

FACILE FABRICATION OF GRADIENT SURFACE BASED ON (METH)ACRYLATE COPOLYMER FILMS

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This paper describes a simple and economic approach for fabrication of surface wettability gradient on poly(butyl acrylate – methyl methacrylate) [P (BA–MMA)] and poly(butyl acrylate – methyl methacrylate – 2-hydroxyethyl methacrylate) [P (BA–MMA–HEMA)] films. The (meth)acrylate copolymer [including P (BA–MMA) and P (BA–MMA–HEMA)] films are hydrolyzed in an aqueous solution of NaOH and the transformation of surface chemical composition is achieved by hydrolysis in NaOH solution. The gradient wetting properties are generated based on different functional groups on the P (BA–MMA) and P (BA–MMA–HEMA) films. The effects of both the surface chemical and surface topography on wetting of the (meth)acrylate copolymer film are discussed. Surface chemical composition along the materials length is determined by XPS, and surface topography properties of the obtained gradient surfaces are analyzed by FESEM and AFM. Water contact angle system (WCAs) results show that the P (BA–MMA–HEMA) films provide a larger slope of the gradient wetting than P (BA–MMA). Moreover, this work demonstrates that the gradient concentration of chemical composition on the poly(meth) acrylate films is owing to the hydrolysis processes of ester group, and the hydrolysis reactions that have negligible influence on the surface morphology of the poly(meth) acrylate films coated on the glass slide. The gradient wettability surfaces may find broad applications in the field of polymer coating due to the compatibility of (meth) acrylate polymer.

Keywords: Copolymer; film; surface; wettability; composition; morphology.

1. Introduction

Materials with surfaces of wettability gradient^{1,2} are of great interests for various applications, such as movement of water droplets,^{3–6} microfluidics,^{7,8}

protein adhesion studies,^{9,10} and cell attachment and growth.^{11–14} The control of surface geometrical microstructure and chemical composition is critical for fabrication of gradient surfaces. So far, a number of

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methods^{15–22} have been developed for preparation of wettability gradient. However, most of them need either complex processes or expensive equipment. Moreover, polymer coating has rarely been used for fabrication of wettability gradient, while their use might possess great advantages in micro–electro–mechanical systems (MEMS) engineering fields. For example, (meth)acrylate copolymers have been reported as novel surface energy materials,^{23,24} because of the fine solubility and compatibility of the chain. Herein, a facile and economical method is developed to prepare a gradient wetting surface on the poly(meth) acrylate films. The gradient surface is fabricated under soft experiment conditions, and involves only cheap materials. Due to the practicability and versatility of (meth)acrylate copolymer films, the obtained surfaces might be used in various engineering fields.²⁵ Moreover, the chemical composition of polymer film surface can be changed by designing and controlling the structure of (meth) acrylate polymers. The poly(meth) acrylate structure has a significant influence on the surface chemistry and the process of ester group hydrolysis reactions. Matsuda *et al.*²⁶ prepared a surface with given directional wettability gradient and demonstrated that the advancing water angle of the surface gradually increases from the treated region of the poly(vinylene carbonate) (PVCa) film to the untreated. Chilkoti *et al.*²⁷ showed that many functional polymer films could be modified to produce a reactive functional group. Laugnas *et al.*²⁸ reported that surface gradients with different chemical compositions prepared on PMMA films by ester group hydrolysis process and WCA measurements demonstrated that a gradual increase from 71° to 78° when measuring from the most hydrolyzed part of the polymer film to the least hydrolyzed one. Besides, Zhang *et al.*²⁹ showed that the construction of surface wettability gradient is dependent on a controlled functional group hydrolysis process on copper slides. It is found that the copolymer structure has a significant influence on the concentration of ester groups on the outermost surface and thus is important for the formation of slope gradients.

In this work, the P (BA–MMA) and P (BA–MMA–HEMA) are first prepared by a free atom radical solution polymerization method and the chemical composition of copolymer films surface is vital to obtain the gradient wettability surfaces. The

gradient wettability surfaces are fabricated by the hydrolysis procedure of ester group in alkaline solution. The hydrolysis reaction is designed to be simply governed by dipping the alkaline solution in the container. In addition, being prepared with curing agent, the P (BA–MMA–HEMA) films surface can exhibit gradient wetting property, which enlarges the range of contact angles as compared to the P (BA–MMA). Surface morphology analysis is carried out using field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). X-ray photoelectron spectroscopy is used to determine the chemical composition along the resultant surface. Contact angles (CAs) of water is analyzed via an optical contact angle system.

2. Materials and Methods

Glass Slides 25 × 100 mm and butyl acetate (99%, A.R.) were obtained from Tianjin Kermel Chemical Reagent Company. Butyl acrylate (BA) (99%, A.R.) and xylene (99%, A.R.) were obtained from Chengdu Kelong Chemical Reagent Company. Sodium hydroxide (96%, A.R.) and absolute ethanol (99.7%, A.R.) were obtained from Guangdong Guanghua Tech Co., Ltd. Methyl methacrylate (MMA) (98%, A.R.) was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. 2-Hydroxyethyl methacrylate (HEMA) (98%, A.R.) was obtained from Guangzhou Shuangjian Chemical Reagent Company. Acetone (99.5%, A.R.) was obtained from Hengyang Kaixin Chemical Reagent Company. BPO (99%, A.R.) was purchased from Guangzhou Huaxue Chemical Reagents Company (Guangzhou, China). The amino curing agent (product name is CYMEL 303) was obtained from Guangzhou Zhuoyu Chemical Reagents Company (Guangzhou, China). And distilled water was used in this work to dissolve NaOH.

P (BA–MMA) copolymer solutions were prepared by the conventional free radical polymerization method. 100 g of xylene, 100 g of comonomers (MMA: BA = 6:4, wt %) and 0.5 g of BPO were added into a 500 ml, three neck, round-bottom container, which included a heat exchange equipment. First, BPO was introduced in the mixture of MMA and BA. The mixture was allowed to agitate for 20 min with 80 rpm mixing to dissolve the BPO. Then the mixture was dipped slowly to the xylene solutions for 60 min with

300 rpm agitation. The temperature of polymerization reaction is 120 °C and the reaction constant stirring for 8 h.

P (BA–MMA–HEMA) random copolymer can be obtained by the same method as the preparation of P (BA–MMA). 100 g of mixed solutions (butyl acetate : xylene=1:1, V:V), 100 g of comonomers (MMA : BA = 6:4, wt %), 15 g of HEMA and 0.5 g BPO were introduced into a 500 ml, four neck, round-bottom container, which included a heat exchange equipment. First, a certain amount of BPO was added to the comonomers (MMA : BA = 6:4, wt%) and HEMA, respectively. The comonomers and HEMA were allowed to stir for 20 min with 80 rpm mixing to dissolve the BPO, respectively. After that, the HEMA was added slowly to the mixed solutions for 20 min with 300 rpm agitation. Then the comonomers were added slowly to the same solutions for 60 min with the same stirring rate. The temperature of polymerization reaction is 120 °C and the reaction is constantly stirred for 8 h.

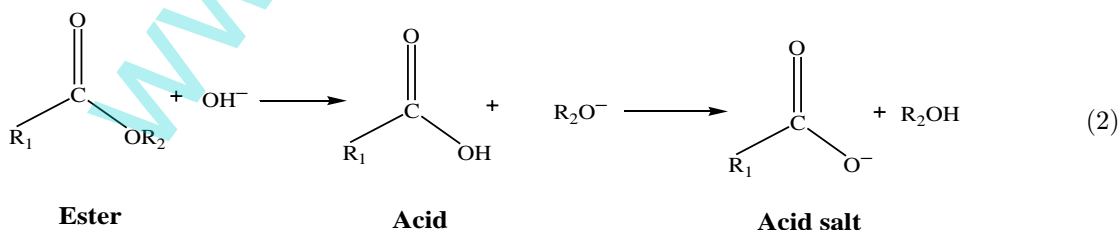
The fabrication procedure of gradient wettability surface on the P (BA–MMA) film is described in Ref. 29. Besides, a 10 g P (BA–MMA–HEMA) copolymer solutions and 1.86 g CYMEL 303 were mixed, firstly. The mixture was allowed to stir for 1 min. Then the cleaned glass slides were immersed into the mixture for 1 min, and dried at 160 °C for about 10 min. The coating process was recycled for 1 time. The adsorption between the polymer and glass substrate was dominated by van der waals force and hydrogen bond. The polymer delamination could

not occur with repeating dip-coating process for the bonding properties. It should be noted that the addition was controlled at such a speed that it took 40 min for the surface of NaOH solution in the container to reach the superior border of the P (BA–MMA–HEMA) coated on the glass slide substrate.

The surface topography of the copolymer film was analyzed by FESEM (LEO 1530 VP, Germany). The three-dimensional measurements and surface roughness parameters of the copolymer film were determined by AFM (CSPM5000, Benyuan, China). XPS (Kratos Axis Ultra DLD, UK, equipped with a monochromator source (Aluminum K α line of 1486.6 eV energy and 150 W)) was employed to study quantitatively the surface chemistry of the copolymer film on glass slide and water contact angles (WCAs) measurement was used to measure the wetting of copolymer film surface. The measured volume of water droplet for the WCA was 3 μ L. The average of three measurements adopted at the same district of the different samples was used to analyze the wettability of copolymer film. The experimental temperature was 25 °C.

3. Results and Discussion

The surface chemical gradients of P (BA–MMA) and P (BA–MMA–HEMA) films can be fabricated according to a controlled hydrolysis process. Two reactions are used to describe the hydrolysis process of ester group as depicted below.³⁰



where R₁ and R₂ represent different alkyl groups, respectively. These equations show that ester hydrolysis reaction to produce acid salt. Equation (1) is an irreversible hydrolysis reaction in basic solution which is called saponification. Equation (2) presents

that ester hydrolysis occurs through a typical nucleophilic acyl substitution pathway in which the tetrahedral intermediate goes through a nucleophilic attack process followed by OH⁻ group. The carboxylic acid is changed to acid salts.

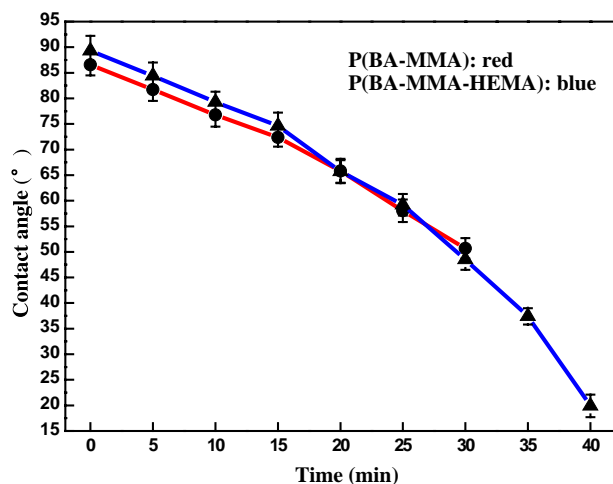


Fig. 1. Relationship between water contact angle and reaction time. With increasing the reaction time, the water contact angle of the copolymer P (BA–MMA) and P (BA–MMA–HEMA) film surface after being modified by alkaline solution decreases. WCA measurements were obtained after the rinse of the measured films with distilled water three times. The measurements were performed on copolymer film with different places. The liquid droplets of 3 μL of water in contact with the surface were recorded immediately after droplet stabilization. 1 mol dm^{-3} NaOH was used for fabrication.

From Fig. 1, it can be found that the P (BA–MMA) and P (BA–MMA–HEMA) films coated on glass slide show an obvious gradient wettability property. The contact angles increase continuously along the substrate surface, when measuring from the most hydrolyzed part of the glass slide to the least hydrolyzed one. Lagunas *et al.*²⁸ prepared surface chemical gradients by a controlled hydrolysis procedure and WCA measured results showed a slight increase from 71° to 78°. Zhang *et al.*²⁹ used the same method to enlarge the slope gradients, indicating that the hydrolysis method causes insignificant change on the morphology of the copolymer film along the

substrate length. Figure 1 shows the relationship between the contact angles of the copolymer film surface and immersion time, when the concentration of NaOH solution is 1 mol dm^{-3} . The contact angle has a dramatical decrease with the reaction time. Since the (meth)acrylate units serve as active points during reaction,³¹ ester group along the main chain of (meth)acrylate copolymer could be hydrolyzed by alkaline solutions, where the ester group on the outermost surface of the copolymer film will produce more active COOH groups and acid salt by controlling ester group hydrolysis process and using NaOH. It can be seen that both lines have similar declining slopes and after the point of inflection, these slopes switch. This may be due to that both the preparation method and the ratio of MMA to BA of P (BA–MMA–HEMA) and P (BA–MMA) are the same. The P (BA–MMA–HEMA) and P (BA–MMA) have similar chemical structure. Besides, the P (BA–MMA) copolymer film is partially dissolved after the point of inflection.

The surface wettability is controlled by both the geometrical microstructure and the surface chemical composition.^{32–35} To determine the surface chemical compositions on the copolymer P (BA–MMA) film, XPS was used as a quantitative way. XPS measurements showed the C 1s XPS analysis results of hydrolyzed film and the C 3 raw area attributed to the methoxy groups carbon,²⁸ as summarized in Table 1. Table 1 reveals a decrease of the C 1s content of the peak centered at 282.5 eV or 282.6 eV, which is assigned to the carbonyl carbon and C 3 content of the peak centered at 284.3 eV or 284.4 eV, which is assigned to the methoxy carbon in methyl methacrylate or the ethoxy group carbon in butyl acrylate.²⁹ Comparing the least hydrolyzed part (Table 1(a)) with the most hydrolyzed part (Table 1(b)), the XPS C 1s intensity decreases from 65055.5 to 53484.4 (Raw Area). This is due to the copolymer dispersion.

Table 1. XPS analysis results of C 1s from the peak areas of (a) the least hydrolyzed part of the P (BA–MMA) film and (b) the most hydrolyzed part, showing the C 3 signal decrease, which can be assigned to the methoxy group carbon (MMA) or ethoxy group carbon (BA).

Sample name	C 1s		C 3		Area conc%
	Position BE(eV)	Raw area	Position BE(eV)	Raw area	
(a)	282.600	65055.5	284.3	8188.917	12.6
(b)	282.500	53484.4	284.4	0.1	0.0

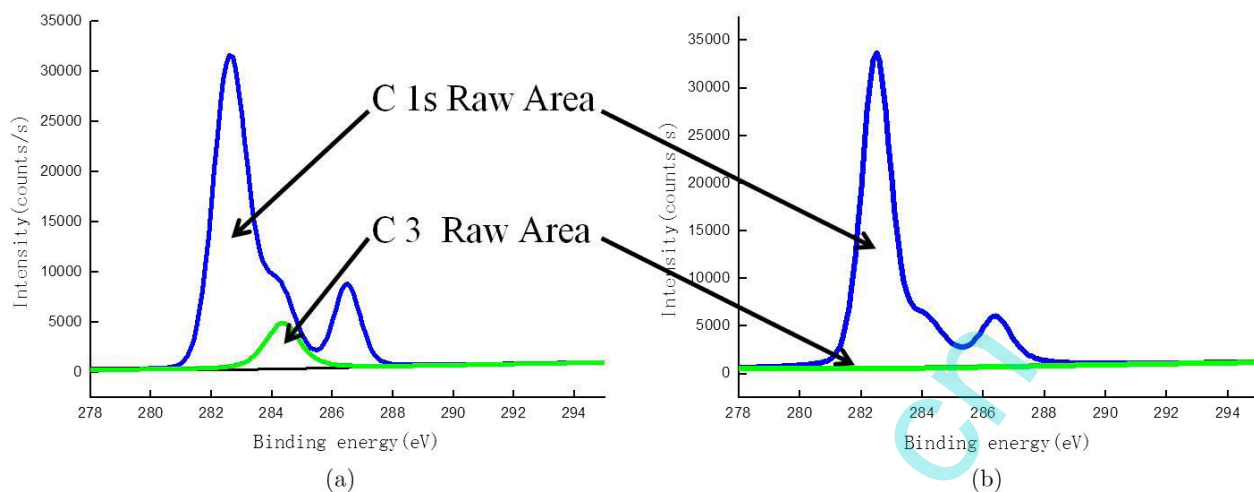


Fig. 2. XPS spectra of the hydrolyzed part of P (BA-MMA) film: (a) the least hydrolyzed region and (b) the most hydrolyzed region.

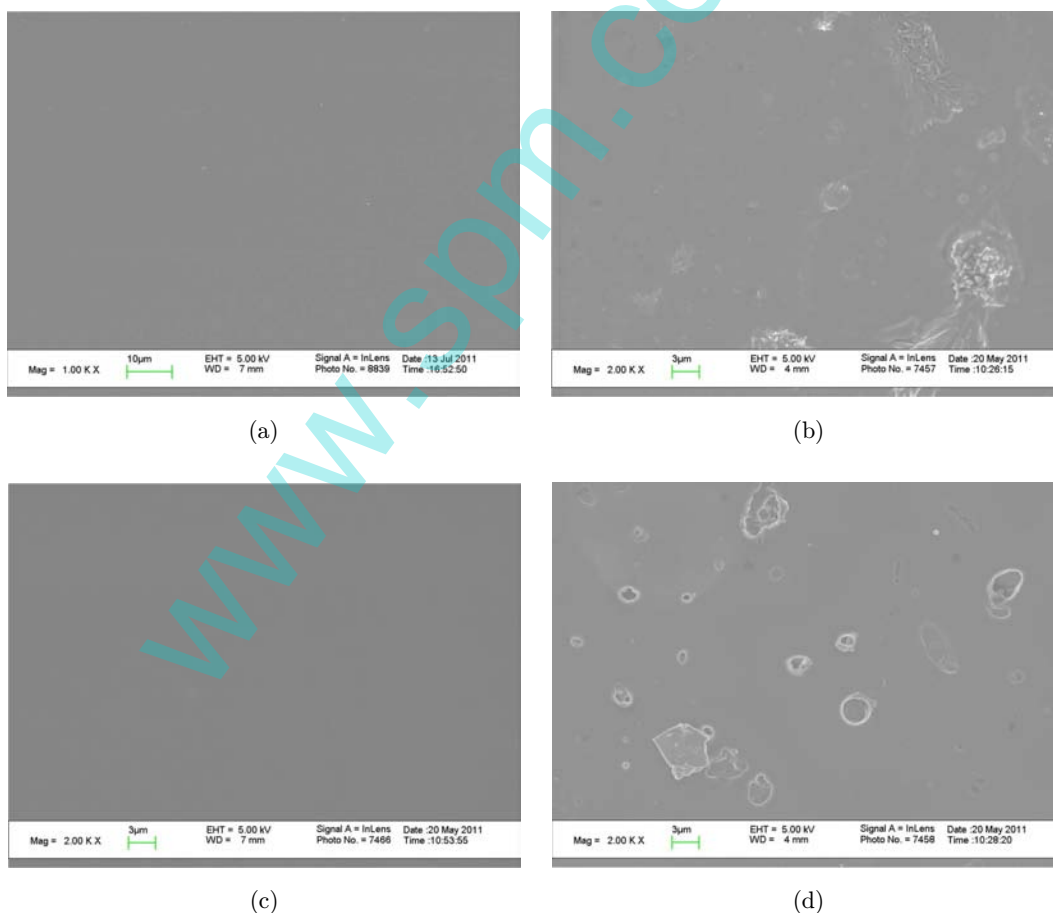


Fig. 3. FESEM images (a)–(d) of corresponding copolymer films on glass substrate: (a) the least hydrolyzed part with P (BA-MMA) film, (b) the most hydrolyzed part with P (BA-MMA) film, (c) the least hydrolyzed part with P (BA-MMA-HEMA) film and (d) the most hydrolyzed part with P (BA-MMA-HEMA) film.

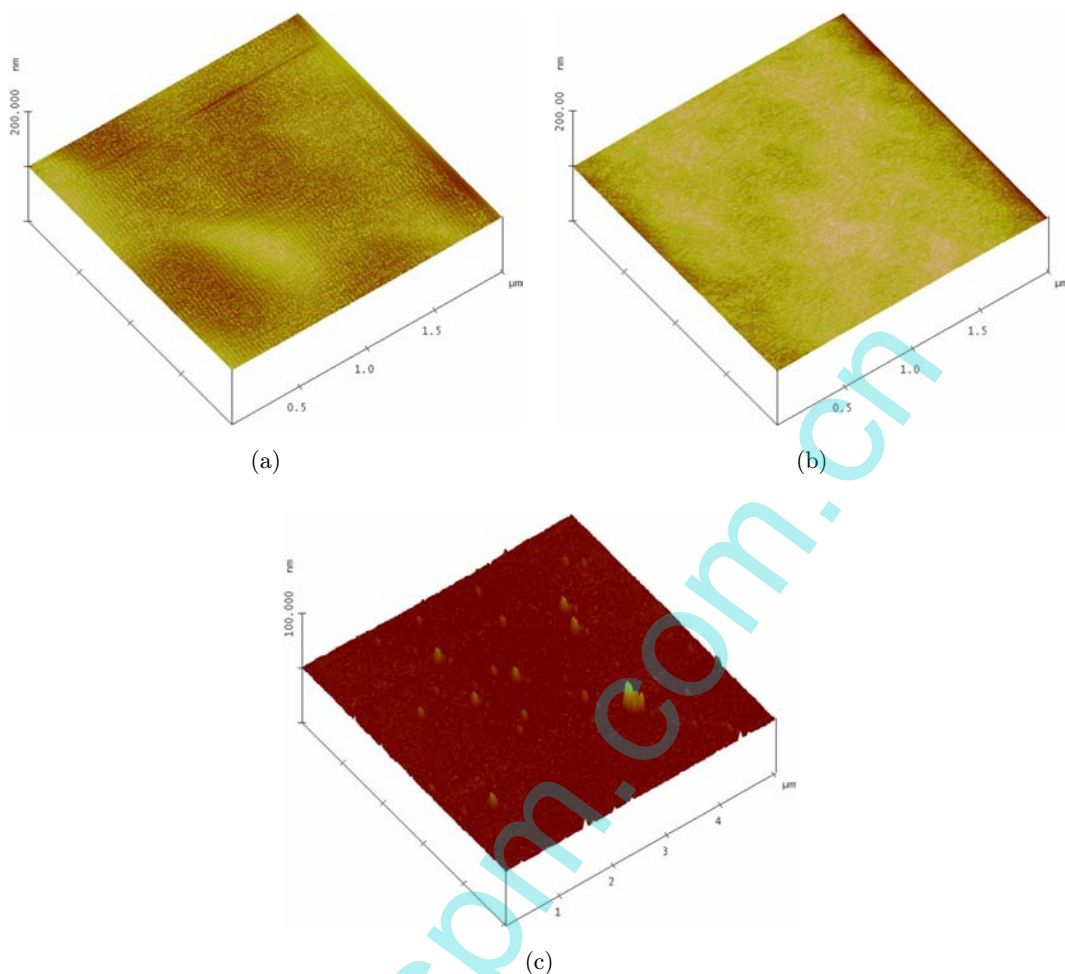


Fig. 4. 3D AFM images on the surfaces of the P (BA-MMA-HEMA) films by alkaline solution with different reaction time: (a) 0 min, (b) 20 min and (c) 40 min.

Additionally, Fig. 2 shows the XPS C 3 intensity also decreases from 8188.917 to 0.1 (Raw Area), attributed to the ester group hydrolysis procedure. From these results, we can find the extent of the carboxylic acid salt along the sample length increases significantly for the C 3 area against the whole copolymer C 1s content permits us to find the extent of the component 3 along the material length, which changes from 12.6% to 0.0%. It should be noted that XPS is only used on P (BA-MMA). This is due to that XPS analysis is affected due to HEMA chemical structure. The surface chemical compositions on the hydrolyzed copolymer P (BA-MMA-HEMA) film are not accurately determined due to the HEMA chemical structure.³⁶

To determine the effect of the surface geometrical microstructure on the wettability of copolymer

film, FESEM analysis was performed on the least hydrolyzed part of the copolymer film and the most hydrolyzed part. The surface morphology on the wettability of copolymer film is given in Figs. 3(a)–3(d). The FESEM results show a surface morphology evolution of the copolymer film on glass slide substrate. The images clearly show that the least hydrolyzed part with P (BA-MMA) film (Fig. 3(a)) is smooth as that the most hydrolyzed part (Fig. 3(b)). And the morphology of the least hydrolyzed part with P (BA-MMA-HEMA) film (Fig. 3(c)) remains almost the same with the most hydrolyzed part (Fig. 3(d)), indicating negligible change of surface morphology after hydrolysis. The copolymer chain with lower molecular weight was dissolved by alkaline solution, which might result in the brighter part in the Figs. 3(b) and 3(d). It can be concluded that the

Table 2. Statistical data of roughness parameters on the P (BA-MMA-HEMA) films.^a

Reaction time (min)	0	20	40
Ra/nm	0.358	0.379	0.448

^aThe WCA of P (BA-MMA-HEMA) film surface decreases with the hydrolysis reaction time; Ra is roughness average. The gradient wettability surface was fabricated on the P (BA-MMA-HEMA) film coating on the glass slides.

chemical modifications only introduced a gradient concentration along the copolymer film surface length and the surface geometrical microstructure along the slide distance barely changed.

Figures 4(a)–4(c) and Table 2 show the three-dimensional measurements of the gradient wettability surface and roughness of the P (BA-MMA-HEMA) films fabricated by the alkaline solution with different reaction time. The Ra (roughness average) of the P (BA-MMA-HEMA) film surface for hydrolysis reaction time of 0, 20 and 40 min are 0.358, 0.379 and 0.448 nm, respectively, which demonstrates that the Ra variations of P (BA-MMA-HEMA) film were negligible and demonstrated the physical properties of the P (BA-MMA-HEMA) negligibly changed.

Additionally, it is observed that Fig. 1 shows the enhancement of P (BA-MMA-HEMA) slope gradients is larger than copolymer P (BA-MMA). It can

be found that the P (BA-MMA) copolymer film was partially dissolved when the reaction time of alkaline solution increased. However, the larger slope gradients of copolymer P (BA-MMA-HEMA) can be found under the same reaction time. This may be due to the pseudo-cross linking reaction between the –OH active group of copolymer P (BA-MMA-HEMA) and the –O-CH₃ group of amino curing agent,³⁷ resulting in a compact film of covering the substrate surface. The more reaction time of alkaline solution with the copolymer P (BA-MMA-HEMA) compact film is ascribed to the pseudo-cross linking reaction. The –O-CH₃ reactive group in the chemical structure of amino curing agent (product name is CYMEL 303) is illustrated in Fig. 5.

4. Conclusions

Two (meth)acrylate copolymers were prepared firstly, then the wettability gradient surface on poly (meth) acrylate films was fabricated by a simply controlled hydrolysis process. The gradual change of chemical composition from the ester group to acid salt by changing the reaction time of the sodium hydroxide solutions, leads to the gradient wettability surfaces. The slope hydrolysis gradients have the vital characteristic of barely changing the surface topography along the glass slide length. The results show that the P (BA-MMA-HEMA) film surface has larger slope gradients than P (BA-MMA). The more reaction time to the copolymer surface would introduce more active COOH groups and acid salt by the ester group hydrolysis procedure using relatively alkaline solutions, which will result in larger slope gradients. The wettability of the poly(meth) acrylate coating film needs to be further validated by research because of the copolymers polydispersity. The (meth) acrylate copolymer film with gradient wettability behavior has been widely used in many industrial areas such as phase change heat transfer, microfluidics fabrication and biomimetic materials.

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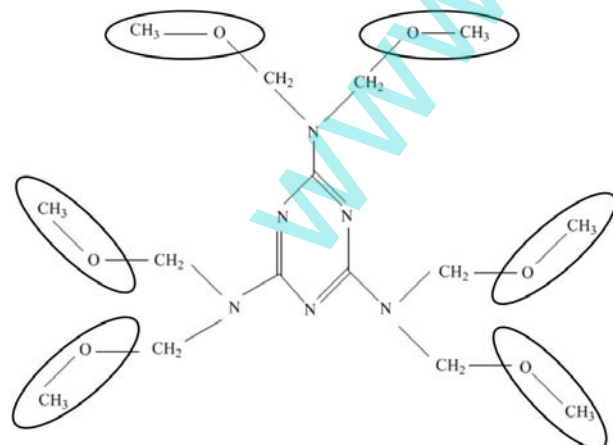


Fig. 5. Chemical structure of amino curing agent (product name is CYMEL 303). The chemical structure of amino curing agent indicated that the amino curing agent contain six –O-CH₃ groups (the black circle).

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