Polymer(Korea), Vol. 38, No. 3, pp. 265-271
http://dx.doi.org/10.7317/pk.2014.38.3.265

ISSN 0379-153X(Print)
ISSN 2234-8077(Online)

불소화 폴리아크릴레이트-폴리우레탄 라텍스 혼성필름의 그레디언트 구조와 표면성질

Min Zhu, Kun Chen, Yufang Zhang, Xiangrong Wang, and Xiangdong Zhou†
College of Textile and Clothing Engineering, National Engineering Laboratory for Modern Silk, Soochow University
(2013년 10월 7일 접수, 2013년 12월 17일 수정, 2013년 12월 20일 채택)

Gradient Structure and Surface Property of Fluorinated Polyacrylate and Polyurethane Latex Blend Films

Min Zhu, Kun Chen, Yufang Zhang, Xiangrong Wang, and Xiangdong Zhou†
College of Textile and Clothing Engineering, National Engineering Laboratory for Modern Silk, Soochow University, Suzhou, JiangSu 215123, China
(Received October 7, 2013; Revised December 17, 2013; Accepted December 20, 2013)

Abstract: In order to investigate the characteristics of the gradient fluorinated polyacrylate and polyurethane latex blend films, the fluorinated polyacrylate emulsion and the polyurethane emulsion were synthesized, and then the both emulsions were blended at a series of ratios. The effects of content of the fluorinated polyacrylate on the gradient structure and surface property of the blended films were assessed by AFM, XPS, SEM-EDX and surface free energy measurements. It appeared that, while the content of the fluorinated polyacrylate latex was up to 30%, the fluorinated polyacrylate particles were selectively gathered on the film-air (F-A) and film-glass (F-G) interfaces at room temperature. When the content of the fluorinated polyacrylate was under 30%, the gradient structure of fluorinated component was not evident. The further increasing of fluorinated polyacrylate in the mixed system facilitated the formation and enlargement of gradient structure, but the adhesion of film decreased a little.

Keywords: fluorinated polyacrylate, polyurethane, gradient structure, self-organization, latex blend.

Introduction

Fluorinated polyacrylate has been widely used in paint industry, textile and leather finishing etc., because of its low surface energy, water and oil repellent.[1-4] However, in most cases poor adhesion and relatively expensive to produce may circumscribe their use. It is one of the important topics of the research on how to make the fluorinated components play a better role and how to increase the bond strength of the material on the premise of maintaining good surface properties of materials. The defects could be improved through these methods: the copolymerization of fluorinated monomer with other monomers,[5-9] preparation of core-shell particles[10-13] and the mixing of fluorinated polyacrylate with other emulsion.[14-16] Furthermore, the blended process was simple which not only maintained the excellent properties of materials, but also reduced costs. In addition, waterborne polyurethane is inexpensive with excellent characteristics of abrasion resistance, suppleness and adhesiveness.[17]

Self-organizing method is widely used in the preparation of gradient structure materials, but the method is mainly used in solution- and melt-system. In latex-system which is environmental, the polymers are covered by emulsifier, and there is little difference among the properties of emulsion particles. This may result in the lack of propulsive effort to form gradient structure. The driving force was provided for the formation of the concentration gradient structure because the phase separation occurred between the fluorinated polyacrylate and polyurethane in the film drying process. In this study, the fluorinated polyacrylate emulsion and the polyurethane emulsion were blended by a series of relative ratios, and then films were built. The effects of the fluorinated polyacrylate content on the gradient structure and surface property of the blended films were investigated.

†To whom correspondence should be addressed.
E-mail: zhouxiangdong@suda.edu.cn

Experimental

Materials. Polypropylene glycol (PPG, industrial grade, molar mass 1000 g/mol) was purchased from Hai'an Petrochemical Corp., and it was dried in vacuum oven at 90 ℃ for 6 h before use. Isophorone diisocyanate (IPDI, industrial grade) was purchased from Sinopharm and used without purification. 2,2-dimethylol propionic acid (DMPA, industrial grade, Sinopharm) were dried in vacuum oven at 90 ℃ for 12 h before use. Triethylamine (TEA, analytically pure, Jiangsu Strong Function Chemical Corp.), 1,4-butanediol (BDO, chemically pure) and dibutyltindilaurate (DBTDL, chemically pure) were used without purification. Hexafluorobutyl methacrylate (HFMA, industrial grade, Xuegia Chemical Corp.), methyl methacrylate (MBA, chemically pure, Lingfeng Chemical Corp.), ammonium persulfate (APS, analytically pure, China Chemical Reagent Factory), sodium dodecylbenzene sulfonate (SDBS, chemically pure, Lingfeng Chemical Corp.), OP-10 (chemically pure, Shanpu Chemical Corp.), sodium bicarbonate ($NaHCO_3$, chemically pure, Shanghai Chemical Corp.). Deionized water was prepared in laboratory.

Preparation of Fluorinated Polyacrylate (FPA). Monomer pre-emulsions of HFMA, MBA and BA were prepared by fast agitation at room temperature. The stoichiometric APS, $NaHCO_3$ and monomer pre-emulsion (1/3 of the total) were added to a 250 mL four neck flask equipped with a mechanical stirrer under the protection of nitrogen gas. The residual monomer pre-emulsion and initiator solution were added dropwise in 2 h when the emulsion grew blue at 70 ℃. Then the emulsion was kept at 80 ℃ for 3 h to ensure complete monomer conversion.

Preparation of Waterborne Polyurethane (WPU). Dewatered PPG and DMPA were added to four neck flask equipped with electric mixer, condensate return device and thermometer under nitrogen atmosphere around 55 ℃. Then the IPDI was added gradually at 55 ℃ with continuous stirring in the presence of DBTDL and kept for 3~4 h at 75~80 ℃. Subsequently, BDO was added, and maintained until the isocyanate (NCO) content in the prepolymer reached a constant value. The product was cooled down to 45 ℃, the distilled water and TEA were added, then stirred under high speed at room temperature for 1 h, the waterborne polyurethane (WPU) emulsion was prepared.

Preparation of Blended Emulsion Membrane. According to the recipe showed in Table 1, diluted each emulsion of FPA or WPU to 5% at room temperature, then blended every diluted FPA and WPU completely by ultrasonic oscillation. The blended emulsion was dropped on clean glass and dried at room temperature, and the blended film of FPA and WPU was acquired. Then the film was dried at the temperature of 105 ℃ or 205 ℃ in vacuum drying box for 2 h. The sample was obtained after cooling.

Table 1. The Recipe of Blends

Designations	FPA (mL)	WPU (mL)	Ratios of FPA/WPU (v/v)
Sample 1	5	45	1/9
Sample 2	10	40	2/8
Sample 3	15	35	3/7
Sample 4	20	30	4/6
Sample 5	25	25	5/5

Measurements. AFM was obtained by tapping mode with Nanoscope IV atomic force microscope (Veeco Co., USA) at room temperature. Element analysis of the samples was carried out in VG Multilab 2000 type X-ray photoelectron spectrometer (V.G. Scientific Ltd., UK), using AlKα rays for the light source at 300 W. SEM-EDX (EDAX 250, Horiba Co., Japan) analysis was carried out to test the element distribution on the surface and cross-section of blended membrane. The contact angles of deionized water and diiodomethane on blended emulsion membrane were measured on OCA-50 Contact Angle Meter, and the surface free energy of the membrane was computed through Fowkes equation.

Results and Discussion

From Table 1, the content of FPA in the blended emulsion of Sample 1-5 was 10, 20, 30, 40, 50%, respectively. The relationship between the fluorine content in the blended emulsion and film gradient structure can be studied through the surface and internal morphology and composition of blended emulsion membrane.

Analysis of Surface Morphology. The membrane of blended emulsion was tested by AFM at room temperature, and the results were shown in Figure 1. The AFM data could reflect the variation of fluorinated component on film surface. The tested surface of the film contacted with the air, and the bright section showed the FPA component and the dark represented the PU component.

It was obvious that there was few particle phase on the sur-

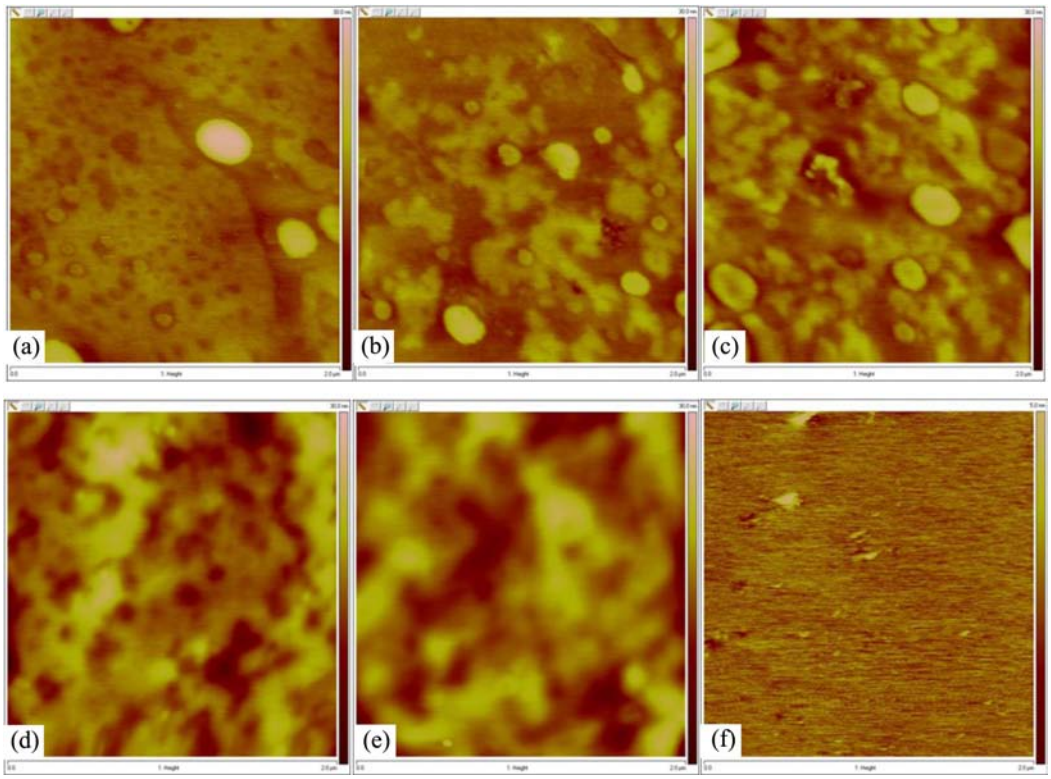

Figure 1. AFM height images of (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4; (e) Sample 5; (f) Sample 4 (Scanning range = 2 μm; a, b, c, d, e: film-air interface (F-A), f: film-glass interface (F-G)).

face contacted with the air in Sample 1 (Figure 1(a)). Most of particle phase were shrouded under membrane surface because the content of FPA emulsion particle was low (10%). Figure 1(b) showed that more than half of the area of F-A had clear bright particle phase, and this was due to the content of FPA in blended system reached 20%, thus flourinated component in the film surface enriched and occupied more than half of the area. See Figure 1(c), almost all of the area was occupied by bright particle phase (FPA component) when the content of FPA reached 30%. FPA component continued to enrich on F-A surface, and part of FPA particle even occupied the space between the PU particles leading to the FPA particle deformed. Figure 1(d) showed that when the FPA content was up to 40%, fluorine components on F-A surface of the membrane continued to accumulate, and FPA particles were squeezed almost completely deformed. The F-A surface was almost entirely occupied by bright particle phase in Figure 1(e), the fluorined component was stretched into a larger area.

In FPA-WPU blended system, the FPA was hydrophobic ingredient and the WPU was hydrophilic ingredient. During the volatile procedure of water, the FPA moved toward the air interface gradually while the WPU moved toward the glass interface and the non-reversible arrangement was formed. With the continuous volatile procedure, the arrangement of WPU particles became closer. A part of FPA particles inserted into the space among the WPU particles, and most part of FPA particles form a non-reversible arrangement on the surface due to the motion of the water. Therefore, when the content of FPA was low, the particles mainly existed among the space of WPU. When the content was high, more and more FPA particles would enrich on the surface. The motion of these two ingredients resulted in the distribution as Figure 1 showed.

Considering Sample 4, different from the situation in Figure 1(d), the F-G surface was smooth and the particle phase can't be seen in Figure 1(f). It means that the FPA particles of Sample 4 were mainly distributed in the F-A surface and internal of the film, and selectively enriched in the F-A surface. We can conclude that there is an influence of concentration gradient of FPA particles from the F-A surface to the F-G surface of the film.

Analysis of Surface Components. The films F-A were characterized by X-ray photoelectron spectrometer (XPS) to analyze the elements. Figure 2 demonstrated that the F1s increased gradually along with the increase in content of FPA

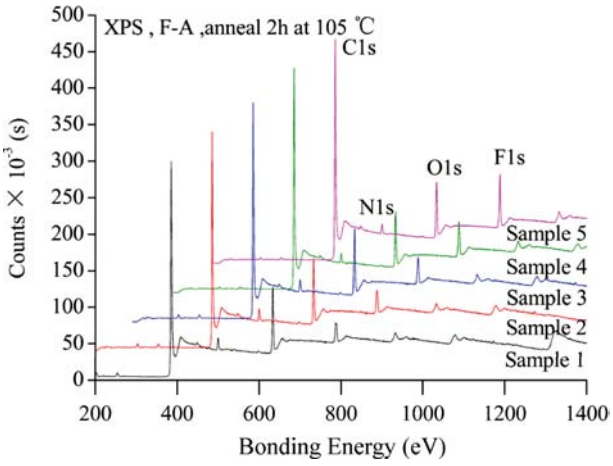

Figure 2. XPS spectra of Samples 1~5 dried at 25 ºC and annealed at 105 ºC for 2 h.

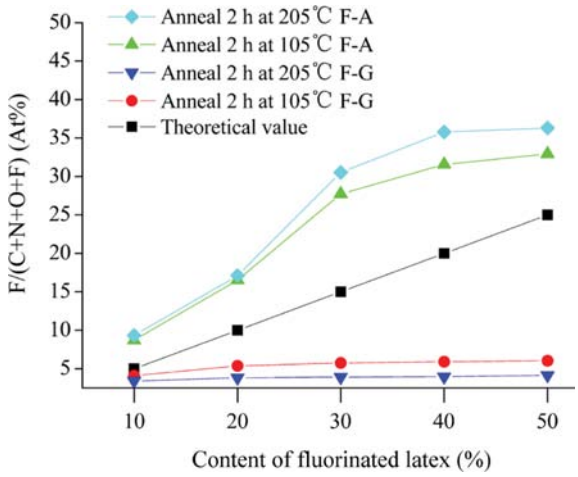

Figure 3. Content of fluorine on the surface of Samples 1~5 annealed at 105/205 ºC for 2 h.

while the peak intensity of N1s and O1s decreased.

The relative contents of fluorine element of F-A and F-G from Samples 1-5 were tested by SEM-EDX in order to characterize the gradient structure on the cross section of the film and the results were shown in Figure 3. With the increase of the content of FPA in blended system, the content of fluorine atom in emulsion membrane F-A also increased greatly. When the content of FPA reached 40%, the relative content of fluorine atoms on membrane surface was above 35%, and the increase in the fluorine atom's content on membrane surface was no longer obvious along with the increase of the amount of fluoride components.

Interestingly, however, when the content of fluorinated component increased from 10% to 50%, the content of fluorine atom in F-G surface did not change significantly. It indicated that the influence of the content of fluorine atom in F-G surface was inconspicuous when the content of fluorined component was changed in the blends. In addition, the F-G surface of the film was mainly occupied by the PU component after heat treatment.

From Figure 3 we can figure out that the contents of fluorine atom in F-A surface of the films after heat treatment in 205 ºC were higher than those in 105 ºC, but the contents in F-G surface were less. It can be explained that the molecular chain after heat treatment can be freely slipped, so the fluorinated components continuously moved from the interface of high surface energy to the low.

Analysis of Surface Energy. The surface energies of FPA and PU films were evaluated to be 20.74 and 37.23 mN/m, respectively. The surface energies of F-A and F-G of FPA-PU blended films were also tested to characterize the variation of fluorine content on both sides of the film and the results were listed in Table 2.

Compared with the surface energies of Samples 1-5 at room temperature, the blended film containing greater content of fluorine showed the lower surface energy of F-A film. This was because more fluorine particle could be beneficial for fluorine component to enrich on the surface of F-A film and thus led

Table 2. Surface Free Energy (mN/m) of the Films before and after Heat Treatment

Sample	1		2		3		4		5	
	F-A	F-G	F-A	F-G	F-A	F-G	F-A	F-G	F-A	F-G
1	37.22	47.18	33.98	46.73	31.45	45.78	30.04	44.77	29.73	44.08
2	27.36	41.29	26.62	42.18	24.29	43.39	23.40	45.69	22.07	46.73
3	26.33	40.77	25.06	39.13	23.17	39.78	22.75	39.02	21.60	40.16
4	25.45	38.75	23.06	36.55	21.77	37.43	21.16	38.18	21.37	37.56
5	25.22	37.89	22.73	39.07	21.03	39.46	20.38	37.06	20.01	37.14

Note: 1-Air dried, 2-Anneal 2 h at 105 ºC, 3-Anneal 4 h at 105 ºC, 4-Anneal 2 h at 205 ºC, 5-Anneal 4 h at 205 ºC.

to the reduction in surface energy. Under the same heat treatment condition, the surface energy of F-A film of Sample 1 was the greatest, and the surface energy of Sample 2 was greater than that of FPA film. Meanwhile, the surface energies of F-A film of Samples 3-5 were almost the same, and slightly decreased and gradually approached to the surface energy of FPA film with the increasing of fluorine-containing in the system. This indicated that the fluorine enriched on the surface of the film, and then tended to be saturated when the fluorine-containing was more than 30% in the blended system, and the increasing fluorine contributed little to the decrease of surface energy. The surface energies of Samples 1-5 were almost the same and were all greater than that of PU film which formed at room temperature. This can be attributed to the enrichment of some emulsifier on the F-G film. The surface energies of F-G film of Samples 1-5 decreased and approached to the surface

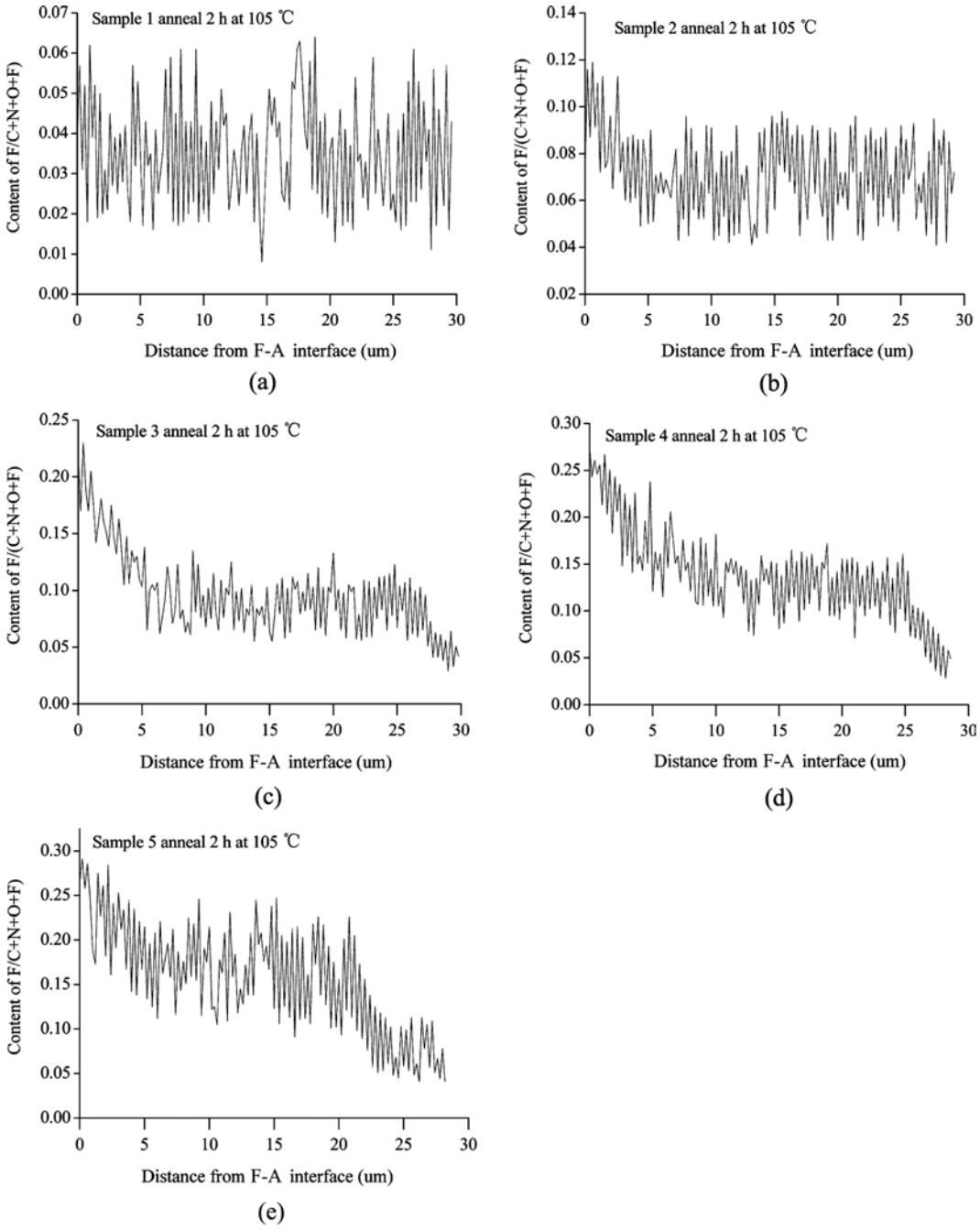

Figure 4. Contents of fluorine in the film transect of Samples 1~5 (a~e) after annealing 2 h at 105 °C.

energy of PU film with the increasing of heat treatment temperature and extending of time. It showed that the surface of F-G film was mainly pure PU component, and small molecule-emulsifier penetrated into the film during the heat treatment.

During the heat process at the temperature of 105 ℃, all of the ingredients in emulsion membrane were the viscoelastic state. It was easy for the molecular chain to move, but difficult to slip. So the ingredients could diffuse and integrate. When the temperature was up to 205 ℃, the viscoelastic state changed to viscous flow state, the molecular chain began to slip, so it was easy for the position of chains to change. It can be seen from the longitudinal comparison of the influences of heat temperature and time on the surface properties of the film that the surface energy of F-A film was between those of FPA film and PU film which formed at room temperature. Because some fluorinated components migrated to the surface of F-A film during the formation of film, which caused the surface energy lower than that of PU film. The surface energy of F-G film was greater than that of PU film, which showed that some emulsifiers may enrich on the surface of F-G film. In conclusion, the data in Table 2 showed that the surface energies of F-A film decreased in different degrees after heat treatment. The surface energy of F-A film gradually approached to that of FPA film with the increasing of heat treatment temperature and the extending of time. Heat treatment made the surface energy of F-G film decreased and approached to the surface energy of PU film. It meant that the heat treatment made the emulsifier migrate into the film and the F-G film was mainly occupied by the PU component.

According to the results in Table 2 and in Figure 1, it could be inferred that the FPA ingredient enriched on the F-A surface and the gradient structure was formed when the content of FPA reached 30% in FPA-WPU blended system.

Analysis of Internal Gradient Structure. The element content and distribution in cross section of Samples 1-5 were tested by SEM-EDX. It can be seen from Figure 4(a) that the fluorine component distributed uniformly and there was no significant enrichment on the film surface when the content of FPA was 10%. When the content of FPA was 20% (Figure 4(b)), the fluorine component enriched on the F-A surface and had a concentration gradient structure at around 5 μm depth in the film. At the same time the fluorine component distributed uniformly from the center of the film to the F-G surface. When the content of FPA reached 30% (Figure 4(c)), the fluorine component enriched on F-A surface and the F-G surface was mainly occupied by PU component. There was a fluorine concentration gradient structure at about 5 μm depth of both sides of the film, and the fluorine component didn't change in the center of the film. What's more, the fluorine component decreased from F-A surface to F-G surface. When the content of FPA reached 40% (Figure 4(d)), FPA component and PU component continued to enrich on the surface of film, and the fluorine concentration gradient became dense. Especially when F-A surface reached 10 μm, both of the two components distributed uniformly at about 15 μm depth in the center of the film. When the content of FPA was 50% (Figure 4(e)), two components continued to enrich on both sides of the film and there was a fluorine concentration gradient at the interface. The layer of fluorine concentration gradient reached 10-15 μm. From all the above, when the content of fluorine component in the system reached 30%, the F-A surface was occupied by fluorine component while F-G surface almost had no fluorine component. The fluorine component decreased from F-A surface to F-G surface. The increasing content of fluorine component made the concentration gradient structure of fluorine component into larger scale. It is consistent with the preceding inference.

Conclusions

After heat treatment, the blended film from a mixture of fluorinated polyacrylate and polyurethane latex on slide glass was obtained. In the film the fluorine component was enriched on F-A interface while the polyurethane component was enriched on F-G interface. The membrane has the concentration gradient structure of fluorine in the film thickness direction.

When the fluorine component in blended system was below 30%, the concentration gradient structure of fluorine was inconspicuous. When the fluorine component was above 30%, the concentration gradient structure in film thickness direction increased. This also resulted in the slight increase of the fluorine content on F-G surface. Furthermore, the heat treatment was beneficial for fluorine component to migrate towards F-A interface then enriched on it. So the concentration gradient of fluorine elements in film thickness direction changed into a bigger scale.

Acknowledgements: This work was funded by the Priority Academic Program Development of Jiangsu Higher Education Institution (China) and by the technology Innovation Foundation of National Engineering Laboratory for Modern Silk (China).

References

1. W. S. Kim, M. W. Kim, E. C. Jung, C. H. Baek, L. S. Park, I. K. Kang, and S. Y. Park, *Polymer(Korea)*, **27**, 364 (2003).
2. C. H. Baek, J. Y. Kong, S. H. Hyun, Y. J. Lim, and W. S. Kim, *Polymer(Korea)*, **29**, 433 (2005).
3. N. Tirelli, O. Ahumada, U. W. Suter, H. Menzel, and V. Castelvetro, *Macromol. Chem. Phys*., **199**, 2425 (1998).
4. Y. J. Chen, C. C. Zhang, Y. F. Wang, S. Y. Cheng, and P. Z. Chen, *J. Appl. Polym. Sci*., **90**, 3609 (2003).
5. Y. J. Chen, C. C. Zhang, and X. Chen, *Eur. Polym. J*., **42**, 694 (2006).
6. S. Yang, J. Wang, K. Ogino, S. Valiyaveettil, and C. K. Ober, *Chem. Mater*., **12**, 33 (2000).
7. H. Li, Z. B. Zhang, C. P. Hu, S. S. Wu, and S. K. Ying, *Eur. Polym. J*., **40**, 2195 (2004).
8. S. S. Kim, S. W. Lee, J. L. Haw, and W. Huh, *Polymer(Korea)*, **26**, 9 (2002).
9. P. Doris, H. Liane, and J. Dieter, *Macromol. Symp*., **198**, 421 (2003).
10. C. C. Zhang and Y. J. Chen, *Polym. Int*., **54**, 1027 (2005).
11. S. Chen, W. C. Yan, L. Chen, Y. J. Chen, and N. P. Xu, *Colloid Polym. Sci*., **284**, 413 (2006).
12. X. J. Cui, S. G. Zhong, and H. Y. Wang, *Colloid Surf. A*, **303**, 173 (2007).
13. L. He and J. Liang, *J. Fluorine Chem.*, **129**, 590 (2008).
14. H. L. Huang, S. H. Goh, D. M. Y. Lai, and C. H. A. Huan, *Appl. Surf. Sci*., **227**, 373 (2004).
15. R. Song, D. Yang, L. B. He, and G. T. Yao, *J. Polym. Sci. Part B: Polym. Phys*., **45**, 138 (2007).
16. K. Koh, S. Sugiyama, T. Morinaga, K. Ohno, Y. Tsujii, T. Fukuda, M. Yamahiro, T. Iijima, H. Oikawa, K. Watanabe, and T. Miyashita, *Macromolecules*, **38**, 1264 (2005).
17. H. J. Lira, Y. T. Lee, I. J. Park, and S. B Lee, *J. Colloid Interf. Sci*., **241**, 269 (2001).