

PREPARATION AND APPLICATION OF PHOTSENSITIVE COPOLYMERS FOR PDP BARRIER RIBS FORMED BY PHOTOLITHOGRAPHY*

Tao Zhang, Qian-wen Dong, Wei Zhang and Jie Wei**
*College of Materials Science and Engineering,
Beijing University of Chemical Technology, Beijing 100029, China*

Abstract In this work, the photosensitive paste was prepared. It was comprised of inorganic particles and a photosensitive organic component. The inorganic particles included glass, ceramics, and metals. The organic component should contain at least the following photosensitive materials: photosensitive monomers, photoreactive copolymer and photopolymerization initiators. The photoreactive copolymer played a role of an adhesive in the photosensitive paste. Meanwhile in the development stage, the carboxyl groups of the copolymer reacted with the alkaline developer. Following this, the unexposed part must be removed and an excellent pattern can be formed. A series of three-component acrylic copolymers (MAA/St/MMA) were designed, and then synthesized *via* free radical polymerization. Subsequently glycidyl methacrylate (GMA) was employed to modify the prepared copolymers through ring-opening reactions between the carboxyl groups and the epoxide groups. Eventually the photosensitive copolymers were obtained and used to form the barrier ribs of PDPs. The chemical structure, glass transition temperature, acid value and molecular weight of photosensitive copolymers had different effects on the structure and pattern of PDP barrier ribs. Through analyzing effects of different polymer performance parameters on the patterns of barrier ribs, the optimal photosensitive copolymer was acquired.

Keywords: Plasma display panel; Barrier rib; Photosensitive copolymer; Photosensitive paste.

INTRODUCTION

A plasma display panel (PDP) is a flat display element, which is mainly used for large-sized display devices over 42 inches because the PDP is thin, light and provides good image quality. Compared with liquid crystal display panels, PDPs allow high-speed display and are more suitable for large-sized display. Therefore, they are used in areas such as office automation (OA) apparatus and public display units. Furthermore, they are highly expected to be applicable in high grade television sets^[1–3].

With such an expansion of application, color PDPs with many fine display cells attract attention. In a PDP, plasma discharge is caused by anodes and cathodes facing each other in discharge spaces which are formed between front and rear glass substrates. The ultraviolet ray is generated by inert gas contained in the discharge spaces. A schematic structure of PDP is shown in Fig. 1. In this case, to keep the spread of discharge in specified cells and to secure uniform discharge spaces, barrier ribs are essential. Barrier ribs of plasma display panels (PDPs), formed in strip and matrix arrangement, function to maintain the discharge space between the two glass plates as well as to prevent electrical and optical cross-talking between adjacent cells. The distance between the barrier ribs defines a subpixel pitch of the PDP. The patterning of barrier ribs is a key in the process of making PDP. The manufacturing process currently uses sand-blasting and screen-printing methods. Both of them involve

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** Corresponding author: Jie Wei (魏杰), E-mail: weij@mail.buct.edu.cn

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complicated steps and limitations including: low aspect ratio for the barrier ribs, poor dimensional and shape control and extensive waste materials^[4, 5]. Recently, new processes such as photosensitive paste, mold-pressing and green tape rolling have been proposed. The photosensitive paste is a pretty good forming route for barrier ribs. In the photolithographic process, photosensitive paste is coated on the rear glass panel of a PDP and dried. After UV exposure and development, the barrier rib pattern is obtained^[6, 7].

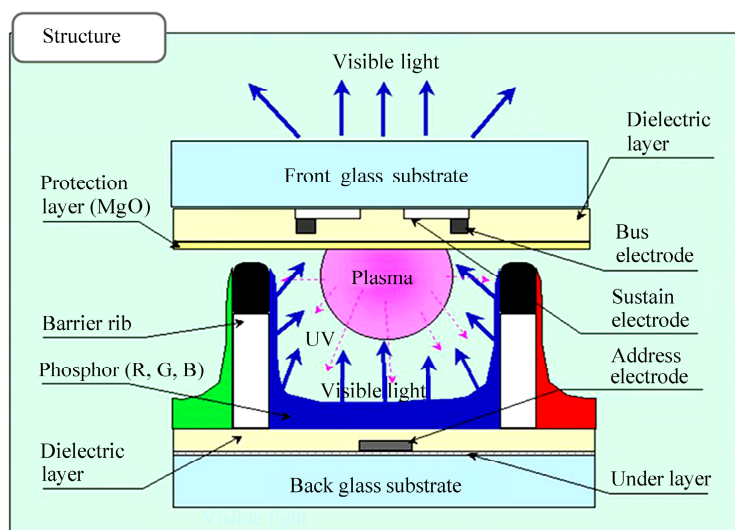


Fig. 1 Structure of a PDP

The photosensitive paste is comprised of inorganic particles and an organic component containing a photosensitive compound. An inorganic pattern is formed by photolithography with the photosensitive organic component and then is sintered. The inorganic particles include glass, ceramics, and metals. Glass and ceramics, as an essential component, contain an oxide of silicon, an oxide of boron, or an oxide of aluminum are particularly preferred^[2]. Being insulators they can be effectively used for producing patterned insulation materials such as barrier ribs for plasma display panels. For the diameter of the inorganic particles, the value is dependent on the shape of the pattern to be formed. For effective pattern formation, however, it is preferable to use inorganic particles with a 10 wt% particle diameter of 0.4–2 μm , a 90 wt% particle diameter of 4–10 μm and a specific surface of 0.2–3 m^2/g as well. The use of spherical inorganic particles permits patterning with a high aspect ratio. Specifically, the sphericity coefficient should preferably be 80% or more. The sphericity coefficient is defined as the proportion of those particles which look spherical or ellipsoidal under a microscope. The organic component should contain at least the following photosensitive materials: photosensitive monomers, photoreactive polymers and photopolymerization initiators^[8]. In addition, it may contain additives such as ultraviolet ray absorbents, sensitizers, polymerization inhibitors, organic solvents, *etc*^[9]. This method rarely causes environmental pollution and enables the production of barrier ribs with fine and complex shapes reducing the material costs required for the barrier rib. Thus, the method is likely to improve quality of PDPs and reduce manufacture costs^[1, 2].

In this work, photosensitive copolymer played a role of an adhesive in the photosensitive paste. Meanwhile in the development stage, the carboxyl groups of photosensitive copolymer can react with the alkaline developer. Following this, the unexposed part must be removed and an excellent pattern can be formed. A series of three-component acrylic copolymers (methacrylic acid/styrene/methyl methacrylate) were designed, and then synthesized *via* free radical polymerization. Subsequently the glycidyl methacrylate (GMA) was employed to modify the prepared copolymers through the ring-opening reactions between the carboxyl groups and the epoxide groups. Eventually, the photosensitive copolymers were obtained and used to form the barrier ribs of PDPs.

EXPERIMENTAL

Materials

Methacrylic acid (MAA), methyl methacrylate (MMA), styrene (St) and glycidyl methacrylate (GMA), as the copolymerization monomers, were distilled at reduced pressure before copolymerization. The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Diethylene glycol dimethyl ether (DGDE) was used as the solvent in free radical solution polymerization. *N,N*-dimethylaniline and 2,5-di-*tert*-butylhydroquinone were used as catalyst and inhibitor respectively in the ring-opening reactions between the carboxyl groups and the epoxide groups. Materials for the preparation of the photosensitive paste include ethoxylated trimethylolpropane triacrylate (TMP(EO)₉TA), photoreactive acrylic copolymers, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure819), inorganic particles, γ -butyrolactone, tetrahydrofuran (THF), ethanol and other additives.

Synthesis and Functionalization of Poly(MAA-co-St-co-MMA)

Free radical solution polymerization was employed to synthesize the three-component acrylic copolymer of MAA, MMA and St. Diethylene glycol dimethyl ether (DGDE) as the polymerization solvent was preheated at 80–85°C and stirred in a nitrogen atmosphere. Then the initiator AIBN was dissolved in appropriate amount of the monomers. The obtained solution of monomers and initiator was dripped into polymerization solvent during 3 h under 80–85°C. The copolymerization would last another 3 h after dripping. The product was then cooled down to room temperature and diluted with tetrahydrofuran (THF). Subsequently, the diluted polymer solution was poured into petroleum ether to induce polymer precipitation. The precipitation procedure was repeated twice to make sure that all the monomers and initiator were washed away. The obtained copolymers were separated by filtration and then dried in vacuum at 60°C. Eventually the three-component copolymer white-powders were analyzed and functionalized with glycidyl methacrylate (GMA) to introduce unsaturated double bonds onto the side chain of the copolymers.

The prepared copolymers were dissolved in diethylene glycol dimethyl ether (DGDE) and preheated at 95–100°C. The solution of *N,N*-dimethylaniline, 2,5-di-*tert*-butylhydroquinone, glycidyl methacrylate (GMA) was added to copolymers solution at 95–100°C in half an hour. Afterwards, the solution was heated up to 115–120°C for 8–10 h. Then the functionalized copolymers were cooled down to room temperature and diluted with tetrahydrofuran (THF), the diluted polymer solution was poured into petroleum ether to induce polymer precipitation. The precipitation process was repeated twice to ensure free of residual catalyst, inhibitor and glycidyl methacrylate (GMA). The white functionalized copolymers powders were separated by filtration and dried in vacuum at room temperature. The product was stored in refrigerator prior to use and analysis. The whole synthetic route of the copolymer was outlined in Fig. 2.

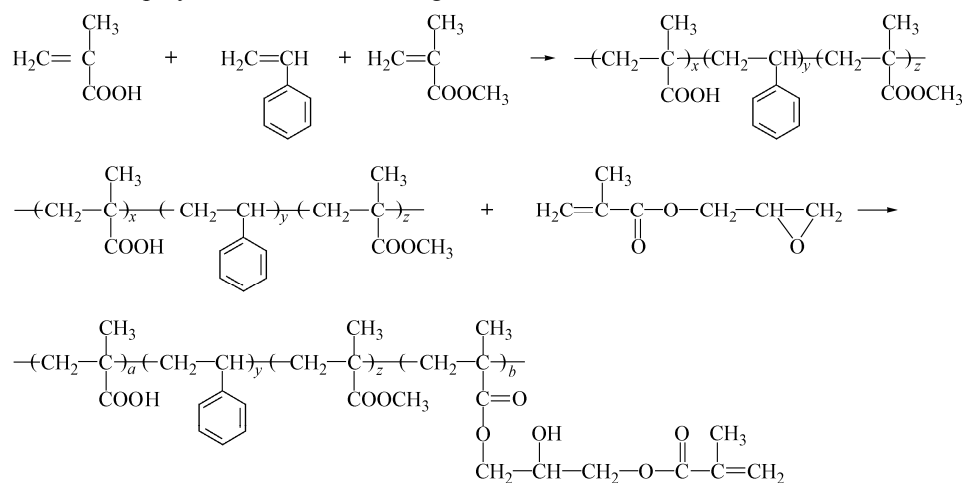


Fig. 2 Synthesis and functionalization of poly(MAA-co-St-co-MMA)

Preparation of the Photosensitive Paste and the Photolithographic Process

The preparation of the photosensitive barrier rib paste and the photolithographic process was carried out in a clean room to avoid dirt contamination^[10]. The photosensitive paste was composed of inorganic particles and photosensitive organic components including: functionalized poly(MAA-co-St-co-MMA) as the binder polymer, ethoxylated trimethylolpropane triacrylate (TMP(EO)₉TA) as the ultraviolet (UV) curable functional monomer, irgacure819 as the photoinitiator, γ -butyrolactone and ethanol as the solvent and other necessary additives. First, the binder polymer was dissolved in γ -butyrolactone solvent with a mechanical stirrer to prevent any gel and coagulum appearing. Appropriate amount of functional monomer, photoinitiator and additives was added to this solution. The resulting mixture was then stirred. To the organic mixture, inorganic particles (about 50 wt%–70 wt% of the photosensitive paste) were added and mixed with a mechanical stirrer. The paste with all ingredients was then kneaded by a three roll mill to achieve the homodisperse and desired viscosity. Viscosity of the photosensitive paste could be adjusted by the amount of γ -butyrolactone and ethanol solvent to give a satisfactory coatability.

The photolithographic process to make barrier ribs with photosensitive paste is shown in Fig. 3. This process was also carried out in a clean room to avoid dirt contamination. The barrier rib paste was coated on the glass substrate with a handy coater at a thickness of 300–400 μm and dried at 110°C to remove the solvent. Then, a photomask was placed on the top of dried barrier rib paste layer and exposed to UV irradiation. This light source was generated from an ultra voltage mercury lamp with varying exposure of 100–300 mJ/cm^2 . After UV exposure, the barrier rib panel was developed with 0.3 wt%–0.5 wt% sodium carbonate aqueous solution at 30°C to dissolve the unexposed portion. This was then dried at 80–100°C. The obtained barrier ribs were fired in an air atmosphere with a box type furnace. The temperature was increased to 580°C at a rate of 3–5 K/min and held for 15 min in order to burn out organic components completely. Barrier ribs with the height of 150–200 μm were obtained *via* this firing process.

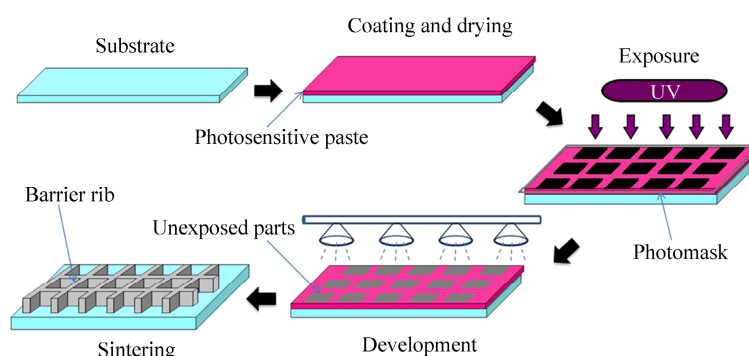


Fig. 3 Photosensitive paste process

Instrument Analysis

Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy were used to analyze the chemical bonds at various stages of the preparation process and the chemical structure of the synthesized polymers. The molecular weights and molecular weight distribution of the binder polymers were measured by Waters gel permeation chromatograph (GPC) with tetrahydrofuran as the eluent at 30°C. Molecular weights of the polymers were reported based on polystyrene standards. Acid values of the prepared photosensitive copolymers were determined by titration with 0.1 mol/L potassium hydroxide (KOH) solution. The definition of acid value is the amount of KOH in milligrams needed to reach the equivalent point for 1 g of the prepared binder (mgKOH/g). Cross section and top view of the barrier rib patterns were examined by scanning electron microscope (SEM) or optical microscope. Differential scanning calorimeter (DSC) was employed to measure the glass transition temperature (T_g) of the synthesized copolymers.

RESULTS AND DISCUSSION

Contribution of the Chemical Structure to Imaging of the Barrier Ribs Pattern

Acrylic monomers used to synthesize the binder contain the desired functional groups, such as phenyl, methyl ester and carboxyl groups. The two former functional groups can improve both the dispersion of inorganic particles and the adhesion of photosensitive paste on the glass substrate. Meanwhile, the carboxyl groups can provide sufficient acid value of the prepared barrier rib paste. The copolymers play a role of an adhesive in the barrier rib paste, in the development stage, the carboxyl groups of copolymers can react with weak alkali aqueous solution dissolving the unexposed part and then the expected patterns were obtained.

A series of three-component copolymers were synthesized from free radical copolymerization of three kinds of unsaturated monomers (methacrylic acid (MAA), methyl methacrylate (MMA), styrene (St)) with different feed ratios, as shown in Table 1.

Table 1. A series of three-component copolymers with different feed ratios

	MAA:St:MMA (feed ratio, mol)	M_w	T_g (°C)	Acid value 1 (mgKOH/g)	Acid value 2 (mgKOH/g)
1	30:30:40	33315	86.5	176	64
2	35:30:35	32728	87.2	205	89
3	40:30:30	30052	88.9	225	114
4	45:30:25	28431	93.6	252	137
5	50:30:20	27427	101.8	288	163
6	55:30:15	24500	118.4	300	184
7	60:30:10	21000	121.8	319	212

M_w = weight average molecular weight;

Acid value 1 = acid value before functionalization; Acid value 2 = acid value after functionalization

Figure 4(a) illustrates the FTIR spectrum of a prepared three-component copolymer. The absorption peaks at 1728 and 1699 cm^{-1} were due to the C=O stretching band of the carboxyl group in MAA and the ester group in MMA respectively. The framework vibration band of the benzene (St unit) was observed at 1600 cm^{-1} , and the $-\text{CH}_3$ asymmetric and symmetric angle vibration bands at 1453 and 1386 cm^{-1} could also be observed. For the MMA unit, the stretching vibration band of the ester group (C—O—C) was observed at 1151 cm^{-1} . The two C—H vibration bands of monosubstituted benzene (St unit) were observed at 701 and 759 cm^{-1} while the absorption peaks of the C=C at 1635 and 810 cm^{-1} did not appear. It is believed that all the residual monomers had been washed away. The spectrum suggests that the three kinds of unsaturated monomers were linked together to form a binder copolymer by the free radical copolymerization^[11–14].

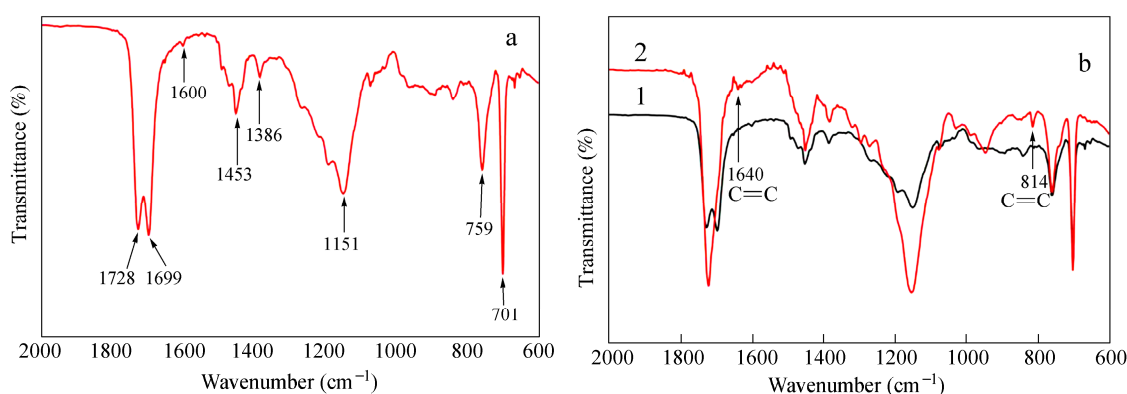


Fig. 4 FTIR spectrum of a three-component copolymer before functionalization (a) and its comparison with that of the copolymer after functionalization (b)

After functionalization, the side chain of copolymers contained a considerable number of reactive unsaturated double bonds, which would react with functional monomers in the photosensitive paste to form a cross-linked network. Figure 4(b) shows FTIR spectra of the three-component copolymer before (spectrum 1) and after (spectrum 2) it was functionalized. By comparison with the copolymer, the bands at 1640 and 814 cm^{-1} for C=C stretching vibrations can be seen in the spectrum 2 of the functionalized copolymer obviously. In other words, the unsaturated double bonds C=C had been introduced onto the side chain of copolymers successfully^[11]. The functionalized polymers would improve the photosensitivity of the barrier rib paste^[10].

Figure 5(a) shows the $^1\text{H-NMR}$ spectrum of a copolymer before functionalization. The phenyl groups of styrene appeared at $\delta = 7.173$. The $\delta = 12.111$ and 3.512 peaks indicated existence of carboxyl group $-\text{COOH}$ and methoxyl $-\text{COOCH}_3$ respectively. Figure 5(b) shows the $^1\text{H-NMR}$ spectrum of the copolymer after functionalization. By comparison with the copolymer before functionalization, the unsaturated double bonds $-\text{C}=\text{CH}_2$ appeared at $\delta = 6.066$ and 5.683 after functionalization. This suggested that the designed photoreactive acrylic copolymers were obtained by free radical polymerization and functionalization. The obtained copolymers were used to prepare photosensitive paste as a binder polymer. The unsaturated double bonds on side chain of copolymers would improve photosensitivity of photosensitive paste and cross-linking density of exposed parts^[15].

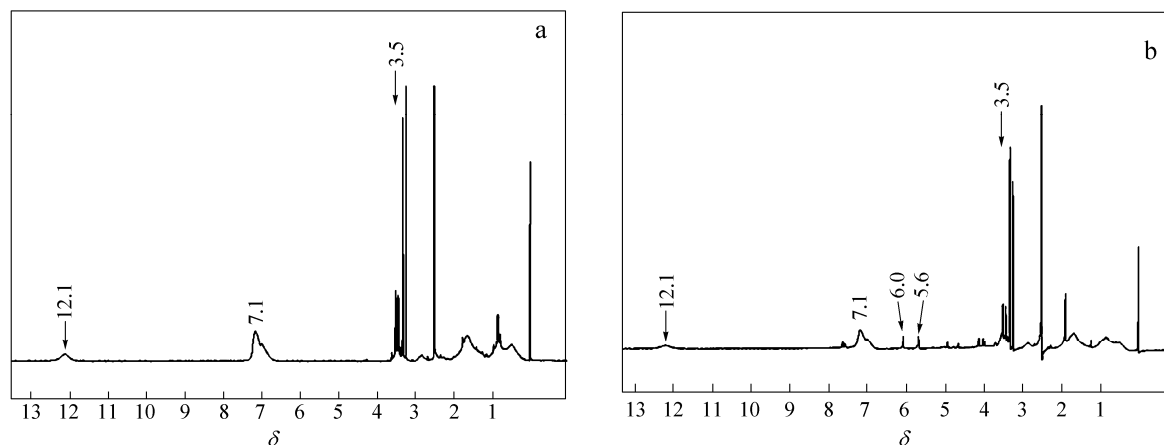


Fig. 5 $^1\text{H-NMR}$ spectra of a copolymer before (a) and after (b) functionalization

Effect of T_g on the Solubility of the Copolymer in the Barrier Rib Paste

Differential scanning calorimeter (DSC) was employed to measure the glass transition temperature (T_g) of the synthesized copolymers, and the results are shown in Fig. 6 and Table 1. For the three-component copolymers it appears that T_g of the binders increased with increasing MAA content. For example, T_g of the three-component copolymer 1 was 86.5°C (MAA = 30 mol%). When MAA content was increased to 60 mol%, T_g of the copolymer 7 became 121.8°C. This suggested that monomer MAA could increase not only the acid value but also the T_g of the binders. It should be noted that when the concentration of polar groups (*e.g.* carboxyl groups) is too high, the solubility of copolymers in organic solvent will decrease^[16, 17], meanwhile, the viscosity of copolymers will increase despite of low average molecular weight and make a negative effect on the coatability of the photosensitive paste.

Effect of Acid Value on the Developing Performance

In the copolymer, the introduction of MAA could improve the developing performance of the photosensitive paste after UV light irradiation. The acid value could be adjusted by changing the amount of MAA in the copolymer. If the acid value of the binder is too low, the solubility of the unexposed photosensitive paste in an alkaline developer liquid would be too low. This may cause an excess amount of residue, *i.e.* poor development (as shown in Fig. 7a). Meanwhile, poor adhesion to the substrate probably will occur if the acid value is too low.

On the other hand, when the acid value is too high the film may dissolve too much in the developer liquid (as shown in Fig. 7b). As expected, the acid value increases as the MAA concentration is increased. That is the solubility of a binder in an alkaline developer liquid is directly related to the MAA concentration of the binder. The resultant polymers with carboxyl groups in their side chains should preferably have an acid value in the range of 100–180 mgKOH/g. The unexposed parts would have much residue if the acid value was less than 100 mgKOH/g. If the acid value exceeded 180 mgKOH/g on the other hand, the exposed portions would be dissolved by alkaline developer liquid. These phenomena are shown in Figs. 7(a), 7(b).

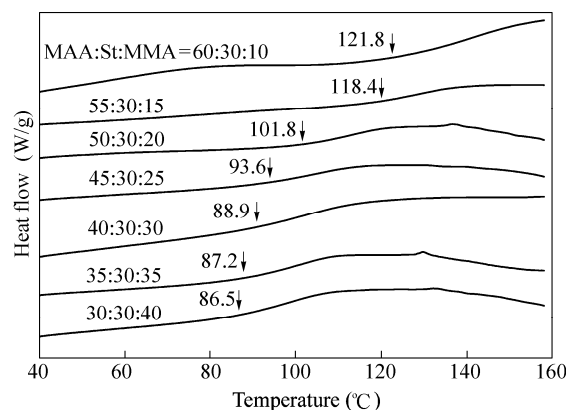


Fig. 6 DSC thermograms of the prepared copolymers

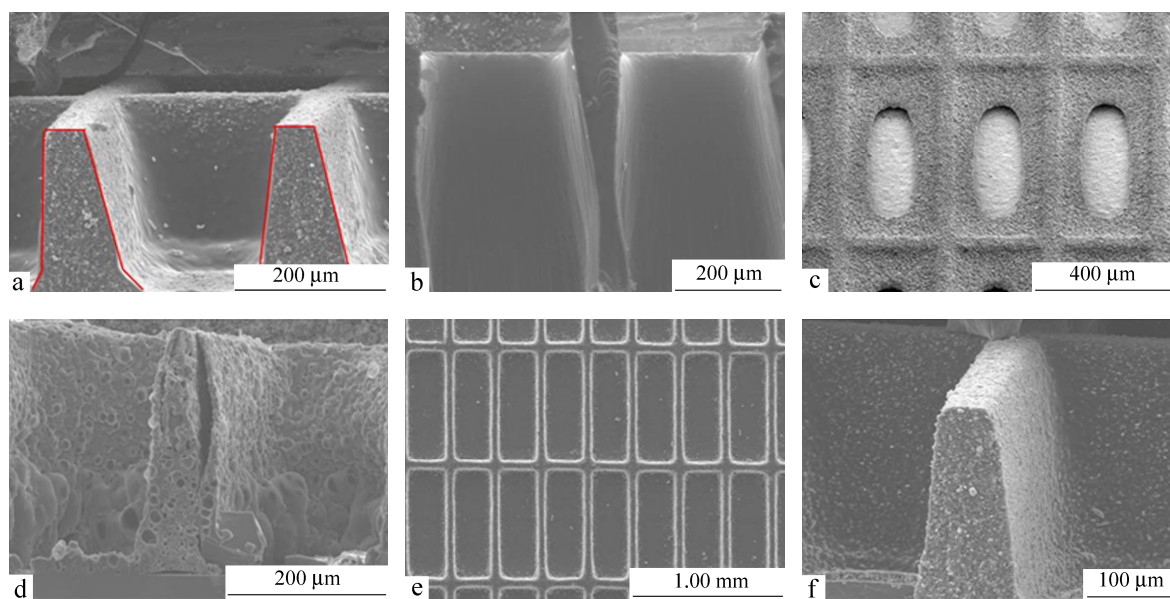


Fig. 7 SEM photographs of barrier ribs: (a) the effect of extra-low binder acid value on the patterns, (b) the effect of extra-high binder acid value on the patterns, (c) the effect of extra-large binder molecular weight on the patterns, (d) the effect of extra-small binder molecular weight on the patterns, (e) (f) fine patterns

Effect of the Molecular Weight on Viscosity and Coatability of the Photosensitive Paste

Weight average molecular weight (M_w) of the prepared three-component copolymers was measured with GPC, and the results are shown in Table 1. The molecular weight could be changed by changing the feed ratios of monomers while keeping other reaction conditions constant. It could be seen from Table 1 that molecular weight reduced with increasing MAA concentration. As the molecular weight of the binder was beyond 40000, the

viscosity of the photosensitive paste would be high. This could affect the coatability and cause an excess amount of residue. Furthermore, the developing performance was apt to deteriorate which made it difficult to form sharp patterns (as shown in Fig. 7c). On the contrary, if the molecular weight of the formed copolymers was less than 20000, the development of the photosensitive paste would be excessively rapid. This made it difficult to control the pattern shape during the development process. Even if patterns could be formed problems such as reduction of the final coating thickness could also occur (as shown in Fig. 7d).

CONCLUSIONS

A series of three-component acrylic copolymers were synthesized *via* free radical polymerization. These were functionalized by the ring-opening reactions between the carboxyl groups and the epoxide groups. Unsaturated double bonds $C=C$ were introduced onto their side chains. The obtained photosensitive polymers were successfully used to prepare photosensitive paste and the fine patterns of barrier ribs (as shown in Figs. 7e, 7f) which were fabricated by the photolithographic process using copolymers 3 and 4 because of their appropriate M_w (30052 and 28431), acid value (114 and 137 mgKOH/g), and T_g (88.9°C and 93.6°C). When keeping other reaction conditions constant, the acid value and T_g increased. Additionally, M_w decreased as the MAA concentration increased in the copolymers. When the MAA concentration in copolymers is 40 mol%–45 mol%, the acid value is 100–150 mgKOH/g and M_w range is 25000–35000, better barrier rib patterns could be obtained with the photosensitive paste by the photolithographic process.

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