

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

Ganghui Li, Xiaorui Li, Yiding Shen, Qinghai Ren

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

Received 21 March 2005; accepted 15 June 2005

DOI 10.1002/app.22450

Published online 19 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cationic polyurethane-fluorinated acrylate hybrid dispersions (PUFA) 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, *N*-methyldiethanolamine, trimethylolpropane, and soft polyester diol block. The influences of hydrophilic monomer on the surface properties, immersion behaviors, particle size and, zeta potential of the dispersions were investigated. The results show that the addition of hydro-

philic monomer can be advantaged to the stability of dispersions and yet will increase the surface free energy by more than 19.9%. The PUFA coating films cured at ambient conditions have the lower surface free energy (less than 0.02033 J/m²). At the same time, there is an obvious mobility of fluorinated groups in fluorinated polymer films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2721–2725, 2006

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

INTRODUCTION

The aqueous polyurethane has been widely used in coating because it has advantages in environmental pollution, fire safety, and soil resistance compared with solvent-based polyurethane.^{1–3} As an important type of the aqueous polyurethane, cationic aqueous polyurethane has attracted particular attention because of its cation.^{4–8} According to the type of hydrophilic chain-extender, the preparation mechanisms of cationic aqueous polyurethane is divided into two types. One is the nucleophilic substitution reaction of halide with tertiary amine, for example, the reaction of 2,3-dibromobutanedioic acids with triethylamine. The other is the simple neutralization reaction after the incorporation of tertiary amine in the polyurethane backbone chain. The tertiary amines usually include triethanolamine, *N*-alkyldiethanolamine, *N*-*tert*-butyldiethanolamine, dimethylethanloamine, etc.

However, during the preparation of polyurethane dispersions, the introduction of hydrophilic groups in polymer segments is necessary. The results are that

some properties of the coating films of polyurethane, such as water resistance and oil resistance, need to be improved further.

The modification of cationic aqueous polyurethane is an effective method to improve its properties and applications. Besides silicones,⁹ acrylates are important compounds to prepare modified polyurethane. Among the polyurethanes modified by acrylates, polyurethane-acrylate hybrid dispersions, because of their excellent properties and environmental advantages, have become one of the major types of materials used in coating, print, adhesive industries, etc.^{10–18} For example, Deckera¹⁹ studied UV-cured aliphatic polyurethane-acrylate (PUA) coatings, which were water-based and exhibited an excellent resistance to accelerated UV weathering, and reported that the addition of UV absorbers and radical scavengers increases the light-stability of water-based UV-cured PUA coatings substantially.

One of the effective approaches to obtain polyurethane-acrylate coating films with lower surface free energies is the incorporation of fluorinated compounds in polyurethane-acrylate. But the studies about the approach are rarely reported, especially the incorporation of fluorinated acrylate in polyurethane-acrylate. In a previous paper, authors²⁰ synthesized a good hydrophobic polyurethane-acrylate coating film with polyurethane prepolymer and a fluorinated macromonomer that contains dihydroxyl groups by the

Correspondence to: Y. Shen (ydshen@sust.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50473049.

Contract grant sponsor: National Natural Science Foundation of Shaanxi province; contract grant number: 2003B02.

TABLE I
Characteristic of Materials

Materials	Chemical composition	Commercial
TDI	Tolyene diisocyanate	Mitsui Takeda Chemical
PEGA ^a	Poly(ethylene glycol adipate), $M_n = 1000$	Zhejiang Chongde Chemical Co. Ltd.
TMP	Trimethylolpropane	BAYER
MDEA ^a	<i>N</i> -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 ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}_2\text{CHFCF}_3$)	Harbin Xeogia Group Co. Ltd.
St	Styrene	Tianjin Kernel 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.

^a Dried at 80°C under vacuum for several hours until no bubbling was observed.

introduction of 1-thioglycol as a chain-transfer agent and long-chain perfluoroalkyl moieties, and the surface free energy was about 20.0 dyn/cm. As yet, reports about cationic PUFA prepared by the copolymerization of vinyl monomers in crosslinked polyurethane were scarcely seen.

In this article, our objective is to study the effects of hydrophilic monomer on the surface properties, immersion behaviors, particle sizes, and zeta potential of the cationic PUFA. 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 PUFA are listed in Table I. All the chemicals were used without further purification, except Poly(ethylene glycol adipate) (PEGA) and *N*-methyldiethanolamine (MDEA).

Preparation of polyurethane (PU)

Polyurethane dispersion based on Tolyene diisocyanate (TDI), PEGA, MDEA, and TMP was synthesized

using solution polymerization. The feed ratios are shown in Table II. PEGA, TDI, and Dibutyltin dilaurate (DBTDL) (0.02 wt % based on the total reaction 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 0.5 h 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 0.5 h. The polyurethane solution was used directly for the next procedure.

Preparation of cationic PUFA

A series of cationic PUFA were prepared by the copolymerization of Styrene (St), Butyl acrylate (BA), and FA in the said polyurethane solution via phase inversion polymerization. The feed ratios are shown in Table II. The mixture of St, BA, FA, and Benzoyl peroxide (BPO) (1.0 wt % based on the total vinyl monomers mass) was added dropwise to the said polyurethane solution. The reaction was carried out for about 4.0 h at 80°C. After the neutralization with proper addition of acetic acid (n (acetic acid): n (MDEA) = 0.92 : 1.0), the mixture was poured slowly into a flask containing cool deionized water and stirred vigorously. Finally, the solvent was evapo-

TABLE II
Theoretical Composition and Properties of PUFA^a

Sample	Molar ratio of TDI/MDEA/PEGA/TMP	Mass ratio of St/BA/FA ^b	w (MDEA) (wt %)	Particle size (nm)	ζ (mV)
PUFA-1	0.21/0.10/0.08/0.01	2.0/2.0/16.0	7.34	—	—
PUFA-2	0.21/0.11/0.07/0.01	2.0/2.0/16.0	8.66	782	22.4
PUFA-3	0.21/0.12/0.06/0.01	2.0/2.0/16.0	10.19	429	33.9
PUFA-4	0.21/0.14/0.04/0.01	2.0/2.0/16.0	14.10	357	36.3
PUFA-5	0.21/0.16/0.02/0.01	2.0/2.0/16.0	19.80	229	39.8
PUFA-6	0.21/0.17/0.01/0.01	2.0/2.0/16.0	23.76	118	42.1

^a The content of BPO was 1.0 wt % based on the total vinyl monomers mass.

^b The content of FA was 16.0 wt % in all samples.

rated. The resulting products were stable dispersions with a solid content of about 30%.

Particle size and zeta potential (ζ) of dispersions

Particle size was recorded on a Coulter-Counter PCS-N5 in which the sample was diluted by water; the test angle was 90° and run time was 200 s. Zeta potential (ζ) of dispersions was measured with BDL-B surface potential particle size analyzer, in which the mass fraction of the sample was diluted to 0.5%; the test voltage was 30.4 V and the temperature of the sample was 18°C .

Contact angle measurements and evaluation of surface free energies of coating films

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

The surface free energies of coating films were calculated by the following equation, which was rearranged from Wu's equation.¹⁶

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

in which $\gamma = \gamma^d + \gamma^p$, $\gamma_{\text{liquid}} = \gamma_{\text{liquid}}^d + \gamma_{\text{liquid}}^p$, γ is the surface tension, d is the dispersion component, and p is the polar component, θ_{liquid} is contact angle of the polymer with water or diiodomethane. The numerical values used are $\gamma_{\text{H}_2\text{O}}^d = 0.0221 \text{ J/m}^2$, $\gamma_{\text{CH}_2\text{O}}^p = 0.0507 \text{ J/m}^2$, $\gamma_{\text{CH}_2\text{I}_2}^d = 0.0441 \text{ J/m}^2$, and $\gamma_{\text{CH}_2\text{I}_2}^p = 0.0067 \text{ J/m}^2$.

Preparation and immersion behaviors of the PUFA films

The PUFA films were prepared by casting the polymer dispersions into clean poly (tetrafluoroethylene) molds, and the molds were kept in an oven at 25°C for 24 h under vacuum. The thickness of the film was about 0.3 mm. After being immersed in water for different time, the film was taken out and sopped up by filter paper. The contact angle measurements were carried out immediately.

RESULTS AND DISCUSSION

Particle size and zeta potential (ζ) of dispersions

Table II shows the mean particle sizes and zeta potential (ζ) of PUFA dispersions, according to the

MDEA contents. From Table II, when the MDEA content is about 7.34 wt %, the polymer cannot be dispersed in water; when the content of MDEA increases, the particle sizes decrease sharply, while the zeta potentials increase quickly. The main reason is that the content ratio of hydrophobic segments to hydrophilic segments decreases with the increasing of MDEA content. The amount of hydrophilic groups introduced in polymer hard segments increases, and the compatibility between the polymer segments and water is increased too. At the same time, from the formation mechanism of the dispersion, we can know that the hydrophilic hard segments of PUFAs form the shells of particles, and the hydrophobic segments including the copolymer of vinyl monomers and the soft segments of PUFAs are packaged into inside of the particles and form the cores of particles. Because of the decrease of the hydrophobic segment contents, the volume of the cores of particles decreases. As a result, the particle sizes of the dispersions decrease markedly. For example, the particle sizes decrease from 782 to 118 nm as the MDEA contents increase from 8.66 to 23.76 wt %. The decrease of particle sizes is more than 660 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 22.4 to 42.1 mV when the MDEA contents increase from 8.66 to 23.76 wt %. The change in the zeta potential is about 19.7 mV. The results indicate that the MDEA content has obvious effects on the particle size and the particle surface charge. This is advantaged to the stability of dispersions.

Surface free energies of the PUFA coating films

The surface free energies of polymers reflect the surface properties directly. The higher the surface free energy is, the better the surface properties are. Table III shows the surface free energies calculated from contact angles of the coating films with water and diiodomethane.

In Table III, though the surface free energy of PUFA-1 is very low (just only 0.01934 J/m^2), it is not dispersion but gel in water. So we omitted it for further study. As MDEA content increased from 8.66 to 23.76 wt %, the surface free energies increased from 0.02033 to 0.02439 J/m^2 . The surface free energies of the coating films were increased by more than 19.9%. At the same time, we also know that with the change of MDEA content, the dispersion component of surface free energy is decreased, with the minimum value of about 0.01445 J/m^2 , and then increases while polar component of surface free energy is increased straightly.

TABLE III
Contact Angles and Surface Free Energies of the Coating Films

Sample	Contact angles (degree)		Surface free energy (J/m ²)		
	Water	Diiodomethane	γ^d	γ^p	γ
PUFA-1	107.5	84.6	0.01541	0.00393	0.01934
PUFA-2	103.6	83.8	0.01465	0.00568	0.02033
PUFA-3	102.8	83.6	0.01455	0.00604	0.02059
PUFA-4	99.7	82.4	0.01445	0.00732	0.02177
PUFA-5	96.2	80.1	0.01487	0.00859	0.02346
PUFA-6	94.4	78.8	0.01516	0.00923	0.02439

The results demonstrate that there will appear more hydrophilic groups on the film surface with the MDEA content increasing. Although the addition of MDEA is adverse to improve the surface properties, the data in Table III show that the coating films have still favorable water and oil repellency. It is clear that the low surface energies of PUFA coating films with FA content about 16.0 wt % come mainly from the chemical structure of FA, which has strong hydrophobic fluorinated groups. According to prior literature,²¹ poly(tetrafluoroethylene) has a critical surface free energy of 0.0185 J/m². The PUFA coating films in our article have also shown relatively low surface free energies. For the PUFA-2 coating film, in which the content of FA is 16.0 wt %, the surface energy of 0.02033 J/m² is obtained. To a great extent, the low surface free energy is due to the CF₃ groups on the outermost coating film surface.²² The results demonstrate that the addition of MDEA has adverse effect on the surface properties of the coating films.

Immersion behaviors of the films in water

The immersion behaviors in liquid can reflect the changes of surface microstructure and macro-properties of polymer films. Table IV 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 contact angle (R_a (°/min)) to describe the immersion behaviors in water. The atten-

uation rate of contact angle is obtained from linear regression analysis of $\theta(t)$ vs. t curve. In other words, the slope of the line is the value of attenuation rate of contact angle. The result was shown in Table IV.

The result shows that the contact angles fall gently according to the immersion time. But the contact angles of the films, which were dried at 100°C for about 4.0 h after being immersed in water at about 25°C for 20 min increase. The changes of contact angles indicate that the fluorinated groups don't escape from films to the water but transfer from the outermost film surface to the bulk.

The results of R_a show that the R_a of the films with high contents of hydrophilic monomer becomes higher. It is clear that the higher the content of hydrophilic groups in fluorinated polymer films, the more obvious is the mobility of fluorinated groups. The phenomenon is related with interface balance. The said films have lower surface free energies. When the films contact water, which is highly polar, strong force produced from the water makes fluorinated groups transfer or flip-flop from the outermost film surface to bulk phase. At the same time, the higher is the content of hydrophilic groups in the film surface, the stronger is the force of the water, the more obvious mobility of fluorinated groups, and the bigger is the value of attenuation rate of contact angle. As a result, the surface free energy increases and then the interface balance is realized.

TABLE IV
Immersion Behaviors of the Films in Water

Sample	Immersion time (min)					Linear regression	
	0	1.0	5.0	20.0	t^a	Correlation coefficient	R_a (°/min)
PUFA-2	103.6	101.8	100.5	97.4	100.2	0.9530	0.2691
PUFA-3	102.8	100.6	99.4	96.3	99.8	0.9372	0.2745
PUFA-4	99.7	99.0	96.4	93.7	97.0	0.9520	0.2809
PUFA-5	96.2	95.3	94.2	89.6	93.6	0.9964	0.3158
PUFA-6	94.4	92.8	91.4	87.3	91.7	0.9776	0.3212

^a The contact angles of the films that were dried at 100°C for about 4.0 h after being immersed in water at about 25°C for 20 min.

CONCLUSIONS

PUFA with good hydrophobic surface properties can be prepared by the copolymerization of styrene, butyl acrylate, and 2,2,3,4,4,4-hexafluorobutyl methacrylate (FA) in the crosslinked polyurethane via phase inversion polymerization. The said polyurethane was synthesized in acetone from TDI, MDEA, TMP, and PEGA. The dispersions with proper hydrophilic monomer content have core-shell structure, small particle size, and high zeta potential. The addition of hydrophilic monomer was very advantageous to the stability of dispersions and adverse to the surface properties. The surface free energy was increase by more than 19.9% with the addition of hydrophilic monomer. There is obvious mobility of fluorinated groups in fluorinated polymer films.

References

1. Mohanty, S.; Krishnamurti, N. *J Appl Polym Sci* 1993, 62, 1996.
2. Chen, G. N.; Chen, K. N. *J Appl Polym Sci* 1999, 71, 903.
3. Chen, G. N.; Chen, K. N. *J Appl Polym Sci* 1998, 67, 1661.
4. Kim, I.; Ahn, J.-T.; Ha, S.; Yang, S.; Park, I. *Polymer* 2003, 44, 3417.
5. Lee, C.-Y.; Ha, J.-W.; Park, J.; Lee, S.-B. *J Appl Polym Sci* 2002, 86, 3702.
6. Asif, A.; Shi, W. *Polym Adv Technol* 2004, 15, 669.
7. Zhu, Y.; Sun, D.-X. *J Appl Polym Sci* 2004, 92, 2013.
8. Chen, Z.; Zhang, R.; Kodama, M.; Nakaya, T. *J Appl Polym Sci* 2000, 76, 382.
9. Shen, Y.-D.; Zhang, C.-X. *China Leather* 2000, 29, 13.
10. Baek, H.; Kim, K. *Colloids Surf A* 2003, 220, 191.
11. Wang, G.-J.; Kangb, S.; Jin, R.-G. *Prog Org Coat* 2004, 50, 55.
12. Li, Ch.; Su, Ch. *Prog Org Coat* 2004, 49, 252.
13. Decker, C.; Vataj, R.; Louati, A. *Prog Org Coat* 2004, 50, 263.
14. Huybrechts, J.; Bruylants, P.; Vaes, A.; De Marre, A. *Prog Org Coat* 2000, 38, 67.
15. Muller, H.; Hille, H.-D. U.S. Pat 6,770,702 (2004).
16. Yoshizumi, M.; Takato, A.; Nobushige, N. *Prog Org Coat* 1999, 35, 117.
17. Decker, C.; Zahouily, K.; Valet, A. *J Coat Technol* 2002, 74, 87.
18. Kim, Y.-B.; Kim, H.-K.; Yoo, J.-K.; Hong, J.-W. *Surf Coat Technol* 2002, 157, 40.
19. Deckera, C.; Massona, F.; Schwalmb, R. *Polym Degrad Stab* 2004, 83, 309.
20. Lim, H.; Lee, Y.; Park, J.; Leey, S.-B. *J Colloid Interface Sci* 2001, 241, 269.
21. Fox, W.; Zisman, A. *J Colloid Sci* 1950, 5, 514.
22. Hare, F.; Shafrin, G.; Zisman, A. *J Phys Chem* 1954, 58, 236.