Asian Journal of Chemistry Vol. 22, No. 10 (2010), 7983-7996

Comparison of Polyurethane-Fluorinated Acrylate Composite Latex Prepared by Two Different Synthesis Technique

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Polyurethane-fluorinated acrylate (FPUA) composite latexes were synthesized from pre-prepared polyurethane seed latex, dodecafluoroheptyl methacrylate (DFMA) and acrylate monomers though monomer pre-emulsification method and monomer dropping method, respectively. Influences of the two different methods on the polymerization stability and the properties of FPUA composite latex film were discussed. The structure of FPUA films were characterized by scanning electron microscopy (SEM) and FT-IR. The mechanical properties of FPUA films were also tested. The results showed that after the incorporation fluorine monomer, fluorine-containing segments transferred to the surface of the FPUA films and produced phase separation subsequently and FPUA films exhibited improved water and solvent durability, soaking resistance and mechanical properties. Compared with monomer dropping method, FPUA composite latex prepared by monomer pre-emulsification method was more stable.

Key Words: Fluorinated monomer, Polyurethane-fluorinated acrylate, Composite latex, Properties.

INTRODUCTION

Polyurethane (PU) dispersions can be tailored to various applications by changing the preparation method and chemical component. In recent years, significant emphasis has been placed on the use of waterborne polyurethane dispersions due to their environmental safety and excellent properties such as the high solid content and molecular weight of the dispersions. Owing to their numerous advantages, aqueous polyurethane dispersions have found applications in various fields, such as construction, automotive, packing, transportation, electronics, textiles, tape, paper and footwear[1-6].

However, the application of waterborne polyurethane dispersions is limited because of their weak properties in solvent and water resistance, high-temperature performance and chemical resistance. Various methods have been employed to improve these disadvantages, such as the change of the type and content of ionic center[7-9], grafting hydrophobic monomers to polyurethane backbone chain[10,11], adjustment of ionic neutralization degree[12], the copolymerization[13-15] and blend of different polymers[16,17] and cross-linking[18,19].

Recently, polyurethane-fluorinated acrylate (FPUA) has attracted much more attentions due to its significantly improved thermal, mechanical and surface properties[20-23]. Because these properties are closely related to the chemical structure and molecular arrangement of the polymer surface, fluorine is usefully employed to improve the surface functionality of materials. By incorporation of fluorine alkyl side-chain, the film of composite latex not only sustains intrinsic characteristics of bulk polymer, but also exhibits excellent surface properties, which can effectively improve the low surface energy, lubricity, chemical inertness, water and oil resistance, stain resistance and biocompatibility of the films[24-29].

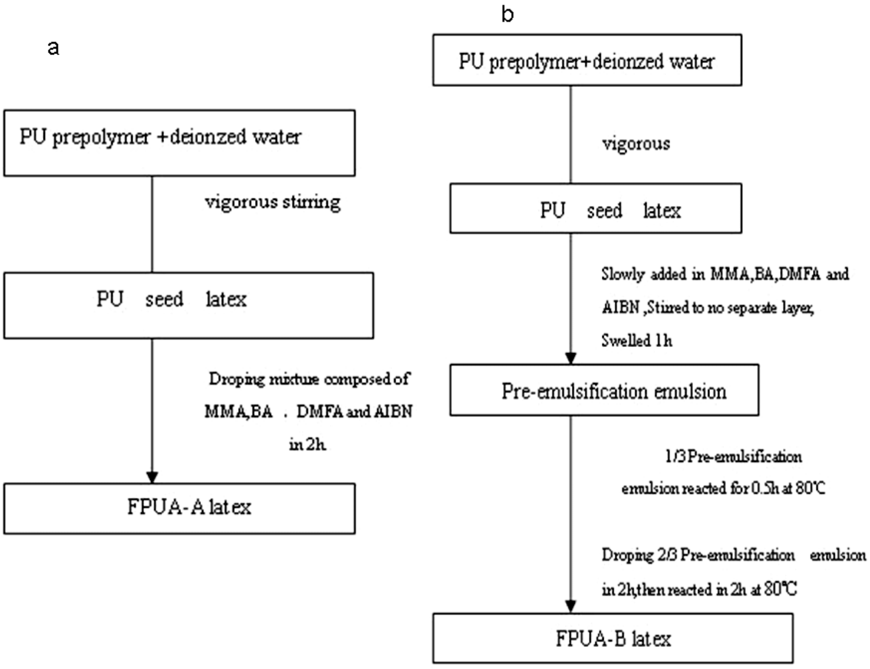
In this study, polyurethane-fluorinated acrylate composite latexes were synthesized from pre-prepared polyurethane seed latex, dodecafluoroheptyl methacrylate (DFMA) and acrylate monomers by monomer pre-emulsification methods and monomer dropping methods, respectively. Influences of synthesis technique on polymerization stability and properties of FPUA composite latex films were discussed. The effect of different methods on polymerization stability of the dispersion, water and solvent resistance and mechanical properties of the films were investigated.

EXPERIMENTAL

Dodecafluoroheptyl methacrylate (DFMA) purchased from Jiaxue Corp. (Haerbing, China), isophorone diisocyanate (IPDI, analytical grade) purchased from Bayer Corp. (Germany) and 2,2-*bis*(hydroxymethyl)propionic acid (DMPA, analytical grade) purchased from Perstorp Corp. (Sweden) were used without further purification. Methylmethacrylate (MMA, analytical grade) and *n*-butyl acrylate (BA, analytical grade) obtained from Dongfang Corp.(Beijing,China), were purified to remove the inhibitor by passing it through a basic alumina column and stored in a refrigerator until use. 2-2'-Azo*bis*(2-methylpropinoitrile) (AIBN) purchased from Shanghai chemical Corp. (China) was used after recrystallization from alcohol. Diethylene glycol (DEG), triethylamine (TEA), stannous octoate and acetone (AT) purchased from Shanghai chemical Corp. (China) were used as received. Polyester diols was prepared in our laboratory. Deionized water was applied for all experiments.

Synthesis of polyurethane seed latex: The synthesis of polyurethane prepolymer was carried out in a 250 mL four-neck flask equipped with a reflux condenser, Teflon stirrer, nitrogen inlet tube and thermometer. Polyester diol, IPDI and stannous octoate were charged in the reactor and allowed to react at 90 ºC for *ca.* 2 h. After the prepolymer was cooled to 70 ºC, stoichiometric amounts of DEG, DMPA and AT were added. The polymerization was carried out for about 4 h until the values of NCO reached to theoretical value. When the temperature was below 40 ºC, the carboxyl groups were neutralized by TEA aqueous solution. The polyurethane seed latex was obtained by pouring deionized water into the above mixtures under vigorous stirring, followed by the removal of AT under reduced pressure.

Preparation of polyurethane-fluorinated acrylate (FPUA) composite latex: Polyurethane-fluorinated acrylate composite latexes were prepared by two different methods. **Scheme-Ia** shows the conventional synthesis process of FPUA composite latexes by monomer dropping method. The mixture of acrylate monomers, DFMA and AIBN were added dropwise into the prepared polyurethane seed latex within 2 h. The polymerization was carried out 85 ºC for 2 h under N_2 atmosphere. A series of composite latexes was prepared after being filtered below 40 ºC, which was referred to as the FPUA-A series. Polyurethane-fluorinated acrylate composite latex prepared by monomer pre-emulsification method is illustrated in **Scheme-Ib**. The pre-emulsification emulsions were prepared by injecting mixed monomers of MMA, BA and DFMA with stoichiometric amount of AIBN into polyurethane seed latex under mechanical stirring for about 0.5 h. One third of the prepared pre-emulsification emulsions was poured in a four-necked flask, stirred for 0.5 h and then heated to about 80 ºC under N_2 atmosphere. After the remaining pre-emulsification emulsions were dropped within 2 h, the polymerization was carried out about for another 2 h at 85 ºC. Then the latex was filtered below 40 ºC. A series of FPUA-B composite latexes were prepared.



Scheme-I: Two different progress in the preparation of polyurethane-fluorinated acrylate (a) Flow chart of monomer dropping technique (the samples prepared by this method marked as FPUA-A); (b) Flow chart of monomer pre-emulsification technique (the samples prepared by this method were marked as FPUA-B)

Characterization: Polymerization stability was assessed by the gel content produced during the polymerization, which was calculated by the eqn. 1. A sample of 0.1 g (m_b) was wrapped in 100-mesh stainless steel mesh and exposed to 100 mL of xylene at 100 ºC for 24 h. The stainless steel mesh was then removed and the mass was measured after vacuum drying at 80 °C for 24 h (m_a). The degree of gel was measured in terms of the percentage of gel content.

$$G = m_a / m_b \times 100\ \% \qquad (1)$$

FT-IR data was obtained with infrared spectroscopy (Nicolet Model210, USA). For infrared analysis each sample was prepared by casting a film on KBr window. Water resistance of FPUA films was measured by determining the degree of water absorption of a film in distilled water. The weighed latex film (W_1) was immersed into distilled water at room temperature for 24 h, followed by wiping off the surface water with a piece of filter paper to determined the weight W_2. The absorbed water ratio Q of the film was calculated by the formula, where W_1 is the original film weight and W_2 is the film weight after water absorption.

$$Q = \frac{(W_2 - W_1)}{W_1} \times 100\ \% \qquad (2)$$

The solvent resistance of FPUA films was investigated qualitatively by alcohol, acetone and toluene respectively. Tensile strength and elongation tests were done using a tensile tester (Model LJ-100). Micro-tensile specimen for the test had the dimensions of 25 mm length, 5 mm width and 1 mm thickness. The specimens were elongated at the rate of 300 mm/min. For each datum point, five samples were tested and the average value was recorded.

Contact angle were measured using a contact angle goniometer (JC2000C1, Shanghai Zhongchen Digital Technical Equipment Ltd., China). The samples for contact angle measure were prepared by casting the polymer latexes onto clean glass wafers. The glass wafers were kept in an oven at 50 °C for 24 h. Contact angles were measured on 1 μL of water and diiodo-methane at 12 °C and the results reported are the mean values of five replicates.

The fracture surface images of FPUA films were studied by scanning electron microscopy (SEM, AIS2100) operating at 20 kV. Samples were made conductive by deposition of a thin gold layer.

RESULTS AND DISCUSSION

Polymerization stability of FPUA composite latex: Polymerization stability of FPUA composite latex was shown in Table-1. It could be seen that the polymerization stability of composite films prepared by monomer pre-emulsification method (FPUA-B) was obviously superior to that prepared by monomer dropping method (FPUA-A). With the increasing of fluorine content, the polymerization stability decreased and gel rate increased rapidly. By using monomer dropping method, after the monomer droplet containing initiator entered into aqueous system, the

TABLE-1
POLYMERIZATION STABILITY OF FPUA COMPOSITE LATEXES

Samples	Fluorine content (wt %)	Gel rate (wt/wt %)	Filtered matter
FPUA-A-0	0	0.7	Elastic film
FPUA-A-1	2.6	2.5	Tofu pulp
FPUA-A-2	5.2	4.6	Round particles and medium hard
FPUA-A-3	7.8	9.8	Round particles and medium hard
FPUA-A-4	10.4	9.8	Round particles and medium hard
FPUA-B-0	0	0	None
FPUA-B-1	2.6	0.3	Elastic film
FPUA-B-2	5.2	0.6	Elastic film and tofu pulp
FPUA-B-3	7.8	0.7	Elastic film and tofu pulp
FPUA-B-4	10.4	0.7	Elastic film and tofu pulp

monomers polymerized in water phase directly. Because there is not enough time for the monomer diffusing into polyurethane seed colloidal particle, part of monomer droplet nucleation led to the gel formation. For the FPUA composite latex prepared by monomer pre-emulsification, the hydrophobicity of colloidal particle increased with the increasing of fluorine content, which made it harder for polyurethane macromolecular emulsifier to stabilize the colloidal particle which nucleated from monomer droplet.

FTIR Spectroscopy analysis: The structure of the FPUA was confirmed by FTIR spectroscopy and the typical spectra for FPUA-B-0 sample and FPUA-B-4 sample were shown in Fig. 1. The characteristic absorption peaks of the functional group were detected and monitored during the synthesis reaction. The spectra showed the absorption peaks of typical polyurethane at 1730 cm^{-1} (C=O) and 1540 cm^{-1} (NH), respectively. Compared with FPUA-B-0, a series of new bands between 1400-1100 cm^{-1} appeared in the ATR spectrum of FPUA-B-4, which was due to the combined absorption bands of C=C and C-F. The characteristic absorption peak of the C-F was detected at 1384 cm^{-1}, which proved that fluorine groups had successfully grafted onto polyurethane main chains.

Water resistance of FPUA film: Polyurethane films always exhibit poor water resistance property because of the hydrophilic monomer in the polyurethane backbone chains. For many practical applications, the key aspect in the modification of polyurethane films is to improve the water resistance.

The relationship between the water absorption rate and soaking time was tested and the results were shown in Fig. 2. It was found that the water absorption increased with the soaking time. But, the tendency of water resistance was increasing while fluorine increased. On the other hand, the water absorption of the films and the decreased with increasing the fluorine content from 60 to 15 %.Compared with pure polyurethane films, FPUA-B films had a lower water absorption rate. The improved water resistance property of FPUA-B films could be due to the presence of fluorine in polyurethane matrix. It could also be found that it was not obvious to

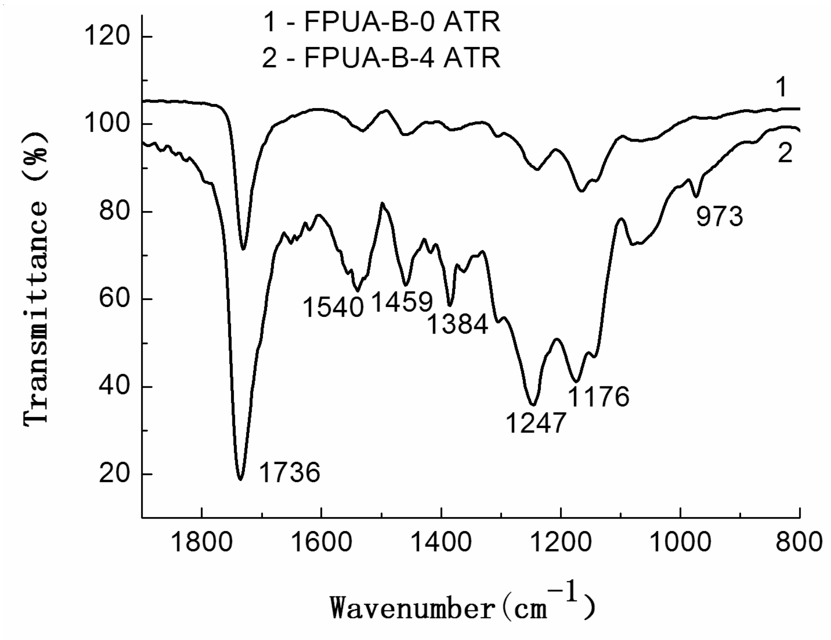


Fig. 1. FTIR spectroscopy for FPUA-B-0 sample and FPUA-B-4 sample respectively. FPUA-B-0 sample means the films were obtained by monomer pre-emulsification technique and there was no fluorine. FPUA-B-4 sample means the films were obtained by monomer pre-emulsification technique and the fluorine content was 10.4 %

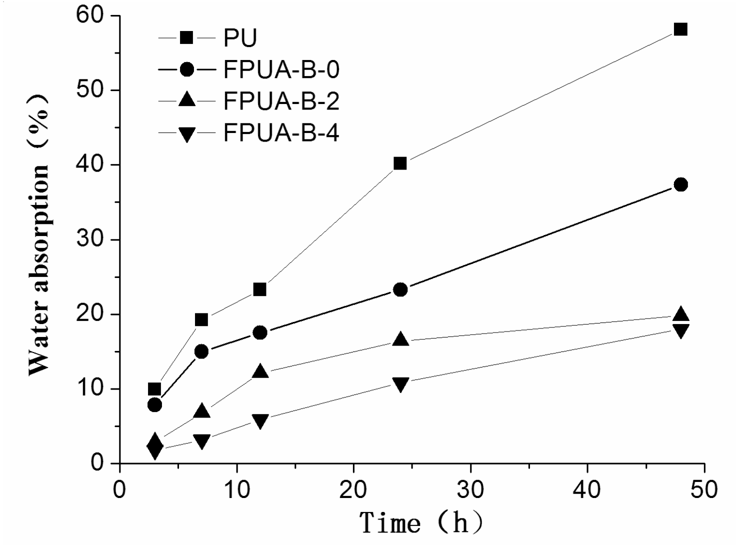


Fig. 2. Water absorption curves of PU and FPUA films as the function of time. In this test all of the FPUA films were prepared by monomer pre-emulsification technique. Fluorine content in FPUA-B-0, FPUA-B-2, FPUA-B-4 were 0, 5.2 and 10.4 %, respectively. PU means both acrylate and fluorine were absent in the films

improve water resistance by the increasing of the fluorine content. Because of the low miscibility between polyurethane and fluorine groups, the fluorine groups migrated to the film surface. Small amount of fluorine groups would cover the film surface effectively and led to the decreasing of water absorption. The optimum percentage of fluorine content is 4 %, but above that point the increase of fluorine content has low impact. The increase of contact angle could be attributed to the surface activity of the hydrophobic DMFA. When fluorine concentration is low, it migrates to the surface to shield the polymer chain with high surface energy and substantially lowers the surface free energy. But when the fluorine content increases to a degree where there is enough fluorine at the surface, their low surface free energy is up to the limit point.

Fig. 3 shows the relationship between the water absorption and fluorine content of FPUA films. As expected, the 48 h water absorption of both FPUA-A and FPUA-B films decreased gradually with increase in fluorine content. It could also be found that the water absorption values of FPUA-A films prepared by monomer dropping method were remarkably larger than those of FPUA-B films prepared by monomer pre-emulsification. Moreover it was found that for FPUA-B, the water absorption reduced sharply when the fluorine content was below 7 wt %, but it decreased slightly above 7 wt %. For FPUA-A, water absorption reduced linearly as fluorine content increased. This was probably due to lower polymerization stability of monomer dropping method. Because more gels generated and the loss of part fluorine monomer in polymerization process, practical content of fluorine in FPUA-A was lower than theoretical content, which led to the higher water absorption of FPUA-A films.

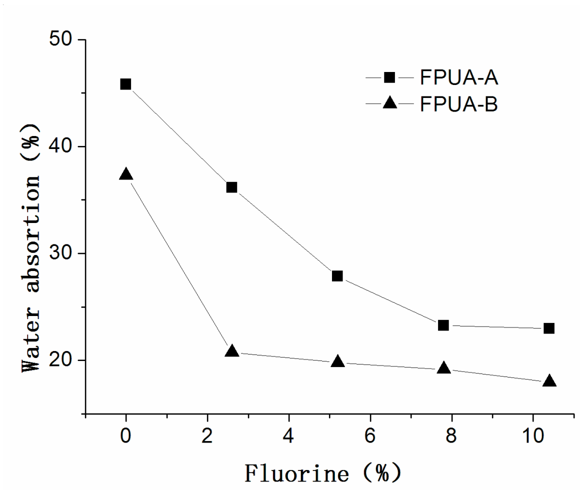


Fig. 3. Effect of fluorine content on water absorption of FPUA films and films samples were immersed into distilled water at room temperature for 48 h. The FPUA-A means the films were prepared by monomer dropping technique and the FPUA-B means the films were prepared by monomer pre-emulsification technique

Solvent resistance of FPUA films: Solvent resistance of FPUA films with various fluorine content (soaking time 48 h) prepared by different polymerization methods are shown in Table-2.

TABLE-2
SOLVENT RESISTANCE OF POLYURETHANE (PU) AND FPUA FILMS

Samples	Alcohol	Acetone	Toluene
PU	Blushing, Swelling	Blushing, Swelling	Blushing, Swelling
FPUA-A-0	Blushing, Swelling	Dissolved Nearly	Dissolved, Nearly
FPUA-A-4	Welling, Slightly	Blushing, Swelling	Blushing, Swelling
FPUA-B-0	Blushing, Swelling	Blushing, Swelling	Dissolved, Nearly
FPUA-B-4	No Change	Welling Slightly	Welling, Slightly

Water and solvent resistance are important properties for many applications in coatings and films, especially for the water-based polymer systems. Compared with polyurethane films, the FPUA films without fluorine groups (FPUA-A-0, FUPA-B-0), the solvent resistance of films was decreased. This suggested that the incorporation of PA did not improve the solvent resistance of composite films. Due to the combined effects of water and oil repellency of fluorine groups, the solvent resistance of films was enhanced after the instruction of fluorine monomer.

Mechanical properties of FPUA films: Figs. 4 and 5 displayed the relationship between fluorine content and tensile strength and the relationship between different polymerization methods and breaking elongation, respectively.

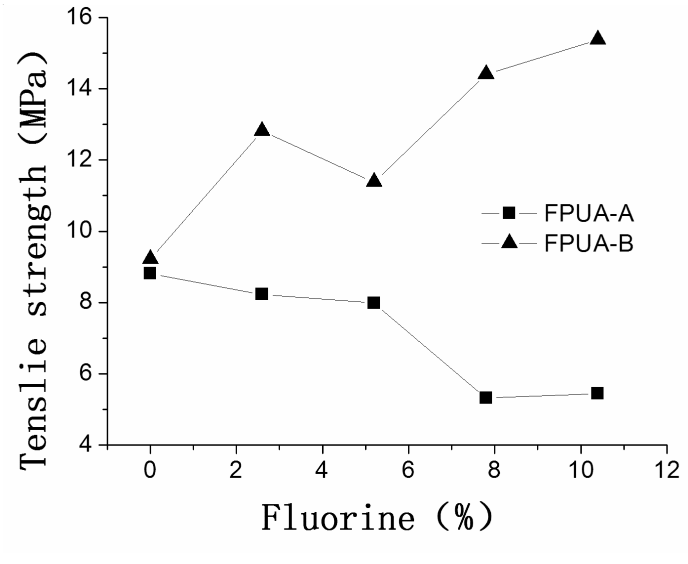


Fig. 4. Effect of prepared methods and fluorine contents on tensile strength. The FPUA-A means the films were prepared by monomer dropping technique and the FPUA-B means the films were prepared by monomer pre-emulsification technique

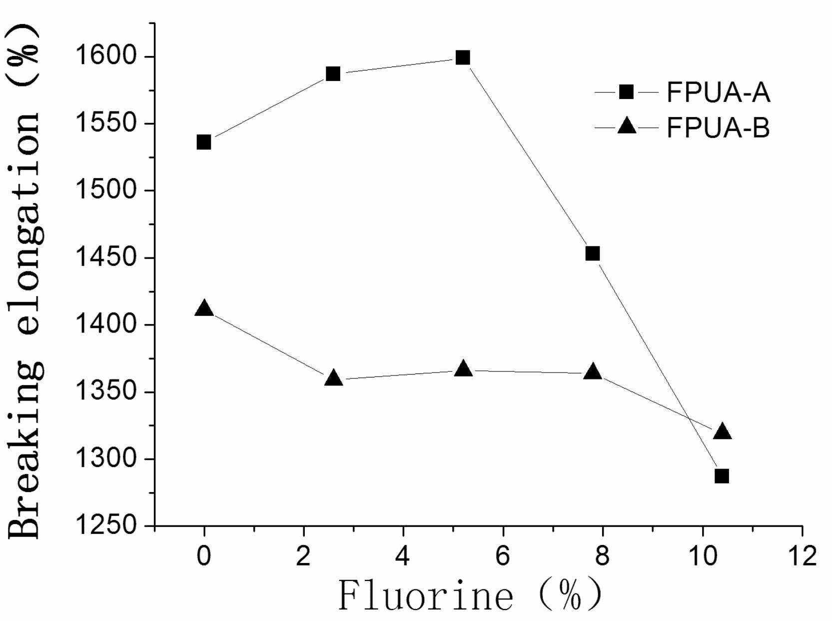


Fig. 5. Effect of prepared method and fluorine on elongation percentage. The FPUA-A means the films were prepared by monomer dropping technique and the FPUA-B means the films were prepared by monomer pre-emulsification technique

As shown in Fig. 4, the tensile strength of FPUA films prepared from different preparation methods was about 9 MPa when there was no fluorine. With the content of fluorine increasing, the tensile strength of FPUA films exhibited two opposite trends. When the fluorine content increased, the tensile strength of FPUA-A films prepared from monomer dropping method decreased gradually, but those of FPUA-B prepared from the other method increased. This can be explained as follows. By means of monomer dropping method, the polymerization stability decreased and the dispersity of particle size increased. This influenced the structure regularity during the film-forming and thus was responsible for the decreasing of tensile strength. However, the increase of fluorine content resulted in the enlarging degree of microphase separation and led to the improved tensile strength of the FPUA-B films.

Fig. 5 shows the breaking elongation curves for FPUA prepared from different methods. It could be seen from Fig. 5 that the breaking elongation decreased gradually with fluorine content increasing. As the fluorine content increased to 5 wt %, the breaking elongation of FPUA-A sharply ascended to a maximum of 1660 % and then decreased. However, with regard to FPUA-BA of fluorine content at 3 %, the breaking elongation reduced to 1350 % and then lowered off. The decreasing of breaking elongation of FPUA films indicated that the fluorine groups resulted in expanded degree of microphase separation.

Figs. 6 and 7 show the tensile strength and elongation percentage curves of the films of FPUA-B composite latex by soaking some time. It was obvious that both tensile strength and elongations at break of FPUA-B films decreased as soaking time increased. When the fluorine content increased, the tensile strength descended sharply. When the immersed time was 24 h, the tensile strength was nearly 2 MPa when the fluorine content increased to about 4 %. However, compared to FPUA-B-0, the tensile strength was reduced by 80 %. After water molecular permeated into film, the crystallization was destroyed and the intermolecular force was weakened. Among the series of FPUA-B films, the FPUA-B-2 and FPUA-B-4 films exhibited slighter downward tendency of elongation percentage. Compared to FPUA-B-0 film, the breaking elongation of FPUA-B-4 was improved by 175 %. So, it could be concluded that fluorine effectively strengthened the properties of soaking resistance of FPUA-B-2 and FPUA-B-4 even after a long time of soaking.

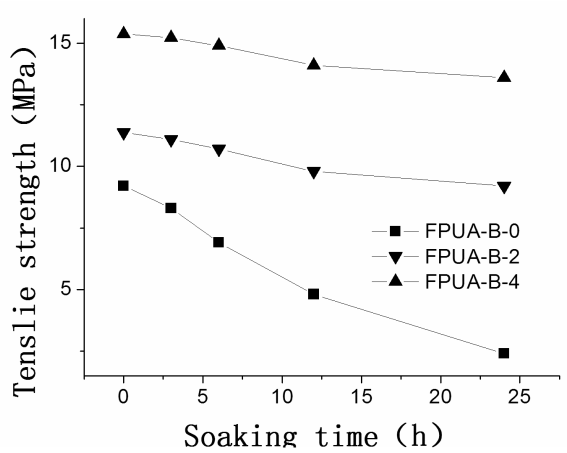


Fig. 6. Relationship between tensile strength of FPUA-B films and soaking time. FPUA-B means the films were prepared by monomer pre-emulsification technique. Fluorine contents in FPUA-B-0, FPUA-B-2, FPUA-B-4 were 0%, 5.2% and 10.4%, respectively.

Measurement of water contact angle: Measurement of water contact angle is the primarily means to characterize the surface properties of films. We estimated the hydrophilic and hydrophobic properties of films by measuring the contact angle between water and films. Fig. 8 shows the contact angle of the films as a function of fluorine content. The pure polyurethane film exhibits a relatively low contact angle of 63.7° at time of 0 s and the values decreased sharply with time. After polyurethane film was modified by polyacrylate, the initial water contact angle rapidly increased to 84.6° and moreover, the values decreased slightly with time. The incorporation of fluorine into PUA significantly increased the contact angle value from 84.6° to 95.4° when the fluorine content was 10.4 wt %. Furthermore, the value was still up to 92.6° after 5 min, implying that acrylate and fluorine groups played an important role in the hydrophobicity of the films.

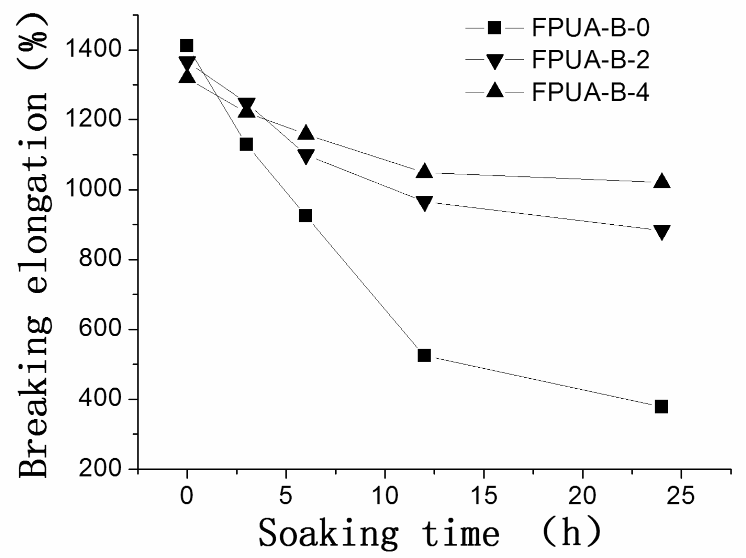


Fig. 7. Relationship between breaking elongation of FPUA-B films and soaking time. FPUA-B means the films were prepared by monomer pre-emulsification technique. Fluorine contents in FPUA-B-0, FPUA-B-2, FPUA-B-4 were 0, 5.2 and 10.4 %, respectively

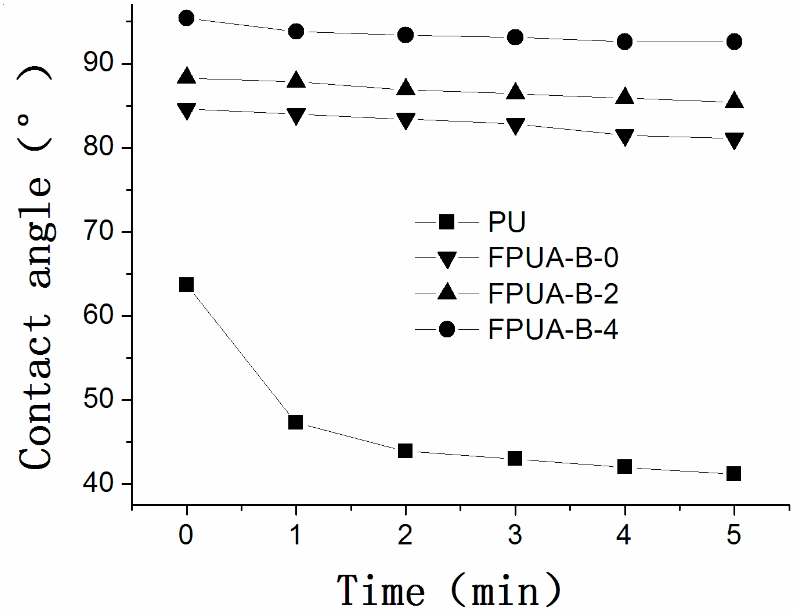


Fig. 8. Relationship between contact angle of PU and FPUA-B films and soaking time. FPUA-B means the films were prepared by monomer pre-emulsification technique. fluorine contents in FPUA-B-0, FPUA-B-2, FPUA-B-4 were 0, 5.2 and 10.4 %, respectively. PU means both acrylate and fluorine were absent in the films

As shown in Fig. 9, water contact angle of FPUA films by both polymerization techniques increased with the increasing of fluorine content. At the same time, the contact angle values of FPUA-B films were higher than those of FPUA-A films, which was in agreement with the results measured by water absorption. At the same fluorine content of 8.0 wt %, the contact angle reached to 93° and 87° for FPUA-B and FPUA-A, respectively. That is to say, the films prepared by monomer pre-emulsification method exhibited a higher hydrophobocity and better surface properties.

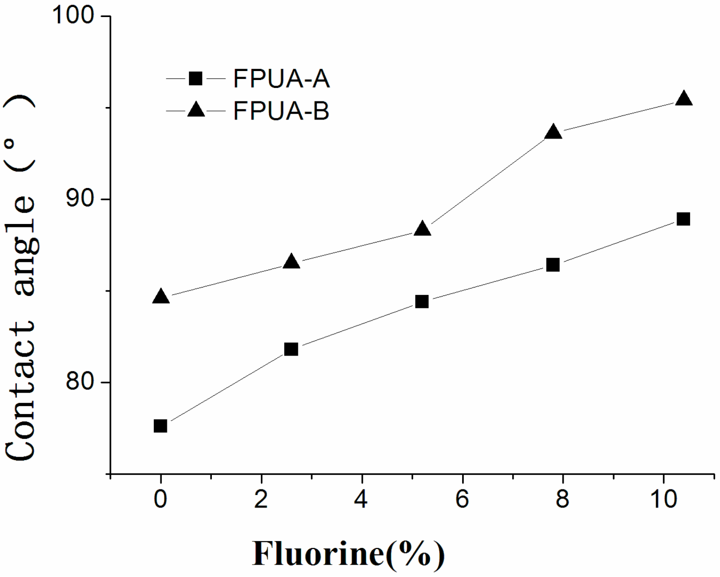


Fig. 9. Effect of polymerization techniques on contact angle with water of FPUA films. The FPUA-A means the films were prepared by monomer dropping technique and the FPUA-B means the films were prepared by monomer pre-emulsification technique

Surface microstructure of FPUA films: The surface structure of FPUA films was investigated by scanning electron microscopy (SEM). At low fluorine content, the surface of FPUA-B-1 (Fig. 10a) was smooth. With the increasing of fluorine content, irregular particles with a size of 1 to 3 μm appeared on the surface of FPUA-B-4 (Fig. 10b). Such results demonstrated that the chain segments containing fluorine transferred to FPUA film surface during the film formation and then the enrichment led to the formation of irregular particles.

Conclusion

The polyurethane-fluorinated acrylate composite latexes were synthesized from prepared polyurethane seed latex, dodecafluoroheptyl methacrylate and acrylate monomers by the methods of monomer pre-emulsification and monomer dropping methods, respectively. The results showed that compared with monomer dropping

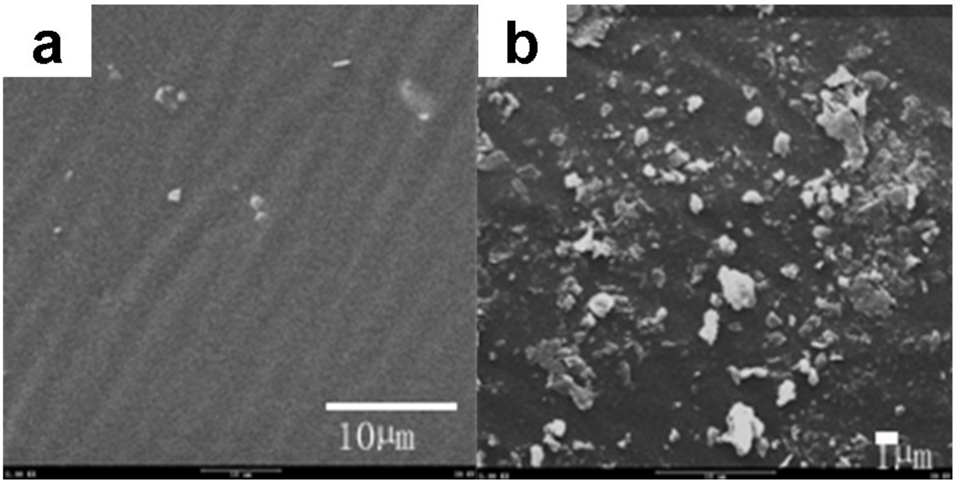


Fig. 10. SEM surface of the FPUA-B films. (a) SEM surface of the FPUA-B-1, which was prepared by monomer pre-emulsification technique and the fluorine content was 2.6 %. (b) SEM surface of the FPUA-B-4, which was prepared by monomer pre-emulsification technique and the fluorine content was 10.4 %

method, more stable FPUA composite latex was obtained by the monomer pre-emulsification method. After the incorporation of fluorine monomer, the contact angle between water and FPUA films increased. The films exhibited superior properties on water resistance, solvent resistance and soaking resistance to that of polyurethane and FPUA films. Compared with monomer dropping method, the FPUA films prepared by monomer pre-emulsification method had the comparative advantages of water resistance, solvent resistance, soaking resistance and mechanical properties, which was due to the enrichment of the chain segments containing fluorine on the FPUA film surface.

REFERENCES

1. H. Du, Y.H. Zhao, N. Yin, Q.F. Li, J.W. Wang, M.Q. Kang, H.W. Xiang and X.K. Wang, *J. Appl. Polym. Sci.*, **110**, 3156 (2008).
2. P. Aruna and D.D.R. Kumal, *J. Appl. Polym. Sci.*, **110**, 2833 (2008).
3. H. Du, Y.H. Zhao, Q.F. Li, J.W. Wang, M.Q. Kang, X.K. Wang and H.W. Xiang, *J. Appl. Polym. Sci.*, **110**, 1396 (2008).
4. M. Barrere and K. Landfester, *Macromolecules*, **36**, 5119 (2003).
5. A. Barni and M. Levi, *J. Appl. Polym. Sci.*, **88**, 716 (2003).
6. B.K. Kim and J.H. Shin, *Colloid. Polym. Sci.*, **280**, 716 (2002).
7. M.A. Perez-Liminñana, F. Arán-Aìsa, A.M. Torró-Palaua, A.C. Orgilès-Barcelo and J.M. Martìn-Martìnez, *Int. J. Adhes. Adhes.*, **25**, 507 (2005).
8. C.H. Lim, H.S. Choi and S.T. Noh, *J. Appl. Polym. Sci.*, **86**, 3322 (2002).
9. S. Turri, M. Levi and T. Trombetta, *J. Appl. Polym. Sci.*, **93**, 136 (2004).
10. D.K. Kim, S.B. Lee, K.S. Doh and Y.W. Nam, *J. Appl. Polym. Sci.*, **74**, 2029 (1999).
11. J.W. Gooch, H. Dong and F.J. Schork, *J. Appl. Polym. Sci.*, **76**, 105 (2000).
12. J.E. Yang, J.S. Kong, S.W. Park, D.J. Lee and H.D. Kim, *J. Appl. Polym. Sci.*, **86**, 2375 (2002).

13. H.H. Wang, Y.d. Shen, G.Q. Fei, X.R. Li and Y. Liang, *J. Colloid Interf. Sci.*, **324**, 36 (2008).
14. M. Jiang, X.L. Zhao, X.B. Ding, Z.H. Zheng and Y.X. Peng, *Eur. Polym. J.*, **41**, 1798 (2005).
15. R. Adhikari, P. A. Gunatillake and S.J. McCarthy, *J. Appl, Polym, Sci.*, **74**, 2979 (1999).
16. T. Bremner, D.J.T. Hill, M.I.O. Killeen, J.H. Donnell, P.J. Pomery, D.S.T. John and A.K. Whittaker, *J. Appl. Polym. Sci.*, **65**, 939 (1997).
17. M.S. Yen and P.Y. Tsai, *J. Appl. Polym. Sci.*, **90**, 233 (2003).
18. W.J. Blank and V.J. Tramontano, *Prog. Org. Coat.*, **27**, 1 (1996).
19. S. Subramani, J.Y. Lee, J.H. Kim and I.W. Cheong, *Compos. Sci. Technol.*, **67**, 1561 (2007).
20. H. Lim, Y. Lee, I.J. Park and S.B. Lee, *J. Colloid Interf. Sci.*, **241**, 269 (2001).
21. Y.S. Kim, J.S. Lee, Q. Ji and J.E. McGrath, *Polymer*, **43**, 7161 (2002).
22. G.H. Li, X.R. Li, Y.D. Shen and Q.H. Ren, *J. Appl. Polym. Sci.*, **99**, 2721 (2006).
23. G.C. Jiang, X.L. Tuo, D.R. Wang and Q. Li, *J. Polym. Sci., Part A: Polym. Chem.*, **47**, 3248 (2009).
24. X.M. Wang and N.H. Long, *Chin. J. Appl. Chem.*, **23**, 1104 (2006) (in Chinese).
25. H. Lim, Y. Lee, I.J. Park and S. Lee, *J. Colloid. Interf. Sci.*, **241**, 269 (2001).
26 X.J. Wang, J.J. Yang, Q.Y. Wu, J.A. Zhang and M.Y. Wu, *Petrochem. Technol.*, **36**, 178 (2007). (in Chinese)
27. G.H. Li, X.R. Li, Y.D. Shen and Q.H. Ren, *Acta Chim. Sinica*, **63**, 2225 (2005).
28. T. Trombetta, P. Iengo and T. Stefano, *J. Appl. Polym. Sci.*, **98**, 1364 (2005).
29. S. Turri, M. Levi and T. Trombetta, *Macromol. Symp.*, **218**, 29 (2004).

(*Received*: 15 March 2010; *Accepted*: 31 July 2010) AJC-8928