Chemical Components and Properties of Core–Shell Acrylate Latex Containing Fluorine in the Shell and Their Films

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ABSTRACT: Core–shell acrylate latices containing fluorine in the shell were prepared by semicontinuous emulsion polymerization. The chemical components of the latices were determined by Fourier transform infrared, ion-selective electrode analysis, and differential scanning calorimetry. The average size and morphology of the latex particles were characterized by photocorrelation spectroscopy and transmission electron microscopy, respectively. The latex particles were mainly composed of a non-fluorine core and a fluorinated shell. The dynamic water contact angles of the latex films from the Wilhelmy method indicated that the latex films containing fluorine in the shell could be wetted by water only with difficulty. The amount of the fluoromonomer played an important role in the modification on the water contact angles, water absorption, and thermal stability of the latex films. In comparison with a random structure, the core–shell structure was more effective for improving the thermal properties of the latex films. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 107–114, 2006

Key words: latices; core-shell polymers; fluoropolymers; component; property

INTRODUCTION

Fluorinated polyacrylate films not only keep the original properties of polyacrylate films, such as good adhesion to matrices, but also have better durability and both antifouling and self-cleaning properties. Thus, fluorinated polyacrylates have been used to a progressively greater extent in surface coatings for water and oil repellency for textiles, paper, and leather. However, the relatively high market prices of fluorinated acrylate polymers are the biggest limitation for their increased use. The reported studies indicate that the special surface properties of fluorinated polyacrylates are attributable to the fact that the perfluoroalkyl side chains [—$(CF_2)_n CF_3$, n = 2–15] of polymers expand in air and occupy the polymer–air interface.[1–5] The low intermolecular force between perfluoroalkyl side chains and air significantly lessens the surface energy of the polymer film. Moreover, given that stable C—F bonds have high bond energy and perfluoroalkyl side chains pack main chains of polymers, the inside molecules are protected and impart good thermal stability to fluorinated polyacrylate. Thus, to obtain fluorinated polyacrylates with good properties and low fluorine contents, most perfluoroalkyl side chains need to occupy the surface of the films as much as possible by the adoption of suitable polymerization techniques.

A core–shell latex is composed of composite particles with at least two different polymers in the core and shell. The polymers forming the core and the shell phase can disperse totally or partially in the final films, so core–shell latices often exhibit improved physical and chemical properties over their single-component counterparts.[6] Because of differences in the hydrophobicity and surface tension, one of the polymers in core–shell latex particles might preferentially migrate to the surface during film formation, and this provides a theory base to design fluorinated acrylate latex with a low fluorine content. Marion et al.[7,8] designed core–shell latex particles containing a short-chain fluoropolymer in the shell and investigated the core–shell structure. Ha and coworkers[9,10] used a cationic emulsifier to prepare the core–shell particles containing perfluoroalkyl acrylate in the shell.

In our previous work, a stable core–shell latex with a core rich in polyacrylate and a shell rich in a long-chain fluorinated copolymer was successfully prepared by semicontinuous emulsion polymerization, with perfluoroalkylethyl methacrylate (Zonyl TM) as a fluoromonomer and sodium dodecyl sulfate (SDS) and fatty alcohol polyoxyethylene ether (OS-15) as a mixed emulsifier system.[11] In this work, the chemical

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TABLE I
Reaction Conditions, Conversion, and Particle Characteristics of the Samples

Sample	Mixed emulsifier system		APS (wt %)	Zonyl TM (wt %)	Dropping time (h)	Final conversion (wt %)	Average particle size (nm)
	Total (wt %)	OS-15/SDS					
1	3.0	2 : 1	0.40	6.67	3.0	94.22	95.9
2	3.7	2 : 1	0.40	6.67	3.0	94.25	90.0
3	4.0	2 : 1	0.40	6.67	3.0	94.36	88.9
4	5.0	2 : 1	0.40	6.67	3.0	94.45	87.0
5	6.0	2 : 1	0.40	6.67	3.0	94.73	86.4
6	3.7	4 : 1	0.40	6.67	3.0	88.86	100.4
7	3.7	3 : 1	0.40	6.67	3.0	93.65	96.9
8	3.7	0 : 1	0.40	6.67	3.0	92.31	59.8
9	3.7	2 : 1	0.25	6.67	3.0	90.84	96.3
10	3.7	2 : 1	0.30	6.67	3.0	92.86	93.7
11	3.7	2 : 1	0.45	6.67	3.0	94.32	106.3
12	3.7	2 : 1	0.50	6.67	3.0	96.85	110.5
13	3.7	2 : 1	0.40	6.67	2.5	93.46	85.8
14	3.7	2 : 1	0.40	6.67	3.5	95.20	98.3
15	3.7	2 : 1	0.40	6.67	4.0	95.82	109.8
16	3.7	2 : 1	0.40	6.67	4.5	96.14	114.5
17	3.7	2 : 1	0.40	0.83	3.0	97.23	89.3
18	3.7	2 : 1	0.40	1.67	3.0	95.89	87.4
19	3.7	2 : 1	0.40	3.33	3.0	94.51	83.8
20	3.7	2 : 1	0.40	5.00	3.0	95.47	87.0
21	3.7	2 : 1	0.40	0	3.0	97.82	83.5

components of the latices were studied by Fourier transform infrared (FTIR), ion-selective electrode analysis, and differential scanning calorimetry (DSC). The average size and morphology of the latex particles were characterized by photocorrelation spectroscopy (PCS) and transmission electron microscopy (TEM), respectively. The properties of the latex films, such as the surface and thermal properties, were also examined in detail.

EXPERIMENTAL

Materials

Zonyl TM samples (fluoromonomers) were obtained from Aldrich (Milwaukee, WI) and used without further purification. The value of n in the C_nF_{2n+1} group ranged from 6 to 8, and the fluorine concentration was 60 wt %. Butyl acrylate (BA) and methyl methacrylate (MMA) were washed with a 5 wt % sodium hydroxide solution to delete inhibitions. The initiator, ammonium persulfate (APS), was purified by recrystallization. The mixed emulsifier system was composed of SDS and OS-15. The deionized water was obtained by ion exchange.

Emulsion polymerization

Just as we reported before,[11] the core–shell latex was synthesized by a two-stage semicontinuous emulsion polymerization. In the first stage, the latex seed composed of poly(BA-co-MMA) was prepared. In the sec-

ond stage, Zonyl TM, as well as the other part of BA, MMA, and APS, was preemulsified by small amounts of the mixed emulsifier. Then, the preemulsifer was slowly added to react with the seed latex to form the latex shell. The designed solid concentration of the final latex was 25 wt %. The total weight ratio of BA, MMA, and Zonyl TM was 3 : 2 when all the samples were prepared. Table I lists the detailed reaction conditions and final conversions of all the samples.

Polymer characterization

The fluorine concentration of the polymer was determined by ion-selective electrode analysis. A standard curve was created through an examination of standard NaF solutions in different concentrations (from 10^{-2} to 10^{-5} mol/L). A linear regression equation was used as follows:

$$E \text{ (mV)} = -5.1 - 58.1 \log [F^-] \text{ (mol/L)} \quad (1)$$

where E is the response voltage and $[F^-]$ is the concentration of fluorine ion in the absorbing solution.

A latex film was extracted for 24 h at 40°C, with 1,1,2-trifluorotrichroloethane as the extraction solvent. The residual film was dried in a vacuum oven at room temperature. Next, a certain amount of the residual film was burned in an oxygen bomb with a 50-mL, 0.1 mol/L NaOH solution as the absorbing medium. The absorbing solution was diluted 1.25 times and determined by a fluorine ion-selective electrode to obtain E.

According to eq. (1) and *E*, the concentration of the fluorine ion in the solution could be calculated. The fluorine concentration of the copolymer (C_F) was calculated with the following formula:

$$C_F(\text{wt \%}) = (1.25[\text{F}^-] \times 0.05 \times M_F)/W \times 100\% \quad (2)$$

where M_F is the molar mass of the fluorine element and W is the weight of the film before burning.

IR spectra of the latex films were recoded with a PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer Cetus Instruments, Norwalk, CT) in the range of 4000–400 cm^{-1}. The glass-transition and thermal decomposition temperatures of the polymers were measured with a PerkinElmer DSC7 differential scanning calorimeter and a TGA7 thermogravimeter, respectively, under a nitrogen atmosphere at a heating rate of 20°C/min.

The latices were diluted, and then their particle sizes were characterized directly by PCS (Malven Co., Ltd., Worcestershire, UK) at a fixed scattering angle of 90°. The morphology of the latex particles was investigated by TEM. The latices were diluted and stained with a phosphotungstic acid solution (pH 6.4). TEM micrographs were obtained at 60 kV with a TEM-100SX transmission electron microscope (JEOL, Ltd. Co., Tokyo, Japan).

The centrifugal stability and electrolyte-resistant stability of the latices were determined by a centrifugal method and by the addition of electrolyte solutions to latices, respectively. The higher the sedimentation ratio was, the lower these two stabilities were. The sedimentation ratio was calculated with the following formula:

$$\text{Sedimentation ratio(wt \%)} = W_1/W_0 \times 100\% \quad (3)$$

where W_1 is the weight of the sedimentation and W_0 is the weight of the original latex samples.

Weighted latex films were dipped in distilled water for 48 h. Then, the water on the surface of the films was removed, and the films were weighed again. The water absorption ratio of the films was calculated with the following formula:

Water absorption ratio(wt%)
$$= (W_1 - W_0)W_0 \times 100\% \quad (4)$$

where W_0 and W_1 are the weights of the films before and after the films absorb water, respectively.

The dynamic contact angles of the latex films were measured by the Wilhelmy method[12] with a Krüss II interface tension meter (Krüss Co., Hamburg, Germany). The latex films were cut into squares, held in a microbalance, progressively immersed in water at a speed of 0.5 mm/s, and then conversely receded to the
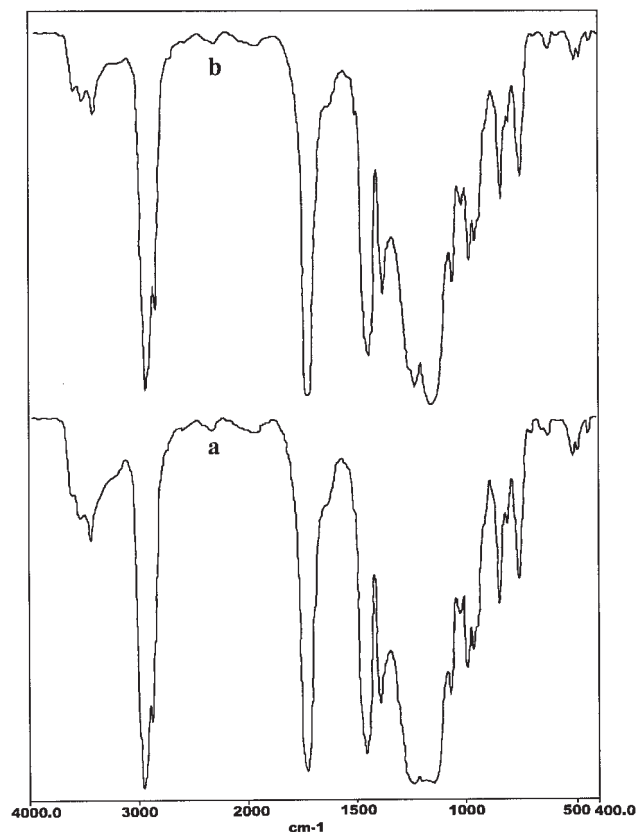

Figure 1 IR spectra of latex films: (a) a film containing fluorine (sample 2) and (b) a film without fluorine (sample 21).

original position. An analysis of the wetting force data yielded both an advancing contact angle and a receding contact angle.

RESULTS AND DISCUSSION

Chemical components of the latex

According to the IR spectrum of sample 2 shown in Figure 1(a), the characteristic absorption of the C=C bond at 1640 cm^{-1} disappears, and this indicates that the monomers polymerized. In comparison with the IR spectrum of sample 21 prepared without Zonyl TM under the same reaction conditions as those of sample 2, the IR absorption peaks at 1000–1260 cm^{-1} are wider and blunter because of the overlap of the stretching vibration absorption of the C—F bond at 1100–1240 cm^{-1} with the stretching vibration absorption of the C—O—C bond of ester groups at 1250 cm^{-1}. This result proves that Zonyl TM participated in the polymerization. To study whether Zonyl TM copolymerized with BA and MMA, the latex film of sample 2 was extracted by 1,1,2-trifluorotrichroloethane to remove the unpolymerized Zonyl TM and its homopolymer. We could expect the detected fluorine in the residual film after extraction to be from the
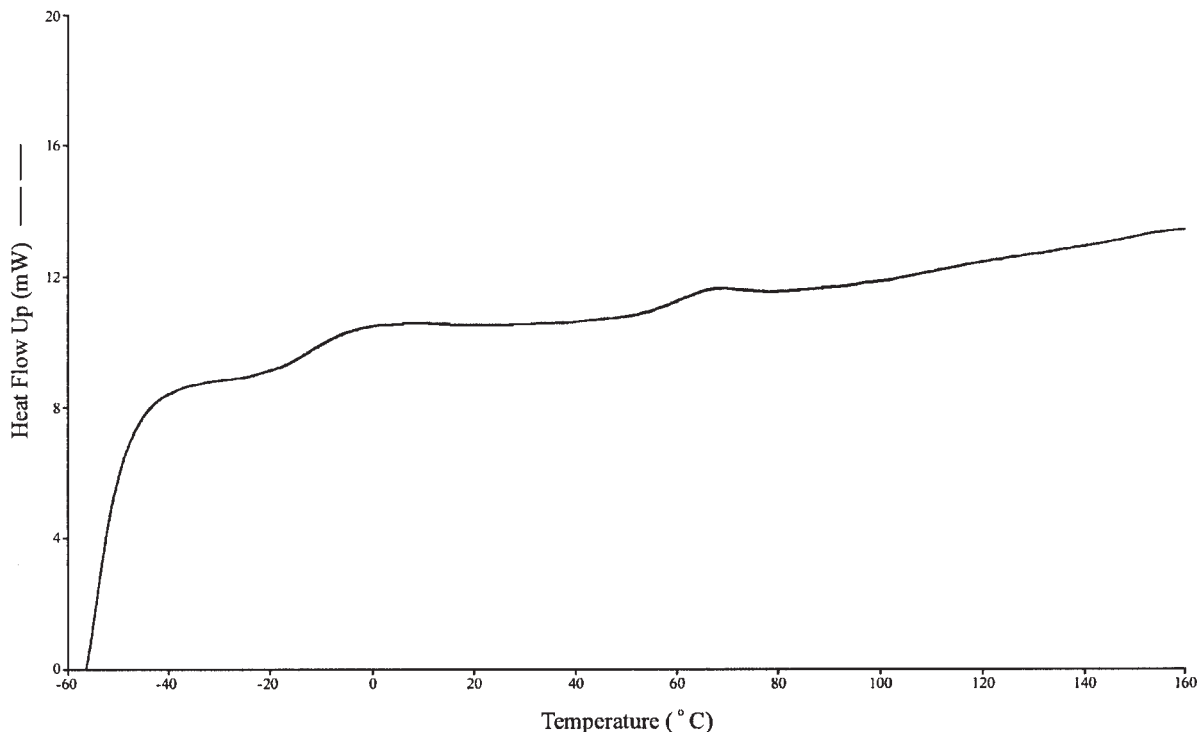
Figure 2   DSC curves of sample 2.

copolymers of BA, MMA, and Zonyl TM. Some of the residual film (0.0126 g) was burned to transfer the fluorine in the copolymer into the fluorine ions of the absorbing solution. Then, the diluted absorbing solution was determined with a fluorine ion-selective electrode. E was 197 mV; thus, the concentration of the fluorine ion in solution was 3.32×10^{-4} mol/L according to eq. (1), and the fluorine concentration of the film was 3.13 wt % according to eq. (2). This result further proved that Zonyl TM took part in the copolymerization. However, the fluorine concentration of this film in theory (4.0 wt %) was higher than the experimental value, and this could possibly be attributed to two factors: the loss of fluorine during the burning process because the oxygen bomb was made of glass and the existence of a Zonyl TM homopolymer trace.

Figure 2 presents the DSC curve of the latex film of sample 2. There are two transform temperatures on the DSC curve, -10 and $60°C$, which reveal that the latex particles had a biphase structure: a core structure and a shell structure. According to the designed experiment recipe, $-10°C$ was the glass-transition temperature of the copolymer in the core, whereas $60°C$ was the glass-transition temperature of the fluorinated copolymer in the shell. The core–shell morphology of the latex particles is shown in TEM images later.

Latex morphology and particle size

Figure 3 shows typical TEM images of core–shell latices with different amounts of the fluoromonomer. The latex particles were round and had a clear core–shell structure. Table I lists the average particle sizes of the latex particles prepared under different reaction conditions. From this table, the effect of the reaction conditions on the particle sizes could be summarized.

As the total amount of the mixed emulsifiers increased, the average sizes of the latex particles decreased. When the total amount of the mixed emulsifiers was constant, the average sizes of the latex particle decreased with a decrease in the ratio of OS-15 to SDS. In the mixed emulsifier system, the amount of the anion emulsifier determined the total area of mixed micelles, whereas the amount of the non-ion emulsifier determined the inner volume. With the same concentration, the overlapping capability of SDS was better than that of OS-15, so the more SDS there was, the lower the volume was of the micelles and the greater the number was of the micelles; this led to the decrease in the latex particle size.

With an increasing amount of APS, the average particle sizes of the latices decreased first and then increased. Increasing the amount of APS increased the concentration of APS in the water phase, and this accelerated the decomposition rate of APS; thus, the concentration of the free radicals increased, and this led to the increase in the odds of micelle nucleation and homogeneous nucleation. Hence, the more latex particles there were, the lower the average particle size was. However, the decomposition products of APS acted as electrolytes in the latex system. The increase in the amount of APS enhanced the concen-
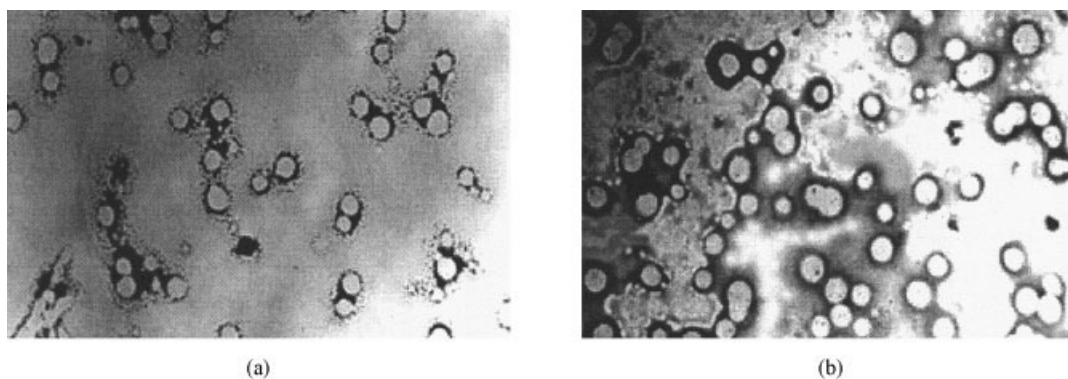
Figure 3 Morphology of the latex particles: (a) magnification $= 2 \times 10^4$ and fluorine concentration $= 0.83$ wt % and (b) magnification $= 2 \times 10^4$ and fluorine concentration $= 6.67$ wt %.

tration of electrolytes in the latices, and this could lead to the increase in the latex particle size. Two contrary effects competed with each other, so the average particle of latex reached the minimum when the concentration of APS was 0.4 wt %.

The amount of Zonyl TM also had two contrary effects on the average size of the latex particles. Because of the very low intermolecular force of perfluoroalkyl groups, the adsorption of the mixed emulsifiers on the latex particle surface became difficult, so the small latex particles showed a trend to integrate to reach a stable state. On the other hand, the high electronegativity of perfluoroalkyl groups led the particles to exclude one another. Thus, Table I shows that the average size of the latex particles was only 83.8 nm when the concentration of Zonyl TM was 3.33 wt %. Moreover, the PCS results also agreed with the TEM images in Figure 3.

Table I reveals that increasing the dropping time increased the average size of the latex particles. In this system, the core–shell polymers were prepared by a semicontinuous addition method, so the excess emulsifiers in the addition part easily induced secondary particles with a smaller particle size to form. However, a very low dropping speed could prevent the emulsifier in the seed emulsion from reaching a saturation state and could reduce the opportunity for secondary particles. Thus, prolonging the dropping time benefited the form of the latices with fine core–shell structures and narrow distributions. The PCS polydisper-

sions of the latices prepared with different dropping times were 0.055 for 2.5 h, 0.049 for 3.0 h, 0.034 for 3.5 h, 0.024 for 4.0 h, and 0.018 for 4.5 h, which agreed with the TEM results reported in our previous research.[11]

Stabilities of the latex

The core–shell latices prepared in this work had good storage, centrifugal, and electrolyte-resistant stabilities. Our previous study indicated that the low fluorine content (<5 wt %) had litter effect on the storage stability of the latices.[11] The effects of the amount of Zonyl TM on the centrifugal and electrolyte-resistant stabilities of the latices are summarized in Table II. The higher the sedimentation ratio was, the lower these two stabilities were. Hence, with an increasing amount of Zonyl TM, the centrifugal and electrolyte-resistant stabilities of the latices increased first and then decreased. When the Zonyl TM concentration was 3.33 wt %, the latex exhibited the best centrifugal and electrolyte-resistant stabilities. Under the same centrifugal condition, the centrifugal stability had a great relationship with the latex particle size. The particle size of the latex with 3.33 wt % Zonyl TM was the least of all the samples, so the centrifugal stability was the best. Because of the two contrary effects of the amount of Zonyl TM on the latices discussed previously, the electrolyte-resistant stability had an optimal point.

TABLE II
Effects of the Amount of Zonyl TM on the Centrifugal Stability and Electrolyte-Resistant Stability of the Latices

	Zonyl TM (wt %)				
	0.83	1.67	3.33	5.00	6.67
Sedimentation ratio (wt %)[a]	22.83	13.91	10.30	13.15	17.78
Sedimentation ratio (wt %)[b]	0.889	0.617	0.485	1.32	2.44

[a] 12,000 rpm, 120 min.
[b] Adding Na_2SO_4 solution and storing 72 h.

TABLE III
Effects of the Amount of Zonyl TM on the Water Contact Angles and Water Absorption of the Latex Films

	Zonyl TM (wt %)					
	0	0.83	1.67	3.33	5.00	6.67
Advancing angle (°)	70.5	98.1	99.8	101.8	102.5	105.4
Receding angle (°)	30.5	36.9	37.5	40.6	41.7	48.2
Water absorption (wt %)	28.72	19.71	18.12	15.60	14.09	13.16

Water contact angles of the latex films

The contact angle has been commonly used as a criterion for the evaluation of hydrophobic surfaces. The water contact angle of a typical hydrophobic surface is always above 90°. Our previous research results[11] indicated that the emulsifier amount, initiator amount, and dropping time had small effects on the water contact angles of the latex films. However, the amount of fluorine played an important role in the modification of the surface properties of the latex films. The water contact angles of the latex films with different amounts of fluorine are listed in Table III. The advancing angles of the fluorinated core–shell latices were all above 90°, even if the Zonyl TM concentration was only 0.83 wt %; this indicated that the fluorine-containing polyacrylate latex films could be wetted by water only with difficulty. The advancing angles of the films significantly increased as the amount of fluorine increased. The fluorinated shell and the nonfluorinated core had great differences in the surface energy and incompatibility, which were a driving force to make the fluoropolymer cover the film's surface.[13] In addition, with respect to this core–shell latex system, the fluoropolymer was concentrated in the shell phase by the control of the polymerization method, so the separation between the fluoropolymer and the nonfluorinated component was accomplished during particle synthesis. As a result, the high-hydrophobicity and low-surface-tension fluoropolymer could more easily accumulate at the film–air interface the during the film formation, and this greatly lessened the surface energy; thus, the latex film could not be wetted by water easily, and the water advancing angles increased with an increase in the amount of fluorine in the bulk.

On the other hand, the water advancing angles were much higher than the receding angles. This was the contact-angle hysteresis, usually caused by the surface roughness and chemical heterogeneity.[14–16] In this work, the films formed under room temperature and were not dealt with by the annealing, so the film surface with initial roughness was not smooth enough, and this resulted in the contact-angle hysteresis. The value of n in the C_nF_{2n+1} group of the fluoromonomer (Zonyl TM) was in the range of 6–8. Undoubtedly, the contact-angle hysteresis was also partly due to the chemical heterogeneity of different fluorinated components with different perfluorinated side-chain lengths. In addition, the fluoropolymer was in a random state of aggregation with no crystal part when n was less than 12.[17,18] Thus, the hydrophobic fluoro groups would migrate to the film inside, and hydrophilic groups would migrate to the surface, when the environment surrounding the latex films changed, such as the films being immersed in water. This may be another possible reason for the significant difference between the advancing angle and the receding angle.

Water absorption of the latex films

The data of Table IV reveal the effect of the mixed emulsifier system on the water absorption of the fluorinated latex films. Short-chain emulsifier molecules are always expelled to the surface during film formation,[19] and this has effects on the nature of the latex films, such as the hydrophilic property. Thus, the water absorption of the latex films increased with an increase in the total amount of the emulsifiers. Moreover, SDS was more hydrophilic than OS-15, so the increasing amount of SDS increased the water absorption of the latex films.

From Table IV, it is noteworthy that increasing the amount of Zonyl TM predominantly reduced the water absorption of the latex films. Because the hydrophobic fluoropolymer in the shell finally assembled to

TABLE IV
Effects of the Mixed Emulsifier System on the Water Absorption of the Latex Films

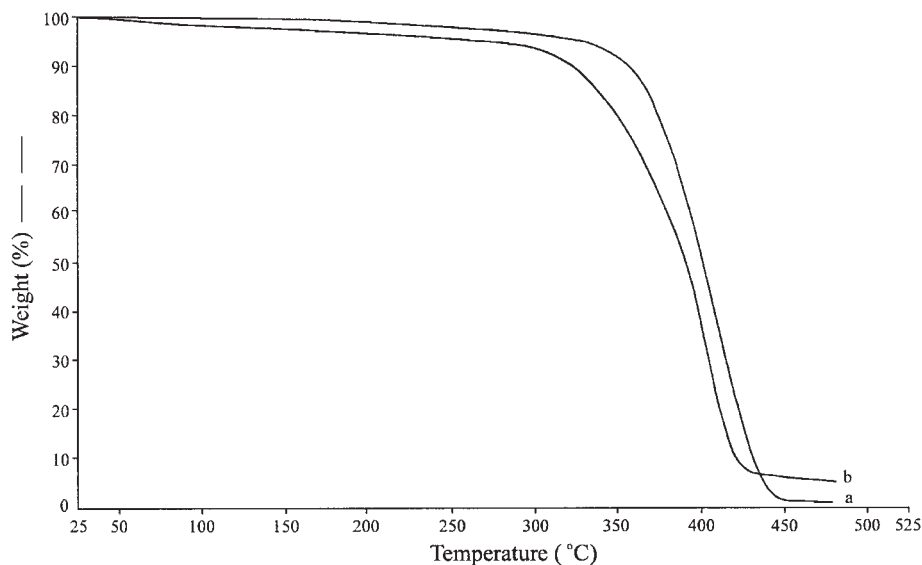| Mixed emulsifier system		Water absorption (wt %)
Total amount (wt %)	OP-15/SDS	
3.0	2:1	10.56
3.7	2:1	13.16
4.0	2:1	13.87
5.0	2:1	14.65
6.0	2:1	17.24
3.7	4:1	19.24
3.7	3:1	16.81
3.7	0:1	38.60

Figure 4 Thermogravimetric analysis curves of latex films: (a) a fluorine-containing film (sample 2) and (b) a non-fluorine film (sample 21).

the film surface as expected, the water absorption of the latex films was significantly modified by the inclusion of the fluorine component.

Thermal stability of the latex films

The thermogravimetric curves of the latex films with fluorine (sample 2) and without fluorine (sample 21) are shown in Figure 4(a,b), respectively. From Figure 4(a), the latex film of sample 2 prepared with 6.67 wt % Zonyl TM began to decompose at 355°C and decomposed completely at 440°C, whereas the decomposition of the latex film without fluorine began at 326°C and ended at 421°C. Only with 6.67 wt % fluoromonomer did the decomposition temperature increase 29°C, and this indicated that the thermal stability of the latex film was significantly modified. This phenomenon was attributed to long-chain perfluoroalkyl groups. Zonyl TM has a terminal perfluoroalkyl chain containing six or more CF_2 units with high bond energy; this was sufficiently long to shield and protect the nonfluorinated segment beneath the fluorinated segment. Our previous study showed that the beginning and ending decomposition temperatures of random copolymers with the same fluorine content were 342 and 428°C, respectively.[20] Thus, the core–shell structure was more effective for improving the thermal stability, in comparison with a random structure.

CONCLUSIONS

Core–shell acrylate latices containing fluorine were successfully prepared by semicontinuous emulsion polymerization with Zonyl TM as a fluoromonomer. The results of FTIR, ion-selective electrode analysis, and DSC indicated that Zonyl TM took part in copolymerization and that the main chemical components of the latex particles were the non-fluorine core and the fluorinated copolymer shell. The average sizes of the latex particles from PCS were 83–115 nm. TEM images of the latex particles further proved the core–shell structure and agreed well with PCS results. The amount of the fluoromonomer had important effects on the properties of the latices and their films. When the fluoromonomer concentration was 3.33 wt %, the latex exhibited the best centrifugal and electrolyte-resistant stabilities. The more fluoromonomer there was, the higher the advancing angles were, the lower the water absorption was, and the better the thermal stability was of the latex films. Moreover, the core–shell structure was more effective for improving the thermal properties of the latex films, in comparison with a random structure.

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