

# Effect of Fluorinated Acrylate on the Surface Properties of Cationic Fluorinated Polyurethane-Acrylate Hybrid Dispersions

Ganghui Li, Yiding Shen, Qinghai Ren

College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi Province, 712081, People's Republic of China

Received 28 January 2005; accepted 5 March 2005

DOI 10.1002/app.21852

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Cationic fluorinated polyurethane-acrylate hybrid dispersions were prepared by the copolymerization of styrene, butyl acrylate, and 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate in the medium of crosslinked polyurethane via phase inversion polymerization. The said polyurethane was synthesized in acetone from 2, 4-toluene diisocyanate, with *N*-methyldiethanolamine as a hydrophilic chain-extender, trimethylolpropane as a crosslinker, and soft polyester diol block. The surface properties, immersion behaviors, particle size, and Zeta potential of the dispersions were investigated. The results show that the particle size of the dispersion particle is less than 450 nm and the Zeta potential is more

than 32.0 mV. The addition of fluorinated acrylate can decrease surface free energy by more than 47.43%, and FPUA films cured at ambient conditions have lower surface free energy (less than 0.02,002 J/m<sup>2</sup>). At the same time, there is an obvious mobility of fluorinated groups in the fluorinated polymer films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2192–2196, 2005

**Key words:** cationic polyurethane-acrylate hybrid dispersions; fluorinated acrylate; immersion behaviors; surface free energy

## INTRODUCTION

Polyurethane-acrylate hybrid dispersions, due to their excellent properties and environmental advantages, have become one of the major types of materials used in coating, print, adhesive industries, and so on.<sup>1–6</sup> For example, Yoshizumi<sup>7</sup> studied the application of a two-component polyurethane coating prepared by graft copolymers with polyacrylate branches as acrylic polyols, and reported that the coating offers the advantages of higher solids, better control of coatings rheology, improvement of applications at the drying process, and improvement in the final film toughness. However, some properties of films of polyurethane-acrylate, such as water resistance and oil resistance, need to be improved further.

One of the important approaches to improve the surface properties is the incorporation of fluorinated compounds in polyurethane-acrylate. For example, Lim and coworkers<sup>8</sup> synthesized a good hydrophobic polyurethane-acrylate film with polyurethane prepolymer and a fluorinated macromonomer that contains dihydroxyl groups by the introduction of 1-thioglycol as a chain-transfer agent and long chain perfluoroalkyl moieties,

and the surface free energy is about 20.0 dyn/cm. As yet, reports about cationic fluorinated polyurethane-acrylate hybrid dispersions prepared by the copolymerization of vinyl monomers in crosslinked polyurethane are scarcely seen.

In this work, we studied the effect of the fluorinated acrylate on the surface properties, immersion behaviors, particle sizes, and Zeta potential of cationic fluorinated polyurethane-acrylate hybrid dispersions. The preparation procedure, particle size, and Zeta potential of the dispersions and surface free energies and immersion behaviors of the films are reported.

## EXPERIMENTAL

### Materials

The materials used in the preparation of the cationic fluorinated polyurethane-acrylate hybrid dispersions (FPUA) are listed in Table I. All the chemicals were used without further purification except PEGA and MDEA.

### Preparation of polyurethane (PU)

Polyurethane dispersion based on TDI, PEGA, MDEA, and TMP was synthesized using solution polymerization. The feed ratios are shown in Table II. PEGA, TDI, and DBTDL (0.02 wt % based on the total reaction

Correspondence to: G. Li (Ligh@sust.edu.cn).

TABLE I  
Characteristics of Materials

Materials	Chemical composition	Source
TDI	Tolyene diisocyanate	Mitsui Takeda Chemical
PEGA <sup>a</sup>	Poly(ethylene glycol adipate), $M_n = 1000$	Zhejiang Chongde Chemical CO., LTD.
TMP	Trimethylolpropane	BAYER
MDEA <sup>a</sup>	N-methyldiethanolamine	Changzhou Taihu Chemical Industry CO., LTD.
DBTDL	Dibutyltin dilaurate	Tianjin NO.1 Chemical Reagent Factory
FA	2,2,3,4,4,4-hexafluorobutyl methacrylate ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}_2\text{CHF}_2$ )	Harbin Xeogia Group CO., LTD.
SFA	Perfluoroalkylethyl acrylate ( $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SO}_2\text{C}_8\text{F}_{17}$ )	Chengdu Qige Chemical CO., LTD.
St	Styrene	Tianjin Kermel Chemical Reagent Development Center
BA	Butyl acrylate	Tianjin Chemical Reagent CO., Inc.
BPO	Benzoyl peroxide	Shanghai Experiment Reagent CO., LTD.
Acetone	Acetone	Tianjin NO.6 Chemical Reagent Factory
Acetic acid	Acetic acid	Jiangsu Changyu Chemical CO., LTD.

<sup>a</sup> dried at 80°C under vacuum for several hours before used.

mass) were charged into a dry vessel fitted with a reflux condenser, a mechanical stirrer, a digital thermometer, and a nitrogen gas inlet. The content was stirred for 0.5h at 90°C. Then the content was cooled to 70°C, and the acetone solution of TMP and MDEA was added slowly to the vessel. The reaction was continued for about 0.5h. A part of the polyurethane solution was neutralized with acetic acid, and then was poured slowly into a flask containing deionized water and stirred vigorously. Finally, the solvent was evaporated, and crosslinking polyurethane dispersion was obtained. The residual polyurethane solution was used directly for the next procedure.

#### Preparation of cationic fluorinated polyurethane-acrylate hybrid dispersions (FPUA or SFPUA)

A series of cationic fluorinated polyurethane-acrylate hybrid dispersions were prepared by the copolymerization of St, BA, and FA (or SFA) in the said polyurethane solution via phase inversion polymerization. The feed ratios are shown in Table II. The mixture of

St, BA, FA (or SFA), and BPO (1.0 wt % based on the total vinyl monomer mass) was added dropwise to the said polyurethane solution. The reaction was carried on for about 4.0h at 80°C. After neutralization with acetic acid, the mixture was poured slowly into a flask containing cool deionized water and stirred vigorously. Finally, the solvent was evaporated. The resulting products were stable dispersions with a solid content of about 30%.

#### Particle size and Zeta potential ( $\zeta$ ) of the dispersions

Particle size was recorded on a Coulter-Counter PCS-N5. Zeta potential ( $\zeta$ ) of the dispersions was measured with a BDL-B surface potential particle size analyzer.

#### Contact angle measurements and evaluation of surface free energy

Contact angles were measured with a JJC-I contact angle goniometer. The samples for contact angle mea-

TABLE II  
Theoretical Composition and Properties of FPUA<sup>a</sup>

Sample	Molar ratio of TDI, MDEA, PEGA, and TMP	Mass ratio of St, BA, and FA	FA (or SFA) Content/wt %	Particle size/nm	$\zeta$ /mV
PU	0.21/0.12/0.06/0.01	—	—	142	40.5
PUA	0.21/0.12/0.06/0.01	10, 10, 0	0	455	31.7
FPUA-1	0.21/0.12/0.06/0.01	8.0, 8.0, 4.0	4.0	445	32.4
FPUA-2	0.21/0.12/0.06/0.01	6.0, 6.0, 8.0	8.0	439	32.8
FPUA-3	0.21/0.12/0.06/0.01	4.0, 4.0, 12.0	12.0	437	33.0
FPUA-4	0.21/0.12/0.06/0.01	2.0, 2.0, 16.0	16.0	429	33.9
FPUA-5	0.21/0.12/0.06/0.01	0, 0, 20.0	20.0	426	34.1
SFPUA-2 <sup>b</sup>	0.21/0.12/0.06/0.01	6.0, 6.0, 8.0	8.0	433	33.8

<sup>a</sup> The content of BPO was 1.0 wt % based on the total vinyl monomer mass.

<sup>b</sup> SFPUA4-2: copolymer of St, BA, and SFA.

TABLE III  
Contact Angles and Surface Free Energies of the Films

Sample	Contact angles/°		Surface free energy/J/m <sup>2</sup>		
	Water	Diiodomethane	$\gamma^d$	$\gamma^p$	$\gamma$
PU	77.2	45.8	0.02828	0.01219	0.04047
PUA	80.4	49.6	0.02703	0.01105	0.03808
FPUA-1	89.7	76.3	0.01559	0.01117	0.02676
FPUA-2	95.6	79.5	0.01504	0.00877	0.02381
FPUA-3	100.2	81.7	0.01489	0.00691	0.02180
FPUA-4	102.8	83.6	0.01455	0.00604	0.02059
FPUA-5	104.2	84.4	0.01450	0.00552	0.02002

surement were prepared by casting the polymer onto clean silicon wafers from 10% (w/v) acetone. The silicon wafers were kept in an oven at 25°C for 24 h under vacuum. Contact angles were measured at 20°C, and the results reported are the mean values of 5 replicates.

## RESULTS AND DISCUSSION

### Particle size and Zeta potential ( $\zeta$ ) of the dispersions

Table II shows the mean particle sizes and Zeta potential ( $\zeta$ ) of PU and FPUA dispersions according to the FA contents. With the content of FA increasing, the particle sizes decrease very slowly, while the Zeta potentials increase. The possible reason is that there are differences of relative density among styrene (St), butyl acrylate (BA), and 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate (FA). The relative density (25/4°C) of St, BA, and FA is 0.9060, 0.8988, and 1.3380, respectively, and the volume of FA is the smallest among those with the same mass. So the volume of the copolymers of St, BA, and FA become smaller when the content of FA increases. At the same time, learned from the formation mechanism of the dispersion, we know that the hydrophilic hard segments of FPUAs form shells of the particles, and the hydrophobic segments including the copolymers of vinyl monomers and the soft segments of FPUAs are packaged inside of the particles and form the cores of the particles. Because of the decrease of the volume of the copolymer, the volume of the cores of the particles decreases. As a result, the particle sizes of the dispersions decrease, while the changes of particle sizes aren't obvious. For example, the particle sizes decrease from 455 nm to 426 nm as the FA content increases from 0.0 wt % to 20.0 wt %. The decrease of particle sizes is less than 30 nm. However, the Zeta potentials increase when the particle size decreases. The particle size decreases and, therefore, the surface charge density of the particle increases. For example, the Zeta potential increases from 31.7 mV to 34.1 mV when the FA contents increase from 0.0 wt % to 20.0 wt %. The change of the Zeta

potential is only about 2.4 mV. The results indicate that the FA content has little effect on the particle size and the particle surface charge.

### Surface free energies of the polymer films

The method developed by Owens and Wendt,<sup>9</sup> which is used to estimate surface tension ( $\gamma$ ) of a solid from contact angle data, has been criticized because the polar interactions depend on the probe liquids chosen.<sup>10,11</sup> Kaelble<sup>12</sup> extended Fowkes' equation, neglecting the polar interaction term to include a polar energy term  $2(\gamma_1^p \gamma_2^p)^{1/2}$ :

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \quad (1)$$

in which  $\gamma_{12}$  is interfacial tension,  $\gamma_1$  and  $\gamma_2$  are surface tensions,  $d$  is the dispersion component, and  $p$  is the polar component. The preferable equation to calculate the interfacial tension between polymers and an ordinary liquid was found by Wu<sup>13</sup> as follows:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (2)$$

Consequently, the equation is used to estimate the surface tension, which is also surface free energy, of fluorinated polyurethane-acrylate. In our article, eq. (2) is rearranged into eq. (3) for water and diiodomethane according to Wu:

$$(1 + \cos \theta_{\text{liquid}}) \gamma_{\text{liquid}} = 4 \left( \frac{\gamma_{\text{liquid}}^d \gamma^d}{\gamma_{\text{liquid}}^d + \gamma^d} + \frac{\gamma_{\text{liquid}}^p \gamma^p}{\gamma_{\text{liquid}}^p + \gamma^p} \right) \quad (3)$$

in which  $\gamma = \gamma^d + \gamma^p$ ,  $\gamma_{\text{liquid}} = \gamma_{\text{liquid}}^d + \gamma_{\text{liquid}}^p$  is surface tension,  $d$  is the dispersion component,  $p$  is the polar component, and  $\theta_{\text{liquid}}$  is the contact angle of the polymer with water or diiodomethane. The numerical values used are

$$\begin{aligned} \gamma_{\text{H}_2\text{O}}^d &= 0.0221 \text{ J/m}^2, & \gamma_{\text{H}_2\text{O}}^p &= 0.0507 \text{ J/m}^2, \\ \gamma_{\text{CH}_2\text{I}_2}^d &= 0.0441 \text{ J/m}^2, & \gamma_{\text{CH}_2\text{I}_2}^p &= 0.0067 \text{ J/m}^2. \end{aligned}$$

**TABLE IV**  
**Contrast of Surface Properties of FPUA-2 and SFPUA-2 Cured at Different Temperatures**

Sample	Contact angles/ $^{\circ}$		Surface free energy/ $\text{J}/\text{m}^2$		
	Water	Diiodomethane	$\gamma^d$	$\gamma^p$	$\gamma$
FPUA-2 <sup>a</sup>	95.6	79.5	0.01504	0.00877	0.02381
FPUA-2 <sup>b</sup>	97.8	81.3	0.01460	0.00804	0.02264
SFPUA-2 <sup>a</sup>	93.5	78.7	0.01506	0.00968	0.02474
SFPUA-2 <sup>b</sup>	100.2	82.5	0.01450	0.00709	0.02159

<sup>a</sup> Cured at 25°C for 24 h.

<sup>b</sup> Cured at 120°C for 24 h.

Table III shows the surface free energies calculated from the contact angles of the films with water and diiodomethane. As FA content increased from 0 wt % to 20.0 wt %, the surface free energies decreased from 0.03808 J/m<sup>2</sup> to 0.02,002 J/m<sup>2</sup>. The surface free energies of the films decreased by more than 47.43%. The results demonstrate that the film surfaces have significant water and oil repellency. It is clear that the low surface energies of FPUA films come mainly from the chemical structure of FA, which has strong hydrophobic fluorinated groups. According to prior literature, poly (tetrafluoro ethylene) has a critical surface free energy of 0.0185 J/m<sup>2</sup>.<sup>14</sup> The FPUA films in our study have also shown relatively low surface free energies. For the FPUA-5 film, where the content of FA is 20.0 wt %, the surface energy of 0.02,002 J/m<sup>2</sup> is obtained. To a great extent, the low surface free energy is due to the CF<sub>3</sub> groups on the outermost film surface.<sup>15</sup>

Table IV shows the effects of cured temperature on the contact angle and surface free energies of the polymer films. The result shows that cure temperature has little effect on the surface free energies of FPUA-2, while it is an opposite result for the SFPUA-2 films. Fluorinated chemicals containing long chain perfluoroalkyl moieties impart a high degree of repellency to a treated substrate because the perfluoroalkyl groups align to form an ordered, low energy, liquid crystalline-like structure at the substrate surface. To form the liquid crystalline-like structure, heating to an

elevated temperature (i.e., more than 100°C) to properly orient the perfluoroalkyl chains is necessary.<sup>16</sup> So the FPUA-2 is preferable to the SFPUA-2 in coatings, especially used on substrates (e.g., buildings) that can't be heated to an elevated temperature.

#### Immersion behavior of the polymer films in water

The immersion behavior in liquid can reflect the changes of surface microstructure and macro-properties of the polymer films. Table V shows the relationship between contact angles of the films and immersion time in water at about 25°C. At the same time, we use the attenuation rate of the contact angle ( $R_a/^\circ/\text{min}$ ) to describe the immersion behavior in water. The attenuation rate of the contact angle is obtained from linear regression analysis of the  $\theta(t) \sim t$  curve. In other words, the slope of the line is the value of the attenuation rate of the contact angle. The result is shown in Table V.

The result shows that the contact angle falls gently according to the immersion time. But the contact angles of the films that were dried at 100°C for about 4 h after being immersed in water of about 25°C for 20 min increase. The changes of contact angles indicate that the fluorinated groups don't escape from the films to the water but transfer from the outermost film surface to the bulk.

**TABLE V**  
**Immersion Behavior of the Polymer Films**

Sample	Immersion time/min					Linear regression	
	0	1.0	5.0	20.0	t*	Correlation coefficient	$R_a/^\circ/\text{min}$
PU	77.2	77.0	77.4	77.3	77.3	—	—
PUA	80.4	80.8	80.2	79.8	80.3	—	—
FPUA-1	89.7	87.4	86.2	82.6	85.4	0.9473	0.3033
FPUA-2	95.6	93.5	90.8	86.7	91.8	0.9509	0.3946
FPUA-3	100.2	97.5	95.4	90.2	94.6	0.9609	0.4395
FPUA-4	102.8	99.6	97.5	92.4	96.3	0.9474	0.4469
FPUA-5	104.2	101.5	99.3	93.4	98.9	0.9691	0.4809

\* The contact angles of the films that were dried at 100°C for about 4 h after being immersed in water of about 25°C for 20 min.

The results of  $R_a$  show that there is no mobility in the PU and PUA films, and the  $R_a$  of the films with high content of fluorinated monomer becomes higher. It's clear that the higher the content of fluorinated groups in fluorinated polymer films, the more obvious is the mobility of the fluorinated groups.

### CONCLUSIONS

FPUA with good hydrophobic surface properties can be prepared by the copolymerization of styrene, butyl acrylate, and 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate in the crosslinked polyurethane via phase inversion polymerization. The said polyurethane was synthesized in acetone from TDI, MDEA, TMP, and PEGA. The particles dispersed in water have a core-shell structure and high Zeta potential. The proper fluorinated monomer content can decrease the surface free energy by more than 47.43%. There is obvious mobility of fluorinated groups in fluorinated polymer films. It was found that fluorinated acrylate had a significant effect on surface properties improvement.

The authors gratefully acknowledge the National Natural Science Foundation of China (grant number: 50473049) and the National Natural Science Foundation of Shaanxi province (grant number: 2003B02) for financial support.

### References

1. Baek, S. H.; Kim, B. K. *Colloids Surf A* 2003, 220, 191.
2. Wang, G. J.; Kangb, C. S.; Jin, R. G. *Prog Org Coat* 2004, 50, 55.
3. Chen, L.; Chen, S. *Prog Org Coat* 2004, 49, 252.
4. Decker, C.; Vataj, R.; Louati, A. *Prog Org Coat* 2004, 50, 263.
5. Huybrechts, J.; Bruylants, P.; Vaes, A.; De Marre, A. *Prog Org Coat* 2000, 38, 67.
6. Muller, H.; Hille, H.-D. U.S. Pat. 6, 770, 702 (2004).
7. Matsuno, Y.; Adachi, T.; Numa, N. *Prog Org Coat* 1999, 35, 117.
8. Lim, H.; Lee, Y. In: Park, J.; Leey, S.-B. *J Colloid Interface Sci* 2001, 241, 269.
9. Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1996, 13, 1741.
10. Fowkes F. M. *J Adhes* 1972, 4, 155.
11. Panzer, J. *J Colloid Interface Sci* 1973, 1, 142.
12. Kaelble, D. H. *J Adhes* 1970, 2, 66.
13. Wu, S. *J Polym Sci Part C* 1971, 34, 19.
14. Fox, H. W.; Zisman, W. A. *J Colloid Sci* 1950, 5, 514.
15. Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J Phys Chem* 1954, 58, 236.
16. Moore, G.; Yandrasits, M. A.; Schulz, J. F.; Flynn, R. M. U.S. Pat. 6, 649, 719 (2003).