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奈米二氧化矽改質負型壓克力彩色光阻之製備

Characterization of Acrylic Copolymers applied in Negative-Type
Photoresist via a Ternary Composition Diagram

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計畫主持人：張正良

共同主持人：鄭廖平

計畫參與人員：張誌民、陳志維

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摘要

本研究成功合成三成份壓克力共聚高分子作為負型光阻之結合劑，並針對其各項性質進行檢測。本研究中首先以自由基聚合法製備雙成分結合劑，並針對其熱性質、黏度及分子量進行檢測。隨後在雙成份結合劑中加入另一單體以製備三成分結合劑。所製備之結合劑藉由 FT-IR 進行化學結構之鑑定，並以 TGA 及 DSC 檢測材料之熱性質。最後可繪製三成分組成座標圖並利用所檢測之結果判定三成分結合劑的最佳組成比例。

關鍵詞：結合劑、三成分組成座標圖、負型光阻

ABSTRACT

Three-component acrylic copolymers used as a binder for negative-type photoresists were synthesized and characterized. First, free radical polymerization was employed to synthesize two-component binders, i.e., acrylic ester copolymers with different ratios of benzyl methacrylate (BZMA) and methacrylic acid (MAA). Thermal behavior, viscosity and molecular weight of the prepared two-component binders were studied. Then, a series of three-component binders were prepared through incorporation of another monomer, 2-hydroxyethyl methacrylate (2-HEMA). FTIR was used to examine the evolution of chemical bonds at various stages of the synthetic process. Thermal analyses, TGA and DSC, were used to evaluate the level of enhancement on thermal stabilities of the prepared three-component binders. Finally, an optimal region in the ternary composition diagram of BZMA, MAA, and 2-HEMA can be identified by comparing the results of acid value, viscosity and molecular weight of the binder.

Key words: binder; ternary composition diagram; negative-type photoresists

INTRODUCTION

Photoresist is generally a type of photosensitive polymer solution. The classification of photoresist is commonly based on the reaction mechanism during the exposure process [1-4]. If a positive-type photoresist is exposed to photo irradiation, the exposed area could be removed by dissolution in an alkaline developer liquid in the developing process. In contrast, the dissolved area of a negative-type photoresist is the unexposed area because the exposed area is crosslinked upon irradiation. After development, the desired circuit or pattern is formed on a substrate. Photoresists are widely used for the manufacture of microelectronics, silk screen printings, printed circuit boards, optical disks, color filter resists and so on [5-7].

Typically, a negative-type photoresist consists of polymer binder, photosensitive polyfunctional monomer, photoinitiator, solvents and additives [8,9]. Acrylic monomers used to synthesize the binder contain the desired functional groups, such as benzyl, hydroxyl, carboxyl groups, etc. The former two functional groups can improve both the dispersion of pigments and the adhesion of photoresist on glass substrate. On the other hand, carboxyl group can provide sufficient acid value of the prepared photoresist. However, it should be noted that when the content of polar functional groups, such as hydroxyl and carboxyl groups, is too high, the solubility of the synthesized binders in organic solvent decreases. A suitable amount of pigment may be added into the photoresist to form colored photoresist, which is termed pigment dispersant color resist (PDCR), and is applied to color filter formation.

As a binder for industrial applications,

there are several basic criteria that should be obeyed. For example, the acid value has to be larger than 100 mg KOH/g and the molecular weight be controlled in the range of $1.5\sim 3.5\times 10^4$ g/mol. Supposed that the binder is to be used for the manufacture of photoresist applied in color filter, the resolution should be less than 10 μm . In this research, a series of binders were synthesized by free radical copolymerization of three kinds of acrylic monomers (BZMA, MAA, and 2-HEMA), and their properties were studied to find the optimal compositions for the binder. More importantly, the optimal composition of the synthesized binders was determined using a ternary composition diagram. Following that a negative-type photoresist was prepared and its resolution was determined.

EXPERIMENTAL

Copolymer binders were prepared by free radical polymerization of three kinds of acrylate monomers, BZMA, MAA, and 2-HEMA in cyclohexanone (solid content = 40 wt%). The monomer solution was preheated at 100°C and stirred under nitrogen atmosphere. Then, initiator (AIBN, 1 wt% of total monomers) and chain-transfer agent (Thiol, 1 wt % of total monomers) dissolved in the same solvent were dropped slowly into the monomer solution. Free-radical polymerization was carried out for 6 h, and then the product was cooled down to room temperature. The obtained acrylate resin, poly(BZMA-MAA-2HEMA), was used as the binder of the photoresist. Binder samples were named according to the rule: the first letter of the monomer name followed by their respective compositions in molar percentage. To prepare samples for characterization of thermal

property, acid value, or chemical structure, the formed binder solution was diluted with tetrahydrofuran (THF) and then poured into hexane to induce polymer precipitation. The precipitation procedure was repeated twice to ensure free of residual monomers. Finally, the white polymer precipitate were separated by filtration and then dried in vacuo at 60°C.

RESULTS AND DISCUSSION

Three-component binders were prepared by incorporation of the third kind of acrylate monomer, 2-HEMA, in the synthesis process. Because of its hydroxyl group, 2-HEMA could enhance the adhesion between photoresist and glass substrate. However, viscosity of the prepared binder will increase as 2-HEMA content increases. In the discussion that follows, thermal behavior, viscosity, M_w and acid value of three-component binders were presented and compared. Compositions of the three monomers in the binder were illustrated in terms of a “ternary composition diagram” (cf. Fig.1 (▲)).

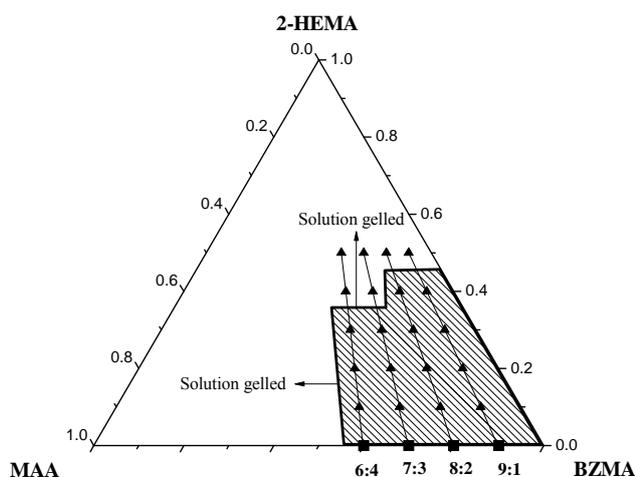


Fig. 1 Ternary composition diagram of the prepared binders.

(a) Thermal behaviors

Glass transition temperatures (T_g) of pure poly(2-hydroxyethyl methacrylate) is 55°C, as obtained from the literature. Previous results of two-component binders showed that T_g increased with increasing MAA content. DSC thermograms of the three-component binders are shown in Fig. 2, and T_g values are collected in Table 1. It appears that T_g of the binders with the same BZMA/MAA ratio were very close to each other, regardless of the 2-HEMA content. Specifically, for the case of BZMA/MAA= 9:1, T_g of the four binders are all closed to 74°C. However, T_g of the B80M20H0 was still slightly higher than that of B56M14H30, ca. 1.4°C, due to the higher content of MAA. On the other hand, for samples of the same 2-HEMA content, T_g increased with increasing MAA content, in accordance with the previous results.

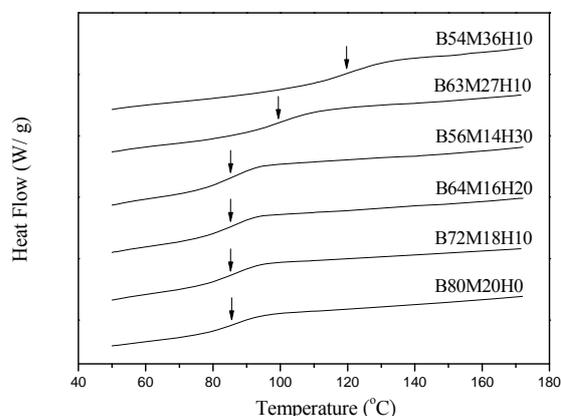


Fig. 2 DSC thermograms of several three-component binders.

TGA was utilized to measure the T_d of the three-component binders. Because thermal decomposition behaviors of the three-component binders were complicate and

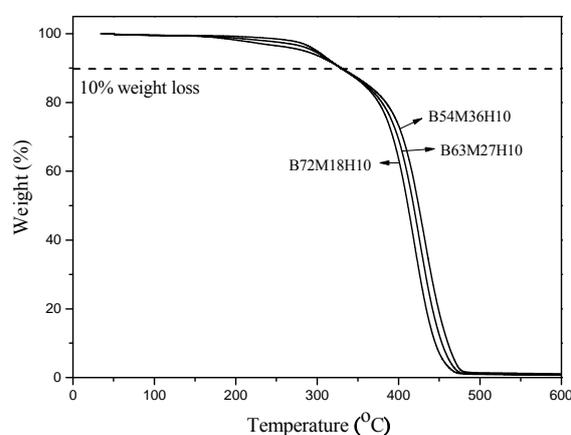
involved several stages, the temperature corresponding to 10 wt% loss was identified as the thermal degradation temperature, T_{d10} , for easy comparison. The results are listed in Table 1. Fig. 3 shows the TGA thermograms of several typical three-component binders, from which it can be seen that the thermal decomposition generally follows a three-stage pattern, which is consistent with the data shown in the literature. For all samples, the first-, second- and the third-stage occurred at about 180-250°C, 250-400°C and 400-470°C, respectively. The weight loss in the first-stage could be attributed to the reactions of MAA with adjacent MAA or 2-HEMA monomer unit, for which water was lost during the formation of anhydride or ester group. Because the ranges of thermal decompositions for poly(2-HEMA) and poly(BZMA) were 250-430°C and 250-400°C, respectively, the second-stage decomposition in Fig. 3 was due to both 2-HEMA and BZMA segments. This explains why the weight loss of the binder containing 72% BZMA, B72M18H10, in Fig. 3(a) was most obvious of the three samples over the temperature range 250-400°C. For the third-stage decomposition, the weight loss could largely be attributed to the MAA units (the thermal decomposition range of poly(MAA) is 370-470°C) in the binders. Therefore, the third-stage degradation temperature increased as the MAA content increased. For example, Fig. 3(a) demonstrates that the highest third-stage thermal degradation temperature of the three samples was the binder B54M36H10. Fig. 3(b) shows that the extent of the first-stage decomposition increased as the 2-HEMA and MAA content increased; furthermore, the decomposition of the binder

“B56M14H30” was most evident over the temperature range of 250-430°C due to its high 2-HEMA content. In addition, T_{d10} also increased with increasing MAA content in the binder, cf. Table 1.

Table 1 Thermal behaviors of the prepared three-component binders.

Sample	BZMA/MAA (molar ratio)	Thermal behaviors	
		T_g (°C)	T_{d10} (°C)
B81M9H10	9:1	74.4	316.8
B72M8H20	9:1	74.7	314.8
B63M7H30	9:1	74.8	310.8
B54M6H40	9:1	73.6	302.5
B72M18H10	8:2	87.1	328.8
B64M16H20	8:2	86.5	314.4
B56M14H30	8:2	86.2	307.9
B48M12H40	8:2	85.8	306.6
B63M27H10	7:3	99.9	329.7
B56M24H20	7:3	99.0	322.9
B49M21H30	7:3	93.8	316.8
B54M36H10	6:4	120.4	329.8
B48M32H20	6:4	110.1	323.5
B42M28H30	6:4	109.9	318.6

(a)



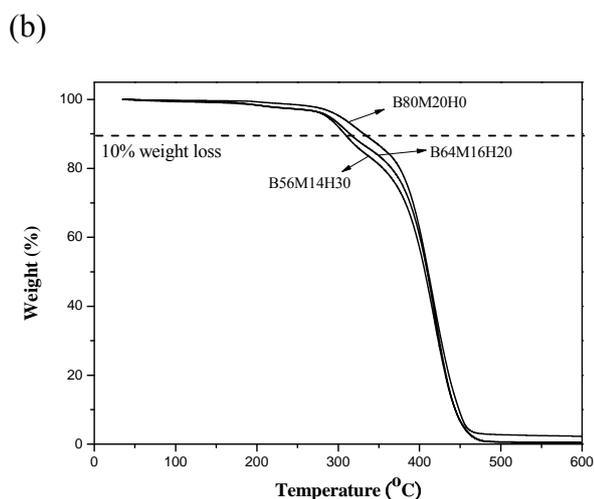


Fig. 3 TGA thermograms of the prepared binders. (a) 10 mol% 2-HEMA (b) molar ratio of BZMA/MAA= 4: 1.

(b) Characterization of chemical structure

Fig. 4(a) illustrates the FTIR spectrum of a prepared three-component binder, B54M36H10. The absorption peaks at 3500 and 3261 cm^{-1} were due to the -OH stretching bands of hydroxyl group and carboxyl group, respectively. The =C-H stretching band of the aromatic ring (BZMA unit) was observed from 2950 to 3065 cm^{-1} , and the C=O stretching band of the carbonyl group at 1729 cm^{-1} (MAA unit) and 1708 cm^{-1} (2-HEMA unit) could also be observed. For the 2-HEMA unit, the stretching band of the ester group (C-O-C) was observed at 1146 cm^{-1} . Furthermore, two C-H vibration bands of monosubstituted benzene (BZMA unit) were observed at 701 and 748 cm^{-1} . The spectrum suggests that the three kinds of acrylate monomers were successfully linked together to form a binder by free-radical polymerization. Fig. 4(b) shows FTIR spectrum of the binder, B54M36H10, that had been baked at 220 $^{\circ}\text{C}$ for 1h. The asymmetric and symmetric stretching vibrations of the two C=O groups of a formed anhydride were observed at

1805 cm^{-1} and 1762 cm^{-1} , respectively; furthermore, the anhydride also had a strong band at 1019 cm^{-1} due to the C-O-C stretching vibration. This result indicates that the anhydride was produced after the binder was baked at 220 $^{\circ}\text{C}$ for 1h. Therefore, as the binder contained more MAA or 2-HEMA, the weight loss in the first-stage degradation of TGA experiment would be more pronounced, in accordance with the TGA results shown in Fig. 3.

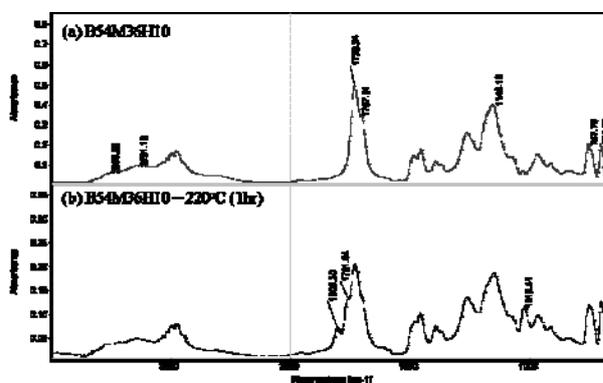


Fig. 4 FTIR spectra of the three-component binder, B54M36H10. (a) before and (b) after baked at 220 $^{\circ}\text{C}$ for 1h.

CONCLUSIONS

In this research, three-component binders composed of MAA, BZMA, and 2-HEMA were prepared by means of free radical copolymerization. The thermal behaviors, chemical structures, and other general properties of the formed binders were investigated. Compositions of the monomers for binder synthesis were determined with the aid of a ternary composition diagram. As the MAA content was increased, not only was the acid value but also the thermal stability of the binders, e.g., T_g and T_d , enhanced.

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計畫成果自評

(1)研究內容與原計畫相符程度

本研究計畫預定完成之內容有：起始劑及鏈轉移劑於 Binder 的添加量、合成不同配方 Binder、酸價、分子量及黏度之分析、Binder 熱分析及探討、最佳化之 Binder 組成及製程，本研究內容與計畫完全相符。

(2)達成預期目標情況

結合劑於光阻組成中為關鍵的成分之一，經過二成份及三成份結合劑的合成及性質比較後，再搭配三成分組成座標圖，本研究已成功獲得最佳化三成份結合劑之比例區塊。

(3)研究成果之學術或應用價值

本研究中所製備之三成分組成座標圖可以提供系統化之比較方式，並且獲得最佳添加比例，因而可應用於製備奈米粒子改質負型光阻，進而達成製備彩色光阻之潛力。

(4)是否適合在學術期刊發表或申請專利

本研發成果將發表於國際性期刊，目前已擇定國際期刊進行投稿。