

Surface Characteristics of Water-Soluble Cationic Fluoro Copolymers Containing Perfluoroalkyl, Quaternized Amino, and Hydroxyl Groups

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ABSTRACT: Various water-soluble cationic fluoro copolymers in quaternized form with perfluoroalkyl, amino, and hydroxyl groups were prepared by varying the contents of perfluoroalkyl ethyl acrylate (FA), 2-(dimethylamino) ethyl methacrylate (DAMA), and 2-hydroxyethyl methacrylate (HEMA). The solvent polymerization was carried out in acetone, with the subsequent addition of acetic acid to form a quaternized polymer. Polyurethanes films were prepared by curing aqueous solutions containing water-soluble cationic fluoro copolymers and a blocked isocyanate at 190°C. The surface characteristics of the water-soluble cationic fluoro copolymers and the polyurethanes were investigated on the basis of FA and DAMA contents. The contact angles

for both water and methylene iodide (MI) on the cationic fluoro copolymer and the polyurethane increase steadily as FA content increases, and decrease gradually with increasing DAMA content. The contact angles on the polyurethane are slightly higher than those on the cationic fluoro copolymer. The cationic fluoro copolymer and the polyurethane with FA content of 40 wt % and DAMA content of <30 wt % show extremely low surface free energies of 13–15 dynes/cm. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3702–3707, 2002

Key words: cationic polymerization; fluoropolymers; polyurethanes; surfaces

INTRODUCTION

Various polymers have been widely used as functional coating materials. The surface properties of polymers are of paramount importance for applications, and many researchers have extensively studied surface properties of functional polymers.^{1,2} The fluoropolymers containing perfluoroalkyl group are widely utilized in industry as excellent surface modification agents for lowering surface free energy and imparting water-and-oil repellency, anti-fouling, and anti-adherent properties.^{3–13} To impart to the building materials water-repellent, oil-repellent, anti-graffiti, and nonstick properties that are stable with respect to ageing and inclement weather, fluoropolymer-coating materials in a solvent medium have been used. However, recently, fluoropolymer-coating materials containing only small amounts of volatile organic compound (VOC) or without VOC are strongly needed because of the environmental regulations against VOC. Although water-soluble fluoropolymers are becoming important in industry, studies on their synthesis and applications have been rarely done. Some patents have been published.^{14–16}

In this study, synthesis and surface properties of water-soluble polymers were investigated. Water-soluble cationic fluoro copolymers in quaternized form with perfluoroalkyl, amino, and hydroxyl groups were prepared from the monomers of perfluoroalkyl ethyl acrylate (FA), 2-(dimethylamino) ethyl methacrylate (DAMA), and 2-hydroxyethyl methacrylate (HEMA). Polyurethanes were prepared using the water-soluble cationic fluoro copolymers and a blocked isocyanate. The surface characteristics of the water-soluble cationic fluoro copolymers and the polyurethanes were analyzed on the basis of FA and DAMA contents.

EXPERIMENTAL

Materials

Perfluoroalkyl ethyl acrylate [$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{-(CF}_2)_7\text{CF}_3$; FA], obtained from Hoechst Company (Fluowet AC-800), was used as a main monomer for the preparation of cationic fluoro copolymers. Comonomers of 2-hydroxyethyl acrylate (HEMA) and 2-(dimethylamino) ethyl methacrylate (DAMA), obtained from Aldrich Company, were used to prepare cationic fluoro copolymers with both hydroxyl and amino groups in quaternized form. The initiator of 2,2-azobisisobutyronitrile (AIBN), obtained from Aldrich Company, was used for free-radical solvent polymer-

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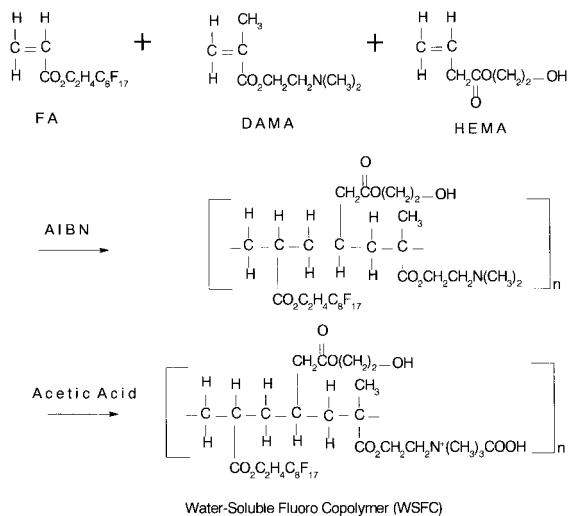


Figure 1 Reaction scheme for the preparation of water-soluble fluoro copolymer (WSFC).

ization after recrystallizing three times from methanol. The solvent polymerization was carried out in acetone obtained from Junsei Chemical Company. Acetic acid, obtained from Junsei Chemical Company, was used as a quaternizing (salifying) agent of the copolymers prepared. Methylene iodide (MI) used for measurement of contact angle was obtained from Aldrich Company. Deionized water was used throughout the experiments.

Synthesis of water-soluble cationic fluoro copolymers

Cationic fluoro copolymers with hydroxyl and amino groups were prepared using the reaction scheme as shown in Figure 1. The monomers of FA, HEMA, and DAMA were charged into a reaction bottle. The concentration of the monomers was maintained as 40 wt %. After purging the reaction bottle with nitrogen, the reaction mixture was heated to 65°C, and then AIBN was put into the bottle to initiate the reaction. The polymerization reaction was carried out at 65°C for 3 h. After analyzing the completion of polymerization by gas chromatography (GC), acetic acid in water was added to form a quaternized copolymer. The reaction mixture was maintained for an additional hour at 75°C. The amount of acetic acid was adjusted so that the DAMA/acetic acid mole ratio became 1.0. The concentration of quaternized cationic fluoro copolymers was maintained at 20 wt % by adjusting the amount of water containing acetic acid. All the reaction mixtures obtained with the method just described were clear and transparent like an aqueous solution. It can be said that the cationic fluoro copolymers prepared are soluble in water containing acetic acid. Various water-soluble cationic fluoro copolymers were

prepared by varying the contents of FA, HEMA, and DAMA.

Preparation of coating solutions and films

Coating solutions for the preparation of films of quaternized fluoro copolymers were prepared by diluting the reaction mixture obtained after polymerization to 1.0 wt % with water. The films for the analysis of surface characteristics were prepared by solvent die casting¹⁷ with the coating solutions. The smooth polymer films were obtained with a uniform thickness of ~100 μm on a glass plate by slow evaporation of water. The evaporation of water was performed in a vacuum oven at room temperature. To investigate the effect of annealing on surface properties, the films annealed at 130 ± 5°C for 3 min were also prepared.

Films of polyurethane polymers with both perfluoroalkyl and quaternized amino groups were prepared with the cationic fluoro polymers and a blocked isocyanate. The blocked isocyanate was diphenylmethane-4,4'-diisocyanate [CH₂(C₆H₄NCO)₂; MDI] blocked by caprolactam and obtained from Korea Fine Chemical Company. The reaction scheme for the preparation of polyurethane film is shown in Figure 2. The blocked isocyanate dispersed in water using a surfactant of sodium dodecyl sulfonate was used to prepare the coating solutions. The concentrations of the blocked isocyanate and the surfactant in the aqueous dispersion of the blocked isocyanate were 1.0 and 0.02 wt %, respectively. Because the dissociation temperature of the blocked isocyanate is known to be ~182°C,¹⁸ the polyurethane films were made by curing aqueous solutions containing the cationic fluoro copolymer and the blocked isocyanate at 190°C. The film was made on slide glass. The slide glass was cleaned with a cleaning solution consisting of sulfuric

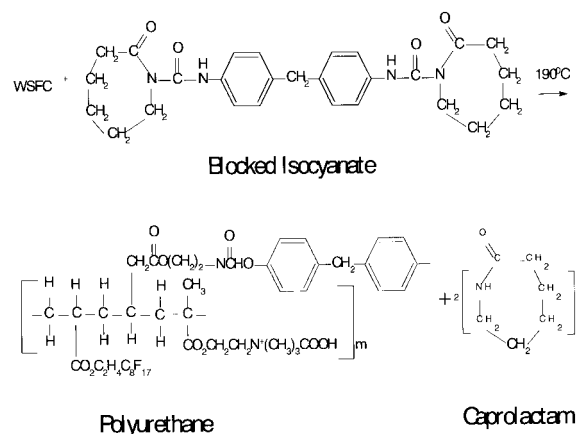


Figure 2 Reaction scheme for the preparation of polyurethane with both perfluoroalkyl and quaternized amino groups.

acid and chromium oxide ($\text{CrO}_3/\text{H}_2\text{SO}_4 = 1/50$ wt ratio) before use.

Measurements

Advanced contact angles on the films of cationic fluoro copolymers and polyurethane polymers with both perfluoroalkyl and quaternized amino groups were measured by the sessile-drop method with an optical goniometer (Rame-Hart, 100-series) at room temperature. At least two drops of liquid were advanced by adding liquid slowly, and the angles were measured immediately after each addition of liquid. The contact angle was defined as average of 5 data points. Swelling and deformation of the polymer during the measurement of contact angle were not observed.

Distilled water and methylene iodide (MI), suggested by Owens and Wendt,¹⁹ were used as wetting liquids. The surface free energies were calculated by Fowkes' theory using the contact angle data.^{6,19}

Adsorption spectra of Fourier transform infrared (FT-IR; Bio-Rad FTS-165) were measured to compare the functional groups of monomers and polymers.

RESULTS AND DISCUSSION

Synthesis of cationic fluoro copolymers and polyurethanes

FT-IR absorption spectra for the monomers of FA, DAMA, and HEMA and the cationic fluoro copolymer are compared in Figure 3. The peaks were assigned according to the literature.²⁰ The most intense bands between 1050 and 1200 cm^{-1} for the FA spectrum (a) are assigned to the C—F stretching of $-\text{CF}_2-$ and $-\text{CF}_3$. The bands around 1455 cm^{-1} for the spectra of

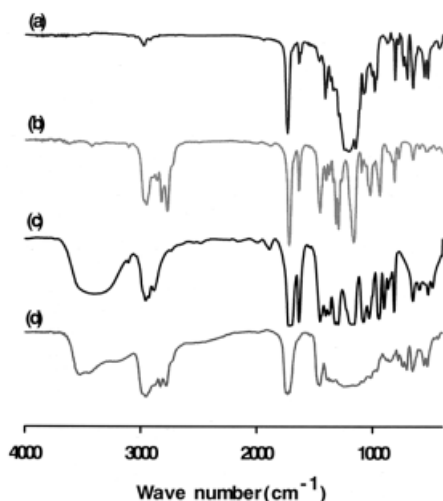


Figure 3 FT-IR spectra of monomers and cationic fluoro copolymer: (a)FA, (b) DAMA, (c) HEMA, (d) cationic fluoro copolymer.

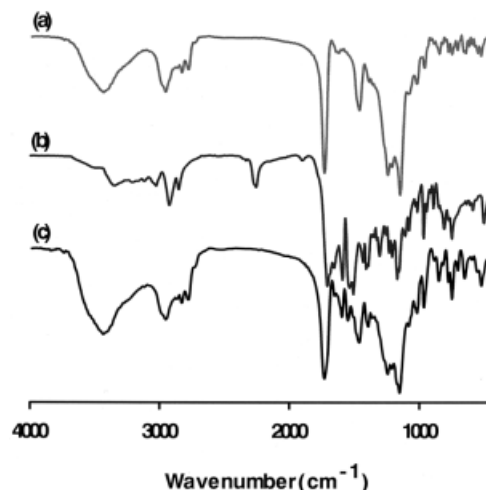


Figure 4 FT-IR spectra of (a) cationic fluoro copolymer, (b) MDI, and (c) polyurethane.

DAMA (b) and HEMA (c) are related to C—H asymmetric deformation and $-\text{CH}_2-$ scissors vibration. The absorption bands between 2970 and 2860 cm^{-1} correspond to the vibration modes of $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The bands around 1690 cm^{-1} for the DAMA spectrum (b) are assigned to the stretching of the $-\text{CH}_2\text{N}=\text{C}$ group. The adsorption bands between 3420 and 3250 cm^{-1} for the HEMA spectrum (c) correspond to the hydroxyl group. The spectrum (d) shows that the cationic fluoro copolymer contains C—F, $-\text{CH}_2-$, $-\text{CH}_3$, $-\text{CH}_2\text{N}=\text{C}$, and $-\text{OH}$ groups originating from the monomers used. These results indicate that the cationic fluoro copolymer was successfully prepared from the monomers.

The FT-IR absorption spectrum of the polyurethane is compared with those of the cationic fluoro copolymer and MDI in Figure 4. The absorption bands between 2285 and 2250 cm^{-1} assigned to free NCO group of MDI can be seen in Figure 4(b). However, the absorption bands assigned to free NCO group cannot be seen in Figure 4(c). This result means that the polyurethane does not contain free NCO groups and the NCO groups in MDI are completely disappeared because of the urethane reaction. The spectrum for the polyurethane shows the adsorption bands of C—F, $-\text{CH}_2-$, $-\text{CH}_3$, $-\text{CH}_2\text{N}=\text{C}$, and $-\text{OH}$ groups originating from the cationic fluoro copolymer. From the results, it can be said that the polyurethane was well prepared from the cationic fluoro copolymer and the blocked isocyanate.

Surface characteristics of cationic fluoro copolymers and polyurethanes

The variation of contact angle for the polyurethane prepared with a NCO/OH mole ratio of 1.0 as a function of reaction time at 190°C is shown in Figure 5.

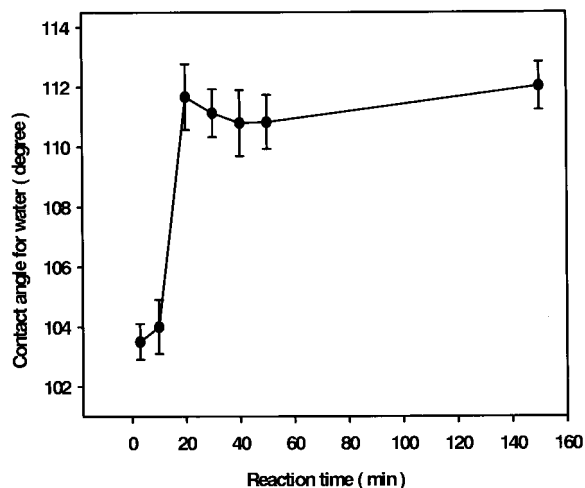


Figure 5 Variation of contact angle according to reaction time (FA/DAMA/HEMA = 40/40/20; NCO/OH = 1.0).

The weight ratio of FA/DAMA/HEMA of the aqueous cationic fluoro copolymer solution used was 40/40/20. The contact angle increases abruptly with the reaction time up to 20 min, but seems to become nearly constant after 20 min. When the polyurethane reaction is not done completely, the film of polyurethane reaction mixture contains unreacted functional groups of —NCO and —OH. Because of the hydrophilic groups of —NCO and —OH, the film containing unreacted groups of —NCO and —OH shows poor hydrophobicity. The polyurethane reaction may be completed within 20 min. Therefore, the reaction time needed for the preparation of polyurethane was fixed to 20 min in the following experiments. The contact angle for the polyurethane exhibits as high as 112°, indicating that the polyurethane is highly hydrophobic. The aqueous cationic fluoro copolymer may have some important applications in the fields of water-repellent coatings.

The effect of NCO/OH mole ratio on the contact angle for polyurethane, shown in Figure 6, was exam-

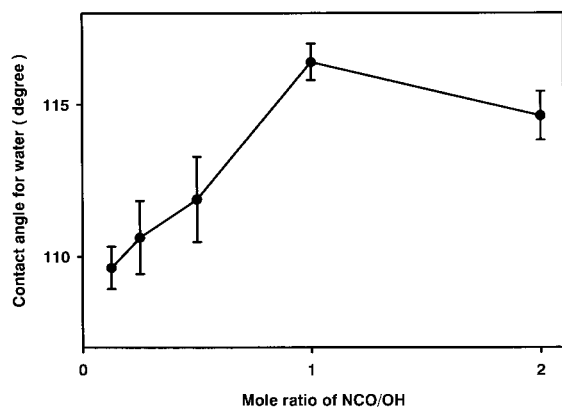


Figure 6 Variation of contact angle according to NCO/OH mole ratio (FA/DAMA/HEMA = 40/5/55).

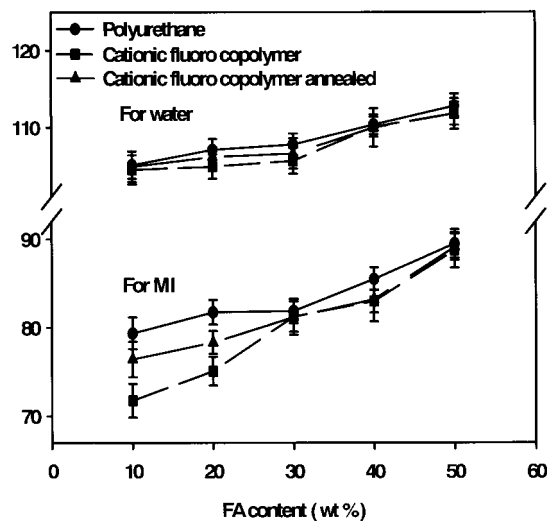


Figure 7 Variation of contact angle according to FA content (HEMA = 20 wt %).

ined using the cationic fluoro copolymer prepared with FA/DAMA/HEMA = 40/5/55 (wt %). As expected, the contact angle for NCO/OH = 1.0 is the highest. As the mole ratio of NCO/OH approaches 1.0, it is well known that the molecular weight of polyurethane increases steeply. The molecular weight may have significant influence on the surface properties.⁹ Because the degree of polymerization (molecular weight) is low, the relative amount of the functional groups of —NCO and —OH in the polymer becomes higher and the effects of the functional groups become more significant. It can be said that the optimum mole ratio of NCO/OH is 1.0. This mole ratio was used to prepare polyurethanes in the following experiments.

The effects of FA content on contact angle for the cationic fluoro copolymer and the polyurethane were investigated and are shown in Figure 7. Five polyurethanes were prepared by increasing FA content from 10 to 50 wt % with HEMA content of 20 wt % (DAMA content decreases from 70 to 30 wt %). The contact angles for both water and MI on the films of the cationic fluoro copolymer and the polyurethane increase steadily as FA content increases. This result confirms that FA content dominates the surface properties. The contact angle of the polyurethane is slightly higher than that of the cationic fluoro copolymer. This result may be due to higher molecular weight and more compact surface structure of the polyurethane than those of the cationic fluoro copolymer. The molecular weight and surface structure may be important variables that significantly influence the surface properties of the polymer.

The effect of annealing on the contact angle for the cationic fluoro copolymer can be also seen in Figure 7. In the case of FA content of <30 wt %, the contact angle for the cationic fluoro copolymer annealed at

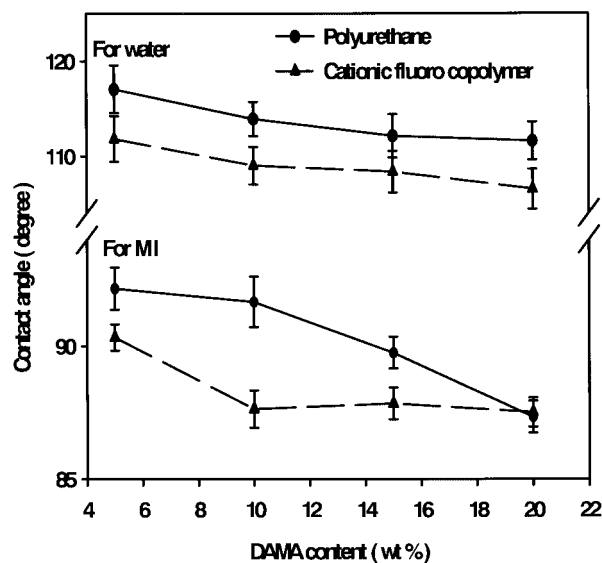


Figure 8 Variation of contact angle according to DAMA content (FA = 40wt %).

130°C for 3 min tends to be higher than that for the cationic fluoro copolymer without annealing. Annealing may enhance the migration of perfluoroalkyl group $[-COO(CH_2)_2(CF_2)_7CF_3]$ to the outermost surface of the cationic fluoro copolymer. The surface migration of perfluoroalkyl group may increase the contact angle by lowering the surface free energy. However, the contact angle between the two cationic fluoro copolymers shows no difference in the case of FA content of >40 wt %. It seems that the surface migration of perfluoroalkyl group is negligible for higher FA content >40 wt %. It is also evident from the results in Figure 7 that the FA content should be >40 wt % to obtain a cationic fluoro copolymer and polyurethane with good surface properties (contact angle for water > 110°; contact angle for MI > 80°).

To investigate the effect of DAMA content on surface properties, the contact angles were measured for the cationic fluoro copolymers and the polyurethanes prepared by varying DAMA content with a constant FA content of 40 wt % (HEAM content varies with DAMA content). The results are illustrated in Figure 8. DAMA was used to endow quaternized amino group $[-COO(CH_2)_2N^+(CH_3)_3COOH]$ to the cationic fluoro

copolymer and the polyurethane. The quaternized amino group may enhance the adhesion ability of polymer to substrates such as ceramic, glass, wood, concrete, tiles, and plastics. The contact angles for both water and MI tend to decrease gradually for the cationic fluoro copolymer and the polyurethane as DAMA content increases. To use higher DAMA content is not desirable for the preparation of polymer-coating materials with good water-and-oil repellency. Because the adhesion of polymer-coating materials to substrate is an important property, DAMA content should be optimized to develop polymer-coating materials with good adhesion property as well as good water repellency. The cationic fluoro copolymer and the polyurethane with DAMA content of 5–20 wt % show excellent water and oil repellency (contact angle for water > 108°; contact angle for oil > 87°).

The surface free energies estimated from the contact angle data shown in Figures 7 and 8 are summarized in Tables I and II, respectively. The cationic fluoro copolymer and the polyurethane with FA content of 40 wt % and DAMA content <30 wt % show extremely low surface free energies of 13–15 dyn/cm. These results indicate that the cationic fluoro copolymer and the polyurethane may exhibit excellent water and oil repellency.

CONCLUSION

The cationic fluoro copolymer and its polyurethane with perfluoroalkyl and quaternized amino groups were successfully prepared from the monomers of FA, DAMA, and HEMA. The contact angles for both water and MI on the cationic fluoro copolymer and its polyurethane increase steadily as FA content increases. FA content used in the synthesis is the most important variable for surface properties of the polymers. The contact angle of the polyurethane is slightly higher than that of the cationic fluoro copolymer. This difference may be due to higher molecular weight and more compact surface structure of the polyurethane than those of the cationic fluoro copolymer. Annealing may enhance the migration of perfluoroalkyl group to the outermost surface of the cationic fluoro copolymer. The contact angles for both water and MI for the

TABLE I
Surface Free Energies of Polymers as a Function of FA Content

Polymer	Weight Ratio of Monomers Used FA/DAMA/HEMA				
	10/70/20	20/60/20	30/50/20	40/40/20	50/30/20
Cationic fluoro copolymer	21.9	20.1	17.1	16.0	13.4
Cationic fluoro copolymer annealed	19.4	18.4	17.0	15.9	13.2
Polyurethane	18.0	16.7	16.6	14.8	13.0

TABLE II
Surface Free Energies of Polymers as a
Function of DAMA Content

Polymer	Weight Ratio of Monomers Used (FA/DAMA/HEMA)			
	40/5/55	40/10/50	40/15/45	40/20/40
Cationic fluoro copolymer	12.7	14.0	14.0	14.4
Polyurethane	11.8	12.1	12.9	14.0

cationic fluoro copolymer and the polyurethane tend to decrease gradually as DAMA content increases. The cationic fluoro copolymer and the polyurethane with FA content of 40 wt % and DAMA content of <30 wt % show extremely low surface free energies of 13–15 dyn/cm.

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