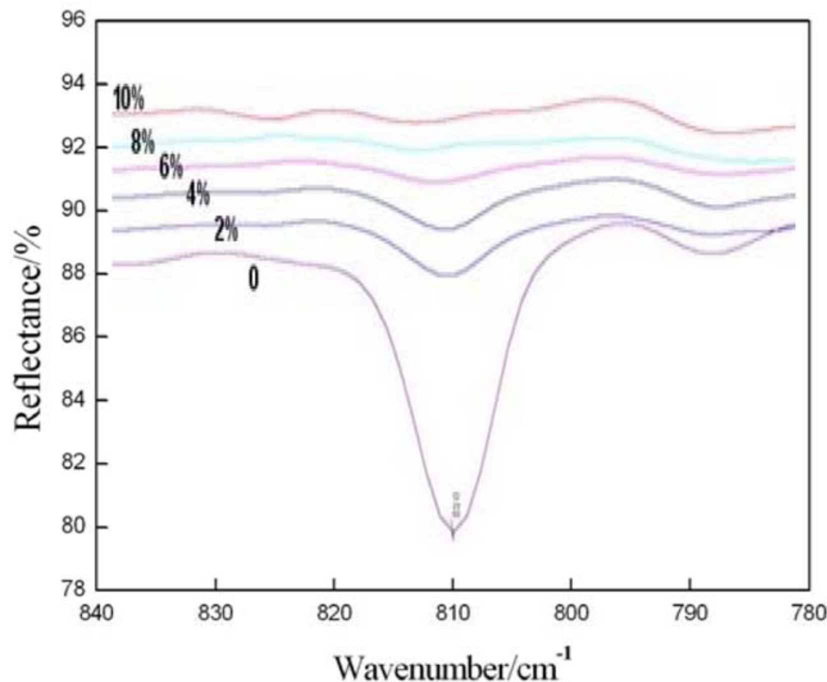

Figure 7. ATR-FTIR spectra of cured film with different concentrations of the photointiator 1173.

This indicates that a higher content of photoinitiator can lead to higher conversion of double bonds on the surface of the film and less influence caused by oxygen inhibition. The conversion values were calculated in accordance with formula (4) and are shown in Figure 8. In a lower content of photoinitiator (2wt%), DC for the film surface was found to be 80.72%. DC however, could achieve about 96% when the content increased to 8wt% and was kept almost equivalent in 10wt%. Therefore, increasing the concentration of photoinitiator has shown to be an effective method in producing higher OI resistance.

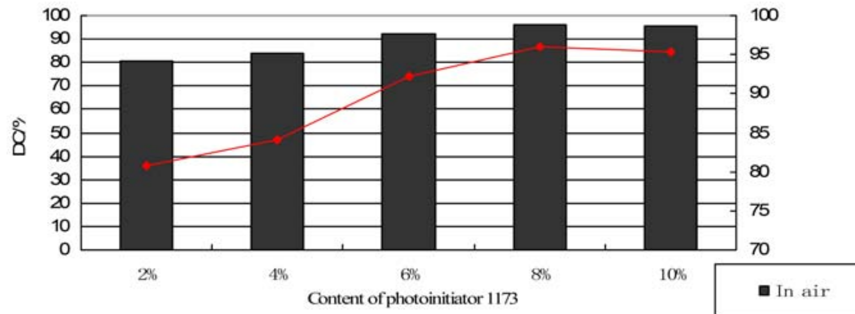

Figure 8. DCs of cured film surface with different concentrations of photoinitiator 1173.

3.6. Thermal stability

As illustrated in Figure 9, the thermal stability of different UV-cured coatings was evaluated by the weight loss thermograms recorded in N_2 atmosphere. From 35ºC to 150ºC, different UV-cured films have a weight loss of about 3%~5%. This can be attributed to the evaporation of moisture absorbed by hydrophilic carboxyl groups. Weight loss in cured PA/HEA and HHPA/HEA films was slightly lower than that of BA/HEA film, mainly because BA/HEA system has a higher yield and more carboxyl groups. Mass weight loss occurred at around 150ºC due to the decomposition of ester groups and unreacted HEA including anhydrides. It is therefore evident that cured films of products can be applied well under 150ºC but should be kept in dry conditions.

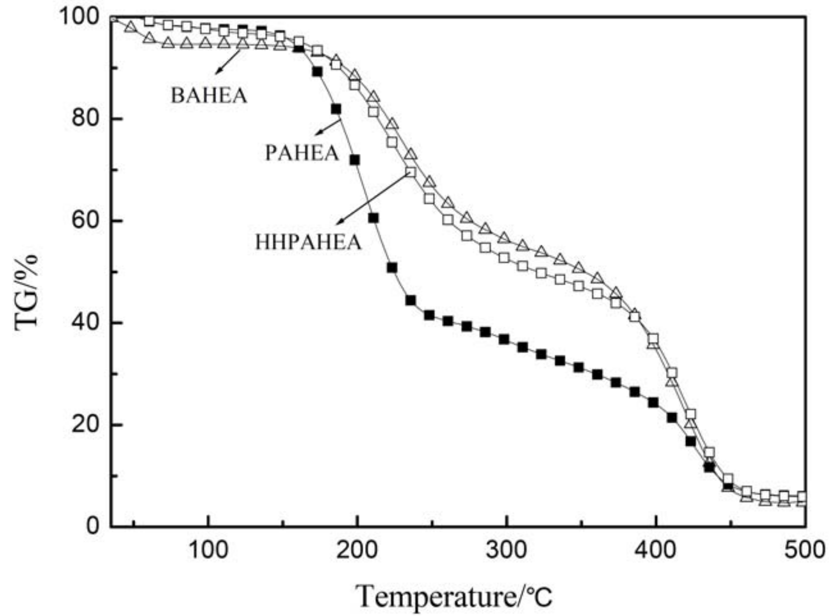

Figure 9. TG curves of different cured films.

3.7. Acid resistance

Good resistance to acid is one of the main advantages of photoresist in the etching process of semiconductors such as ITO. The cured photoresist can thus protect semiconductors from etching by strong acid like hydrochloric acid. In this work, 10wt% hydrochloric acid was selected to evaluate the property of acid resistance at room temperature of about 27°C. Different cured films were prepared in the same UV dosage and immersed in acid; the results are shown in Figure 10. After 5min, BA/HEA cured film was partially stripped from glass substrate. PA/HEA and HHPA/HEA were able to keep the film smooth and of integrity for at least 30min. After 60min, cured HHPA/HEA film began wrinkling, far ahead of PA/HEA film. This could be related to the strong adhesive force associated with substrates and the excellent surface hardness of PA/HEA and HHPA/HEA resulting from the presence of the benzene ring and cyclohexyl.

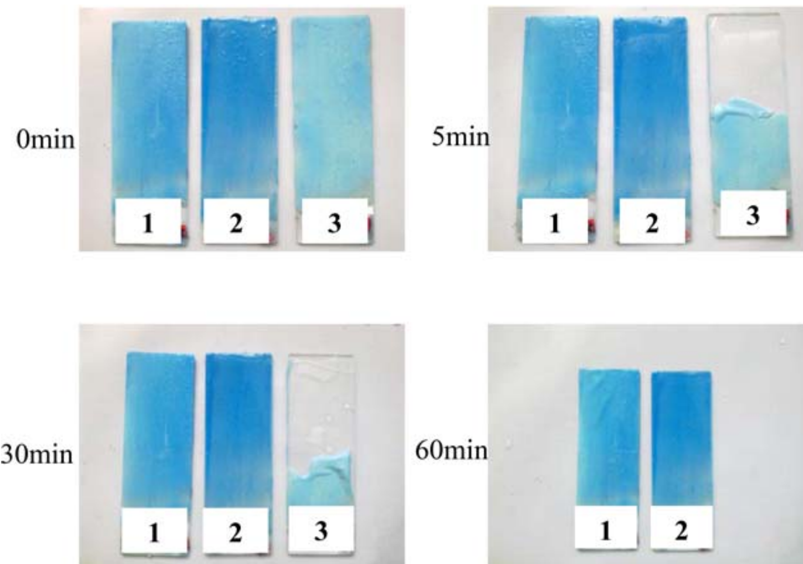

Figure 10. Acid resistance of UV cured film on glass in different system (1) HHPA/HEA, (2) PA/HEA, and (3) BA/HEA.

3.8. Stripping film in alkali aqueous solution

Good properties for stripping film after the etching process can earn more time to promote industrial productivity. Lower concentrations of alkali aqueous solution and a shorter time span represent advantageous properties for stripping. Different cured films were immersed in 1wt% NaOH aqueous solution at room temperature. The results of stripping after 2min without any external forces are shown in Figure 11. The under part without immersion was treated as a matched group. As can be seen from the picture, BA/HEA film was stripped faster than PA/HEA and HHPA/HEA film in alkali solution. This can be attributed to the lower adhesive force of BA/HEA with substrate and more carboxyl groups, making alkali aqueous react more easily with polar carboxyl group and leading to the stripping of substrates.

Figure 11. Property of stripping film in NaOH aqueous solution (1) HHPA/HEA, (2) PA/HEA, and (3) BA/HEA.

4. Conclusion

Different UV-curable/alkali-soluble resins were prepared by esterification between the OH groups of HEA and anhydrides. The conversion of reaction diminished as follows: MA > HHPA > BA > PA. Before performing the UV curing experiment, 907/ITX composite photoinitiators were selected and the ratio of 907 to ITX was determined by ultraviolet absorption spectra. The optimal was identified as 4:1. The UV-curing process was investigated by FT-IR spectrum; conversion of the double bonds was shown to jump dramatically in the early stage and could reach 94.47% after exposure for 24s. The effect of photoinitiator on OI was investigated by ATR-TTIR. It was evident that increasing the concentration of photoinitiator was effective in producing a higher OI resistance. The cured films possessed good thermal stability under 150°C;

PA/HEA and HHPA/HEA could resist 10wt% hydrochloric acid for at least 30min and strip the film in 1wt% NaOH aqueous solution. From the above, it can be concluded that HHPA/HEA would be more highly appropriate as a main resin in negative photoresist.

References

[1] L. E. Schmidt, S. Yi, Y. H. Jin, Y. Leterrier, Y. H. Cho and J. A. E. Manson, J. Micromech. Microeng. 18 (2008), 045022;

DOI:10.1088/0960-1317/18/4/045022.

[2] R. Yang, S. A. Soper and W. Wang, Sens. Actuators A 135 (2007), 625-636.

[3] M. Sharma, A. A. Naik, M. Gaur, P. Raghunathan and S. V. Eswaran, J. Chem. Sci. 121 (2009), 503-508.

[4] H. H. Liu, W. T. Chen and F. T. Wu, J. Polym. Res. 9 (2002), 251-256.

[5] A. M. El-Demerdash and W. A. Sadik, J. Appl. Polym. Sci. 118 (2010), 1933-1942.

[6] J. S. Lee and S. I. Hong, Eur. Polym. J. 38 (2002), 387-392.

[7] L. Feng and B. I. Suh, J. Appl. Polym. Sci. 112 (2009), 1565-1571.

[8] K. Dietliker, R. Husler, J. Birbaum, S. Ilg, S. Villeneuve, K. Studer, T. Jung, J. Benkhoff, H. Kura and A. Matsumoto, Prog. Org. Coat. 58 (2007), 146-157.

[9] H. Q. Xie, X. G. Zhan and D. Xie, J. Appl. Polym. Sci. 98 (2005), 1607-1614.

[10] R. F. Bartholomew and R. S. Davidson, Part I, J. Chem. Soc. (1971), 2342-2346.