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Synthesis and evaluation of a moisture-promoted healing copolymer

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1. Introduction

As we know, skin plays a role of protection for the body in the biological systems, and it can also be self healed and recovered its protection ability again when it suffers damage. Inspired by this biological repairing system, coating material with self healing ability may perfectly protect the substrates and itself simultaneously [1–5], which attracted more and more interests of researchers [6.7].

As the mainstream of self healing systems, the extrinsic healing system which embedded liquid healing agent into microcapsules [8-23], hollow fibers [24,25], microvascular [26], core-sheath structure [27] and so on [28-32] was intensively focused on all the time. The embedded active healing agent would be released to the crack once mechanical damage occurred [33]. Afterwards, the healing agent can polymerize when contacting with the catalyst or hardener, which either dispersed in the matrix or released from other ruptured containers, resulting in rebinding of the crack faces. This approach, despite the sophistication in chemistry and manufacturing, has been quite successful in achieving high mending efficiencies and is applicable to various types of polymeric materials. Aside from the healing agent embedded system, the intrinsic self healing system can be achieved by physical interaction [34], reversible chemistry, which can recover itself by the formation of new covalent bonding [35-38] or weaker interactions, such as hydrogen bonding [39–44], $\pi - \pi$ interactions [45,46] polyelectrolyte multi layers [47,48] and so on. For example by incorporated an active

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ABSTRACT

We report a homogeneous self-repairing copolymer system that exhibits self healing characteristics upon exposure to moisture environment. The copolymer consists of an isocyanate containing methacrylate monomer served as the repairing component and a fluorine-containing monomer as the protection component. Upon a mechanical damage of the coating copolymer, the isocyanate residue groups like the meshes of a zipper will exposure to generate reactive ends with environmental water like a faster of a zipper, thus form new crosslinking and repair the coating film. These materials with merits of easy-preparation and temperate repairing condition, can be used in decorative and anti-corrosion coatings.

precursor into the polymeric network, material could be well healed by the reaction of the active function groups on the both sides of the crack under the sun exposure after mechanical damage [49]. Because there was no heterogeneous "containers" in the polymeric network, the mechanical property could not be influenced; moreover, the healing trigger was UV light existed in the open air, which provided an ambient temperature approach to self healing.

For the metal anti-corrosion self healing coating materials the material structure designs are mainly focus on the systems with encapsulated reactive components in polymeric matrices. For example, Garcia et al. [50] synthesized a water-reactive healing agent based on a silyl ester and encapsulated it into an organic coating. The silyl ester could locally released at the damage site, wets both the metal and polymer surface, reacts with moisture which protects the metal at the scribe from further corrosion attack; Samadzadeh et al. [51] encapsulated Tung oil as an oxidative healing agent the epoxy coating; and Huang et al. [52] reported a facile microencapsulation preparation approach for liquid isocyanates hexamethylene diisocyanate monomer via an interfacial polymerization method in oil-in-water emulsion, which makes the instant healing possible.

Herein, we report a novel self healing coating system based on only one designed copolymer, which can heal itself under moisture environment. This copolymer consists of two components, isocyanate groups containing monomer (ITEGMA) and fluorinated monomer, 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate (HFBMA). In this system, the fluorine-containing segments in HFBMA component, due to their low surface free energy, are prone to gather on the solid—air interface, to form a good water barrier during the





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coating preparation and application process [53–55]. And the isocyanate containing segments in ITEGMA component, due to their strong polarity, are prone to locate on the solid–substrate interface, to form a reparable layer. Once the coating is broken, isocyanate groups exposed can react with H_2O in air and form a urea crosslink. The reactions are depicted in Equations (1) and (2), making the moisture self healing process possible.

$$\mathbf{R} - \mathbf{N}\mathbf{C}\mathbf{O} + \mathbf{H}_2\mathbf{O} \rightarrow \mathbf{R} - \mathbf{N}^{\mathrm{H}} - \mathbf{C}\mathbf{O}\mathbf{O}\mathbf{H} \rightarrow \mathbf{R} - \mathbf{N}\mathbf{H}_2 + \mathbf{C}\mathbf{O}_2$$
(1)

$$R - NH_2 + R' - NCO \rightarrow R - N^H - C^O - N^H - R'$$
⁽²⁾

In this work, first, an isocyanate containing metharcylate monomer ITEGMA was synthesized according to the scheme as shown in Fig. 1. Then various compositions of poly (HFBMA-co-ITEGMA) copolymers were synthesized, and then the characteristics and the self healing property of the copolymers as metal protection coating were investigated. Finally, we speculate as the possible healing mechanism for this kind of self healing behavior.

2. Experimental section

2.1. Materials

Isophorone diisocyanate (IPDI, Degussa Co. LTD., German) was used as received. 2-Hydroxyethyl methacrylate (HEMA, Beijing Chemical Works, China) and 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate (HFBMA, Xeogia Fluorine-Silicon Chemical, Harbin, China) were purified by vacuum distillation before use. 2, 2'-azobis (isobutyronitrile) (AIBN, Tianjin Fuchen Chemical, China) was recrystallized from ethanol. Triethylene glycol (TEG, Tianjin No.1 Chemical Reagent Factory, China) was dried under vacuum oven at 80 °C for 4 h. Tetrahydrofuran (THF, Tianjin Chemical Reagent Wholesaling Company, China) was soaked with CaCl₂ overnight, refluxed with sodium and then distilled. Hexane and acetic ester (analytical reagent) were dried with 4A molecular sieve overnight and distilled prior to use. Fluorescein isothiocyanate (FITC, Shanghai Shize Biotech Company) was used as received.

2.2. Preparation of diisocyanate intermediate BITEG

The reaction was carried out in a glass reactor under nitrogen. 80 mmol IPDI and 0.44 mL benzoyl chloride were added to the reactor. The mixture was pre-stirred for 5 min at 450 rpm. When the temperature was raised to 65 °C, 20 mmol TEG was added dropwise to the mixture within 30 min. After that, the reaction was carried out at 65 °C for 2 h. The final reaction mixture was cooled to room temperature and poured in hexane-ethyl acetate 2:1 (v:v) mixture to extract out the unreacted IPDI. The reaction is depicted in Fig. 1, and the aim product was named as BITEG.

2.3. Preparation of isocyanate containing monomer ITEGMA

7 g BITEG was dissolved in 10 mL anhydrous THF in a glass reactor under nitrogen protection and stirred at 40 °C. With a molar ratio of NCO:OH = 4:1, 0.6 mL HEMA was introduced drop-wise to the solution of BITEG in THF within 30 min. The reaction was further carried out for 4 h. The final reaction mixture was cooled to room temperature and then poured in hexane-ethyl acetate 2:1 (v:v) mixture to extracted out the unreacted BITEG. The reaction is depicted in Fig. 1. And the aim product was named as ITEGMA.

2.4. Preparation of poly (HFBMA-co-ITEGMA) copolymer

HFBMA and ITEGMA with molar ratio of 0:10, 2:8, 3:7, 5:5, 7:3, 10:0, respectively were dissolved in 15 mL dry THF under nitrogen and then the initiator AIBN was added. The temperature was raised to 65 °C and the reaction was carried out for 12 h. The final reaction mixture was cooled down to room temperature and precipitated twice in hexane-ethyl acetate 1:1 (v:v) mixture. Copolymers with different copolymerization molar ratio of HFBMA:ITEGMA = 0:10, 2:8, 3:7, 5:5, 7:3 10:0 were named as PITEGMA, poly(HFBMA-co-ITEGMA)(2-8), poly(HFBMA-co-ITEGMA)(3-7), poly(HFBMA-co-ITEGMA)(5-5), poly(HFBMA-co-ITEGMA)(7-3), and PHFBMA, respectively.

2.5. Coatings on aluminum sheets

Aluminum sheet treatment: Aluminum sheets were cut into the same size with 2 cm \times 4 cm, then polished with a 600 mesh abrasive paper to move off the oxide layer on the surface. After degreased in a mixture solvent of isopropyl alcohol and acetone (1:1, v/v), the sheets were flowed and rinsed with deionized water. Afterwards, the sheets were further etched by ultrasound for 10 min in deionized water [46] and dried in nitrogen atmosphere.



Fig. 1. Synthetic steps of isocyanate containing monomer and the functional copolymer.

Coating preparation: 1 g copolymer was dissolved in 10 mL dry THF under ultrasonic condition. Then polymer solution was dispensed to the aluminum sheets using a drip pipe under nitrogen atmosphere in a shielded glove box. After 24 h evaporation, the samples were transferred to vacuum oven and further dried for 12 h at room temperature.

Annealing process: The copolymer coated aluminum sheet samples were transferred to a bake oven and treated at 120 $^{\circ}$ C for 10 min.

Stability experiment: The coating samples were placed in a sealed beaker with the relative humidity at 95% under 30 °C for several days to test the stability of the coatings.

2.6. Self healing test

Crack formation: The micro cracks were induced by applying a flexing load on the coating around a 2 cm radius of round column [56].

The poly (HFBMA-co-ITEGMA) copolymer coated aluminum sheets with cracks were maintained in a sealed container and treated for 12 h with relative humidity RH% = 95% at 30 °C and then dried for further characterization. After treatment, the situation of cracks was observed with optical microscope and compared with that before healing.

2.7. Characterization

The mass spectra of were recorded on electrospray ionization spectrometer (ESI-MS) Varian QFT-ESI (American). ESI spectra were obtained by using the (CH₃OH + THF) as a mobile phase. Only the positive ions were recorded enlarged by the mass of Na⁺ (23) or NH₄⁺ (18) originating essentially from impurities.

FT-IR spectra were measured in the range from 4000 to 450 cm⁻¹ with a Bio-Rad FTS-6000 (American) FT-IR spectrometer.

Structures of the copolymers were determined by nuclear magnetic resonance (¹H NMR) spectra on a Varian UNITY-plus 400 spectrometer operated at 400 MHz with CDCl₃ as a solvent.

Molecular weights of the copolymers were measured on a gel permeation chromatograph (GPC) instrument (Equipped with Waters 2414 refractive index detector and Waters 1525 Binary HPLC Pump, using Waters styragel HT2, HT3, HT4 THF 7.8 \times 300 mm² columns). THF was used as an eluent solvent and polystyrene standard samples were used to calibrate the results.

Quantera PHI 5300 XPS (American) X-ray photoelectron spectroscopy was used to characterize the surface composition of the copolymer coatings.

Water contact angles (WCA) were measured using the sessile drop method on Dataphysics OCA ISEC contact angle meter (German).

The surface morphologies of coatings were investigated by Hirox digital optical microscope KH 7700 (Japan) and scanning electron microscope (SEM) Hitachi X-650 (Japan).

The electrochemical testing was carried out at a multichannel Potentiostat/Galvanostat Wona Tech WMPG1000 (Korea). Linear sweep voltammetry and chronoamperometry were evaluated in a three electrode electrochemical cell in 1 M KCl aqueous solution equipped with Pt as a counter electrode, Calomel electrode as a reference electrode and coated aluminum substrate as working electrode, respectively. The test samples were coated with epoxy resin in order to seal the naked aluminum sheet and just let the copolymer coating expose to the outside. Linear sweep voltammetry was evaluated from -600 mV to +1100 mV at a rate of 20 mV s⁻¹ and a chronoamperometric curve was performed at 0.3 V for 200 s.

Fluorescence of the cracks was observed using an Olympus BX41 microscope (Japan). The cracked copolymer coatings of PHFBMA, poly (HFBMA-co-ITEGMA) (7-3), poly (HFBMA-co-ITEGMA) (5-5) and poly (HFBMA-co-ITEGMA) (3-7) were placed under moisture for 2 h and 12 h respectively, and then treated with the FITC solution for 2 h. After washing in deionized water for several times, and dried, the coatings were observed under both optical and fluorescent microscopes. Both optical and fluorescent photos were taken.

3. Results and discussion

3.1. Synthesis of isocyanate containing monomer

In this work, first, an isocyanate containing metharcylate monomer ITEGMA was synthesized according to the scheme as shown in Fig. 1, which is confirmed by infrared (IR) (Fig. 2) and electrospray ionization spectrometer (ESI-MS). From the ESI-MS spectrum of BITEG, the molecular ion peak is 617 ($M + Na^+ = 617$). The measured molecular mass is in good agreement with calculated molecular weight of BITEG (M = 594). The molecular ion peak, 742 $(M + NH_4^+ = 742)$, also matches the calculated ITEGMA (M = 724) molecular mass. From the FT-IR spectrum of BITEG in Fig. 2, absorption peaks of 1706 cm⁻¹(-C=O), 2271 cm⁻¹ (-NCO) and 3349 cm⁻¹ (-NHCOO-) can be identified clearly. And peaks at 1703 cm^{-1} (-C=O), 2266 cm⁻¹ (-NCO) and 3341 cm⁻¹ (-NHCOO-) can also be seen in the spectrum of ITEGMA (Fig. 2). Besides, wave numbers of 3080 cm⁻¹ and 1649 cm⁻¹ incorporated with the ESI-MS datum can prove that the vinyl group $(-C=CH_2)$ was introduced to the ITEGMA successfully.

3.2. Preparation of poly (HFBMA-co-ITEGMA) copolymers

HFBMA and ITEGMA with different molar ratio (HFBMA:ITEGMA = 0:10, 2:8, 3:7; 5:5; 7:3 and 10:0) were copolymerized using radical polymerization. Their FT-IR and ¹H NMR spectra are shown in Figs. 3 and 4, respectively. From Fig. 3, we can infer that, the absorption band $\nu = 1707-1721$ cm⁻¹ (-C=O), $\nu = 2252 - 2262 \text{ cm}^{-1}$ (-NCO), $\nu = 3341 - 3355 \text{ cm}^{-1}$ (-NHCOO-) and v = 2862-2863(-CH-O) are corresponding to the isocyanate containing component; and the band of $v = 1100-1289 \text{ cm}^{-1}$ is related to the C–F group. From ¹H NMR spectra in Fig. 4, the chemical shift of 5.1 ppm is related to CF₂-CFH-CF₃ (P_F), which is identified in all the copolymer spectra but not shown in PITEGMA spectrum; the



Fig. 2. FT-IR spectra of ITEGMA and BITEG.



Fig. 3. FT-IR spectra of poly(HFBMA-co-ITEGMA) copolymers with different copolymer compositions; A) 7:3; B) 5:5; C) 3:7; D) 2:8 and E) PITEGMA.

chemical shift of 3.25 ppm is attributed to the existence of NCO–CH– (P₁), which is also found in all spectra. All these results have confirmed the copolymerization of ITEGMA with HFBMA. The real copolymerization molar ratio of HFBMA and ITEGMA can be calculated from the ¹H NMR spectra with the equation of P_F/P₁ = HFBMA/ITEGMA in molar ratio in the copolymer. The data of molecular weights and the copolymer compositions are listed in Table 1.

3.3. Properties of copolymer coating

Coatings were prepared by dispensing the copolymer solution of THF on aluminum sheets. After placed in an undisturbed circumstance of a glove box for 12 h, the coating samples were further dried in vacuum oven for 24 h and then annealed for 10 min at 120 $^{\circ}$ C.

The results of water contact angles for the copolymer coatings were shown in Fig. 5. We can see that the water contact angle of coatings increases with the increase of HFBMA content. The more is



Fig. 4. ¹H NMR spectra of poly(HFBMA-co-ITEGMA) copolymers with different copolymer compositions; A) 7:3; B) 5:5; C) 3:7; D) 2:8 and E) PITEGMA.

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15	hI	P	1
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Data of molecular weight and composition (measured by ¹H NMR) of copolymers.

Copolymers	Mn	Mw	PDI	Composition measured (¹ HNMR)
PITEGMA	6660	12,902	1.93	_
Poly (HFBMA-co-ITEGMA)(2-8)	12,143	27,117	2.23	22.4/77.6
Poly (HFBMA-co-ITEGMA)(3-7)	17,734	33,199	1.87	31.3/68.7
Poly (HFBMA-co-ITEGMA)(5-5)	43,156	107,176	2.48	50.1/49.9
Poly (HFBMA-co-ITEGMA)(7-3)	17,817	32,071	1.80	69.8/30.2



Fig. 5. Relationship of water contact angles of coatings before and after 120 $^\circ$ C annealing with HFBMA monomer content of the copolymer.

the HFBMA amount contained in the coatings, the larger is the water contact angle. But we can also see that when the ratio of HFBMA component is over 30% in the copolymer, the increase tendency of the water contact angle slowed down. In other words, further increase of the HFBMA ratio has only a little help to enlarge the contact angle. The reason may be attribute to that the content of fluorine segments have reached a relative high level when the content of HFBMA is over 30% in the copolymer composition. Thus further increase of HFBMA content has only a little help to the decrease of the coating surface energy. As we know, in the coating formation process, some polymer chains would not be able to arrange to the most probable conformation with the solvent evaporation. And the heat annealing treatment will make polymer side chains move slowly under the enthalpy driven. Results in Fig. 5 show that the contact angles of the copolymer coatings after heat annealing for poly (HFBMA-co-ITEGMA) (5-5) and poly (HFBMAco-ITEGMA) (7-3) can reach to 102.8° and 106.5°, respectively, which indicates that the annealing process could lead the fluorinecontaining segments of the copolymers to gather on the surface

Table 2	
Tested data and theoretic data of F% and N% on the surface of copolymer coating	gs by
XPS.	

Poly (HFBMA-co-ITEGMA)	F% tested data	F% theoretic data	N% tested data	N% theoretic data
2:8	8.84	2.73	3.75	7.27
3:7	10.12	4.42	2.54	6.88
7:3	12.51	15.85	2.07	4.53



Fig. 6. Stable properties of copolymer coatings with different copolymer compositions under high wet environment. (A, A'): PITEGMA; (B, B'): poly(HFBMA-co-ITEGMA)(2-8); (C, C'): poly(HFBMA-co-ITEGMA)(3-7); the right two sections b' and c' are the SEM photos of the coatings of poly(HFBMA-co-ITEGMA)(2-8) and poly(HFBMA-co-ITEGMA)(3-7), respectively. (D, D', D''): coatings of poly (HFBMA-co-ITEGMA) (3-7), poly (HFBMA-co-ITEGMA) (5-5), poly (HFBMA-co-ITEGMA) (7-3) before treatment and after high wet environment treatment for 1 and 2 weeks, respectively.



Fig. 7. Optical photos of healing results for three copolymer coating samples before and after healing; (A, A'): poly(HFBMA-co-ITEGMA)(3-7); (B, B'): poly(HFBMA-co-ITEGMA)(5-5); (C, C'): poly(HFBMA-co-ITEGMA)(7-3). The bar in the Figure is 100 μm.

areas, so the hydrophobic property of the coating would be enhanced.

The XPS was used to further characterize the surface composition of the coatings. The results are shown in Table 2. From the XPS data, as a whole, the content of N atom is grown larger with the increase of the ITEGMA content in the copolymer; and the content of F atom is grown larger with the increase of the HFBMA content. Furthermore, we can found that the tested F concentration is much higher than the theoretic data for poly (HFBMA-co-ITEGMA) (2-8) and poly (HFBMA-co-ITEGMA) (3-7), and the tested N concentration is much lower than the theoretic data. These data indicate that there is obvious gathered tendency to the film surface for F elements, which is in a good agreement with the water contact angle results. This further indicates that when poly (HFBMA-co-ITEGMA) copolymer was coated on the aluminum sheet, on one side, the fluorine-containing segments, because of its low surface free energy, would be prone to go to the air/solid interface, and form a moisture barrier layer, which would protect the isocyanate groups in the bulk matrix away from the outside moisture attacking. On the other side, isocyanate groups, because of its high polarity and the property to react easily with -OH group on the aluminum surface would be prone to locate on the substrate/solid interface, to form a healing function layer.

The environment stability of the copolymer coatings was tested, in order to validate if the fluorinated component in copolymers can support the practical protection for the coatings. Samples were placed in a sealed beaker with the relative humidity at 95% under 30 °C. After 48 h, it can be seen that the color of the coating films for PITEGMA and poly(HFBMA-co-ITEGMA)(2-8) was turned from transparent to white, as shown in Fig. 6A' and B', which indicates that the samples were sensitive to the humidity. The samples of the copolymer coatings would absorb water under high moisture environment, and the water reacted with the isocyanate groups inside the coatings to form urea groups and CO₂, which then could make the film become white. The SEM photo of poly (HFBMA-co-ITEGMA) (2-8) coating film after humidity processing in Fig. 6b' provides further evidence to the above deduction. There are lots of micro holes existed on the film which would be generated from the quickly production of CO₂ because of the reaction between isocyanate groups and water. But for the samples of HFBMA monomer content was over 30% (in molar ratio), the coating films were nearly not influenced and kept transparent, as shown in Fig. 6C and C'. This phenomenon indicates that the coating films can be protected well from the high moisture environment by the fluorine-containing surface barrier. The SEM photo in Fig. 6c' also shows that the coating film is still in a good state. In addition, after placed in the sealed container for 2 weeks under 95% humidity and temperature at 30 °C, the samples of poly(HFBMA-co-ITEGMA)(3-7), poly(HFBMA-co-ITEGMA)(5-5) and poly(HFBMA-co-ITEGMA)(7-3) still maintained in a good state, as shown in Fig. 6D' and D", which indicates that the HFBMA segments have a good protection to the copolymer coatings from exposing to the high moisture environment when HFBMA



Fig. 8. SEM photos of copolymer coating of poly (HFBMA-co-ITEGMA) (5-5) after healing.

segments is over 30% in the copolymer composition. So the samples of poly (HFBMA-co-ITEGMA) (3-7), poly (HFBMA-co-ITEGMA) (5-5) and poly (HFBMA-co-ITEGMA) (7-3) were chosen for the following self healing test experiments.

3.4. Self healing performances

Fig. 7 shows the optical microscope photographs of the morphology of cracks for the copolymer coatings before and after healing. We can see that all the cracks for poly (HFBMA-co-ITEGMA) (3-7) were repaired completely with almost no scar left (Fig. 7A'), indicating the good self healing ability of the coating. Fig. 7B and B' refer to the coating of poly (HFBMA-co-ITEGMA) (5-5). The crack was also healed, but a slight healing scar can be found. SEM photos in Fig. 8 for poly (HFBMA-co-ITEGMA) (5-5) coating after healing process also confirmed the self healing result. From Fig. 8A, the crack was almost healed, only a little light scar left. And with further amplification, Fig. 8B shows that a small amount of white protuberance existed. With a further amplification of the protuberance, Fig. 8C and D show that some place of the crack is not healed completely, and the crack is approximate 1 µm in width. For samples poly (HFBMA-co-ITEGMA) (7-3), as shown in Fig. 7c and c', there is no healing phenomena occurred.

From the experimental data shown above, we can conclude that among the three different ratios of HFBMA and ITEGMA for the copolymer coatings, poly (HFBMA-co-ITEGMA) (3-7) shows the best self healing behavior. The self healing properties of the copolymer systems are mainly related to two factors. On one hand, the more isocyanate groups the coating contains, the better the self healing effect is. On the other hand, the more fluorine groups the coatings contains, the better the protection effect is. But with only a little content of fluorine (30% in molar ratio) containing monomer employed, the fluorine segments of the surface layer can reach a relative high value. So the self healing ability of the coatings is mainly decided by the isocyanate group content of the coatings once the fluorine segment reaches an appropriated amount.

3.5. Electrochemical testing

Electrochemical testing can provide further evidence of passivation property for the self healed coatings [27]. The test was conducted in a three electrode system by using electrochemical workstation. In the three electrode system, Pt equipped as a counter electrode, Calomel electrode equipped as a reference electrode and coated aluminum substrate as working electrode. respectively. When the voltage swept from -0.6 V to 1.1 V, the coated aluminum sheet was under an oxidation process which is charging to the coated aluminum. Results of linear sweep voltammetry and chronoamperometry are shown in Fig. 9. Three samples including self healing processed coating samples of poly(HFBMAco-ITEGMA)(7-3), poly(HFBMA-co-ITEGMA)(3-7), and coating sample of poly(HFBMA-co-ITEGMA)(3-7) just after crack formation as a control were tested. From Fig. 9a, we can infer that the sample of poly (HFBMA-co-ITEGMA) (3-7) after self healing exhibited a passivation property with current of 1.35 \times 10 $^{-9}$ A. Meanwhile, the current of poly (HFBMA-co-ITEGMA) (7-3) counterpart is 0.05 A, and the current of control sample new cracked poly (HFBMA-co-ITEGMA) (3-7) is linear with voltage.

The chronoamperometry curves are shown in Fig. 9b, The currents of healed samples poly(HFBMA-co-ITEGMA)(3-7), sample poly(HFBMA-co-ITEGMA)(7-3), and the control sample poly(HFBMA-



Fig. 9. (a) Linear sweep voltammetry curves. A): poly (HFBMA-co-ITEGMA) (3-7) after crack formation as control; B): poly (HFBMA-co-ITEGMA) (7-3) and C): poly (HFBMA-co-ITEGMA) (3-7) after moisture healing process. The in section is the magnification of healed poly (HFBMA-co-ITEGMA) (3-7) with voltage from from -600 mV to + 1100 mV at a rate of 20 mV s⁻¹; (b) Chronoamperometry curves. A): poly (HFBMA-co-ITEGMA) (3-7) after crack formation as control; B): poly (HFBMA-co-ITEGMA) (7-3) and C): poly (HFBMA-co-ITEGMA) (3-7) after moisture healing process. The in section is the magnification of healed poly (HFBMA-co-ITEGMA) (3-7) with evaluation time for 200 s.

co-ITEGMA)(3-7) just after crack formation are nearly 1.45×10^{-9} A, 0.04 A and 0.19 A, respectively, which also reveals the same tendency consistent with the voltammetry test results. The obtained similar results by the above two types of different electrical testing models suggest that the current data under the same testing conditions as the quantization index cannot only illustrate the healing effects of the coating materials before and after repairing process, but also be acted as the quantization index of repairing degree of the materials. For the well repaired sample of poly(HFBMA-co-ITEGMA)(3-7), the current is very small (10^{-9} A), and for the partly repaired sample of poly(HFBMA-co-ITEGMA)(7-3), the current has an outbreak increases (to 0.04 A). And for the un-repaired sample, there is a complete conduction path in the sample, and the current value is the biggest one correspondingly.

The electrochemical testing results indicate that the coating film of poly (HFBMA-co-ITEGMA) (3-7) is healed well after healing process under moisture environment; moreover, the healed coating film still has good electrochemical protection ability to the metal substrate.

3.6. Analysis of self healing mechanism

In this homogenous copolymer system, the preconditions for self healing process are that the isocvanate groups inside the coating matrix are exposed to the outside when the coatings suffer crack damage and the surface fluorine-containing barrier layer is opened up. And then isocyanate groups reacted with moisture water in air and generated amine groups, finally the amine groups reacted with another isocyanate group and form the urea crosslink to heal the crack. In order to characterize this process more clearly, FITC which is an amine-reactive fluorophore was used to functionalize the post-moisture cracks on the copolymer coatings. From the photos in Fig. 10, coating film of PHFBMA was observed no fluorescence phenomena; however, obvious fluorescence phenomena was observed for all the other three copolymer coatings, which proves the generation of amine groups after the isocyanate groups exposed to the outside moisture. From Fig. 11B and B', the cracks on poly (HFBMA-co-ITEGMA) (7-3) coating were almost not healed, and the fluorescence signal was observed all



Fig. 10. Optical and fluorescent photos on cracks of the different coating after treated under moisture for 2 h; then treated with FITC: (A, A'): PHFBMA; (B, B'): poly(HFBMA-co-ITEGMA)(7-3); (C, C'): poly(HFBMA-co-ITEGMA)(5-5) and (D, D'):poly(HFBMA-co-ITEGMA)(3-7). The multiple of zoom in is 100.

over the cracks. And we can also infer from the Fig. 11C and C', the cracks on poly (HFBMA-co-ITEGMA) (5-5) coating were partly healed in some place where a little amount of fluorescence signal was observed. However, from Fig. 11D and D', we can see that after healing process under moisture for 12 h, the cracks on poly(HFBMA-co-ITEGMA)(3-7) coating were well healed, and almost no fluorescence phenomena was observed, which indicates that the amine groups were consumed by isocyanate groups to form urea groups.

Another important factor to heal the crack is that the isocyanate groups on the two sides of the crack can contact with each other effectively, and then react with H_2O to form urea crosslink. In

a whole crack, the possible contact areas between the two sides of the crack may be the ends, the bottom and some possible areas nearby between the both sides of the crack. These effective contact areas are called part A, and the other areas of the crack are called part B. Area A and area B can be summarized in Fig. 12a. Part A includes the bottom and the end of the crack, as shown in Fig. 12a (1) and (2), which are the main reactive areas where the self healing reactions are carried out. There are also some other possible part A areas existed as shown in Fig. 12a (3) and (4). These possible parts A areas will contribute greatly to the self healing process because they could increase the amount of reactive spots. In part B areas, the isocyanate groups between two sides of the crack cannot contact



Fig. 11. Optical and fluorescent photos on cracks of the different coating after treated under moisture for 12 h; then treated with FITC: (A, A'): PHFBMA; (B, B'): poly(HFBMA-co-ITEGMA)(7-3); (C, C'): poly(HFBMA-co-ITEGMA)(5-5) and (D, D'):poly(HFBMA-co-ITEGMA)(3-7). The multiple of zoom in is 100.

easily and the reactions have no contribution to the self healing behavior.

Along with the repairing process going, part A areas are gradually extending to part B areas. The part A areas are enlarged and part B areas are reduced gradually, which makes the crack grow narrower and shorter, thus the healing process are carrying on. However, when the parts A areas are conducting the healing process, part B areas are also exposed to the moisture. Then, the isocyanate groups on the same side will react with H₂O. Under this situation, isocyanate groups are consumed but no healing effect shows. And this will bring down the healing effect especially to the coating systems with low content of isocyanate groups such as poly (HFBMA-co-ITEGMA) (7-3). For the system with low content of isocyanate groups, the consuming of isocyanate groups in part B will be a fatal side reaction, which leads to no healing phenomena (Fig. 7c and c'). And for poly (HFBMA-co-ITEGMA) (5-5) copolymer coating film, the side reaction influences to a certain degree, which results in that some places in the crack are also unhealed. However, the side reaction to the coating of poly (HFBMA-co-ITEGMA) (3-7) nearly does not affect to the healing process due to the existence of the enough amount of isocyanate groups.

The above self healing process can be described as a slider meshes together the opposing rows of teeth in a zipper as shown in Fig. 12b. The isocyanate groups on the both sides of the crack act as



Fig. 12. a) Illustration of the crack self healing process. A: 1) the bottom of the crack; 2) the ends of the crack; 3, 4) possible contact areas between the two sides of the crack; B: no contact areas. b) Illustration of the zipper model mechanism.

the teeth whereas the H_2O acts as the slider in the zipper. Along with the self healing process conducting, the slider H_2O meshes the isocyanate group teeth together automatically to form a stable urea crosslink. Comparing with the zipper in real world, this "zipper" may consist of several sliders, which are in the different part A areas in the crack.

This zipper-like model can also be used to explain other self healing systems, such as the active precursor containing system of Ghosh et al. [49] In their work, the crack was self healed under UV exposure by couple reaction between two crack faces. The width of the crack grew narrower, and the length of the crack became shorter along with the self healing process, until the crack is healed completely finally. Thus the "zipper model" should be a universal mechanism to explain the self healing systems, which can heal themselves in virtue of contained active functional groups in the homomatrix.

4. Conclusion

In this work, a novel poly (HFBMA-co-ITEGMA) copolymer composed of fluorine segments and isocyanate groups containing components has been synthesized. The self healing property was demonstrated when using the copolymer as a protect coatings on aluminum sheet. When the fluorine segment containing monomer is over 30%, the coating film of the copolymer can be protected well against the environment moisture. The optimized ratio of the self healing coating film was found out to be HFBMA:ITEGMA = 3:7. A zipper-like self healing mechanism has been proposed to explain the healing behavior for this copolymer system. The isocyanate groups on the two sides of the crack within the effective contact areas are coupled under the moisture mediated condition and this process can be extended to the areas which are ineffective contact, and finally the entire crack is healed. This work provides a simple and effective method with a fine prospect to prepare a kind of anticorrosion coatings with high self healing performances.

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