

Synthesis and characterization of fluorine-containing polyurethane-acrylate core-shell emulsion

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ABSTRACT: Fluorinated polyurethane-acrylate (FPUA) hybrid emulsion was prepared by copolymerization of polyurethane, methyl methacrylate, and 1*H*,1*H*,2*H*,2*H*-heptadecafluorooctyl acrylate (FA) via emulsion polymerization in the presence of a perfluorinated reactive surfactant. The polyurethane was synthesized from isophorone diisocyanate, poly(propylene glycol)-1000, dimethylolpropionic acid, 1,4-butanediol, and 2-hydroxyethyl methacrylate. The influence of the monomer on the surface properties, wetting behaviors, particle size, and viscosity of the emulsion was investigated. The mechanical properties of FPUA latex films were improved, and water absorption and contact angle were improved with the addition of methyl methacrylate and FA. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43357.

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INTRODUCTION

Waterborne polyurethanes (PUs) have been widely used in many fields such as elastomers, fibers, coatings, and adhesives.^{1–3} Coatings based on these systems witnessed satisfactory mechanical properties.² In addition, the hardness and flexibility of these films could be balanced by selectively varying the compositions of hard and soft segments.^{4–6} However, they have drawbacks, such as weak water resistance and limited outdoor durability,⁷ which limit their scope of applications in certain aspects.

Acrylic polymer emulsions could yield water-repellent films resistant to weathering, due to the presence of a chemically stable backbone.⁸ Therefore, it is rather imperative to integrate these features into PUs by preparing PU/acrylic hybrid emulsions.

Fluorinated polymers have been characterized by a series of interesting properties, such as environmental stability, self-lubrication, water/oil repellency, biocompatibility, thermal stability, chemical resistance, and low surface free energy.^{9–13} PUs could also be functionalized via introduction of fluorine-containing chemicals, and properties similar to other fluorinated polymers could thus be expected to result.^{9,11} Hydrolytic, thermal, and oxidative stability were promoted, and improved permeability to oxygen was identified.^{14–16} The surface of these fluorinated PUs became less adhesive to foreign substances upon direct contact.¹⁷

To introduce fluorine into functionalized PUs, three components were primarily attempted previously: fluorinated soft segments of PUs, fluorinated hard segments of PUs, and fluorine-containing acrylate.^{18–21} In this paper, the third strategy was reconsidered to introduce fluorinated groups via emulsion polymerization.

During preparation of a fluorine-containing PU emulsion, a reactive fluorocarbon emulsifier was considered as a substitute for a conventional fluorocarbon emulsifier such as perfluorooctanoic acid ammonium (PFOA) or perfluorooctanesulfonic acid (PFOS). The polymerizable emulsifier could be chemically bonded to the PUs to avoid long-term leaching, and it is therefore more environmentally friendly than conventional emulsifiers. In addition, since the PU emulsion was dispersed in water via self-emulsification, the preparation of fluorinated polyurethane-acrylate (FPUA) emulsions could be considered as a soap-free emulsion polymerization.^{22,23} Transmission electron microscopy (TEM) was used to observe the morphology of PU and FPUA emulsions, and the results showed that fluorine could aggregate onto the surface of FPUA particles during the formation of the core-shell structure.

In this paper, several FPUA core-shell emulsions were prepared by free-radical copolymerization of methyl methacrylate, perfluoroalkyl ethyl acrylate, and PU macromonomers terminated by 2-hydroxyethyl methacrylate. The structures and properties

of FPUA emulsions and latex films were characterized by a laser particle size analyzer, TEM, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, contact angle goniometry, and a mechanical universal tester.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was supplied by Bayer Company (Leverkusen, Germany). Poly(propylene glycol) (PPG-1000) and poly(tetramethylene oxide) glycol (PTMG-1000) were supplied by Kabitechemical of Shanghai, China. Dimethylolpropionic acid (DMPA), *N*-methyl-2-pyrrolidone (NMP), triethylamine (TEA), and 1,4-butanediol (BDO) were supplied by Aladdin Reagents (Shanghai, China). Dibutyltin Dilaurate (DBTDL), 2-Hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) were supplied by Sinopharm Chemical Reagent Co (Shanghai, China). Perfluoroalkyl ethyl acrylate (FA; $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$) was purchased from AGC Chemicals Trading Co. (Shanghai, China).

Perfluoro(4-methyl-3,6-dioxaoct-7-ene) sodium sulfonate (PSVNa) was synthesized in our lab.

PPG and PTMG were dried at 90°C under 0.1 mm Hg for 3 h prior to use. IPDI, BDO, TEA, DBTDL, and HEMA were dried with 4-Å molecular sieves for 72 h prior to use. DMPA was dried and degassed at 120°C under 1–2 mm Hg for 8 h prior to use. MMA was distilled under reduced pressure.

Preparation of Polyurethane Dispersion

The PU prepolymer was synthesized in a four-neck glass reactor equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a pressure-equalizing dropping funnel in a thermostatic oil bath. PPG was added into the reactor followed by dropwise addition of IPDI and DBTDL (0.02 wt % based on the overall mass of IPDI and PPG), and the mixture was kept at 75–80°C for 1 h. BDO was then added, and the temperature was kept constant for another 1 h. The DMPA solution in NMP was added dropwise into the mixture slowly, and the mixture was stirred at the same temperature for about 3 h additionally. When the prepolymer solution was cooled down to 40°C, HEMA was added slowly, and the reaction was performed for 1 h. Eventually, the PU dispersion was obtained by mixing these PU prepolymers with an aqueous solution of TEA at a high shearing rate.

Preparation of Fluorine-Containing Polyurethane–Acrylate Core–Shell Emulsion

Polymerization was performed in the same four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a pressure-equalizing dropping funnel with a nitrogen gas inlet. A series of fluorinated polyurethane–acrylate hybrid dispersions were prepared by copolymerization of PU, FA (2.5–12.5 wt %), and MMA (10–40 wt %) in the presence of PSVNa as an emulsifier. PSVNa served as a reactive surfactant that could be chemically bonded to FPUA, and therefore the resulting FPUA emulsion was environmentally friendly, free of byproducts of fluorocarbon emulsifier. Emulsion polymerization was also performed in the presence of ammonium perfluorooctanoate (APFO) as a control for comparison purposes. The core–shell emulsion was

initiated by $\text{K}_2\text{S}_2\text{O}_8/\text{NaHSO}_3$ at 60°C and polymerized for 3 h, and the total conversion of MMA and FA was 98%.

Characterization

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) spectra were recorded on a MAGNA-IR550 FTIR spectrometer (Nicolet, Madison, WI). For each sample, 32 scans at a 4 cm^{-1} resolution were collected in absorption mode.

Particle Size and Its Distribution. The particle size and particle size distribution of PU and FPUA hybrid emulsions were measured with photon correlation spectroscopy on a Malvern Zetasizer 3000 HS (Malvern, United Kingdom). The samples were diluted to a designated concentration with distilled water prior to measurement. Each sample was measured twice.

Transmission Electron Microscopy. The samples for TEM were prepared by diluting the emulsion in an aqueous medium with pH = 7.4 followed by ultrasonication and collection with copper grids. The morphology was visualized with a JEOL 1400 TEM (Tokyo, Japan) after negative staining with phosphotungstic acid, and the image was recorded on a charge-coupled device camera.

Mechanical Properties. PU and FPUA films were prepared by pouring the freshly prepared emulsion into clean poly(tetrafluoroethylene) molds followed by setting at room temperature for 24 h. The films were then dried under vacuum by a gradient heating process and were finally kept at 60°C for 2 h in the oven.

The tensile properties of the samples were measured with a 3300 material testing machine from Instron Co. (Boston, MA) according to ISO 37-1994 under ambient temperature. The tensile speed was 200 mm/min.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was performed on a Q2000 differential scanning calorimeter (TA Instruments, New Castle, DE). The heat flow was recorded at heating rate of 10°C/min from –70 to 150°C.

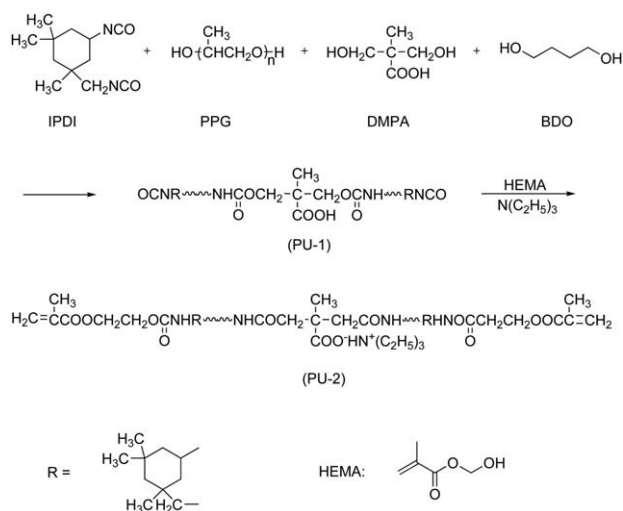
Wetting Behavior and Mechanical Properties of the Polymer Films. Contact angles were measured on a JC-2000A contact angle goniometer at room temperature (20°C), and the results reported were averaged over five replicates.

The films were cut into the dimensions of $30 \times 30\text{ mm}$, and the pieces were weighed as m_1 , the dry mass. Then the pieces were soaked in water for 24 h at 25°C and weighed as m_2 , the hydrated mass. The water absorption of the films can be calculated with the formula $S(\%) = [(m_2 - m_1)/m_1] \times 100\%$.

The mechanical properties of the polymer films were measured at 25°C on an AGS-J Table-top Type Universal Tester (Shimadzu, Japan) under tensile mode.

RESULTS AND DISCUSSION

During preparation of the waterborne PU dispersion (Scheme 1), despite serving as a chain extender, DMPA introduced the hydrophilic groups (carboxyl groups) into PU. Under high-speed stirring, the carboxyl groups combined with water to achieve the self-emulsification of PU. TEA was added to neutralize 90% of



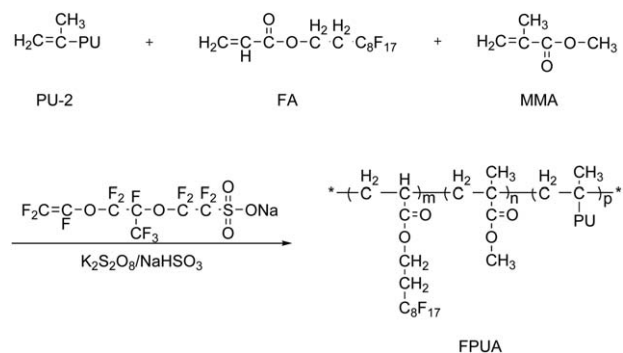
Scheme 1. Preparation of water-based PU.

the carboxyl groups, and the remaining 10% could crosslink in the resulting emulsion, which was advantageous in improving the mechanical properties of the FPUA latex films. The HEMA was added to introduce polymerizable methacrylate into PU so that the PU prepolymer could be polymerized with MMA and FA by a free-radical mechanism. In the final FPUA polymer, the soft segment is composed of PPG, while the hard segment is composed of the other reactants, including MMA and FA.

In recent years, the use of PFOS has been challenged by increasing restrictions, and most of its substitutes for emulsion polymerization have been achieved by limiting the length of their perfluorocarbon chains.^{1,3,8} But those substitutes could not completely avoid contaminating of the environment, especially in their long-term service periods. The reactive surfactant used in the emulsion polymerization (Scheme 2) could be chemically bonded onto the fluorinated polyurethane-acrylate macromolecule to achieve self-emulsification in water. Therefore, the fluorine-containing monomers would never leach to the environment and thus are environmentally friendly.

The structure evolution of the FPUA during its synthetic procedures was verified by FTIR, as shown in Figure 1.

Figure 1 presents representative FTIR spectra of IPDI, PU prior to methacrylation (PU-1), methacrylated PU by HEMA (PU-2), and FPUA, in which absorption bands at 2900–3000 cm^{-1} for stretching of the C—H bond were mostly used for reference.



Scheme 2. Preparation of FPUA emulsion.

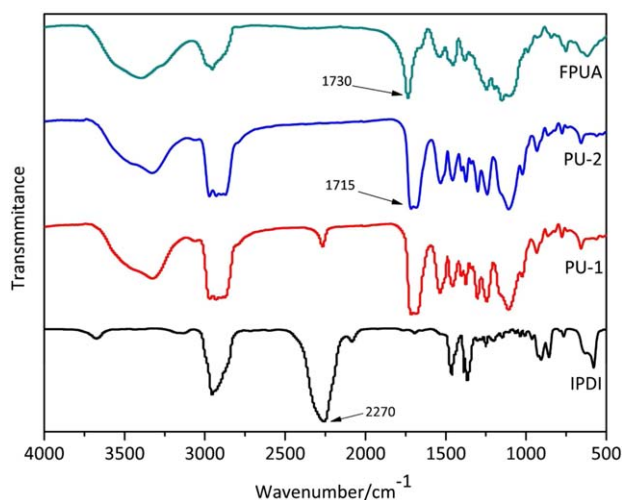


Figure 1. FTIR spectra of IPDI, PU before end-capping (PU-1), PU terminated by HEMA (PU-2), and FPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The absorption band of the —NCO group at 2270 cm^{-1} was prominent in the spectrum of IPDI. For PU-1, however, the absorption band of the —NCO group declined dramatically in intensity, while the absorption corresponding to the stretching vibration and bending vibration of N—H in urethanes at 3300 cm^{-1} and 1537 cm^{-1} emerged respectively. The absorption bands corresponding to the stretching vibration of C=O in urethane at 1690 cm^{-1} and C=O in DMPA at 1715 cm^{-1} were also observed. In addition, an absorption band at 1110 cm^{-1} originating from C—O—C in PPG also confirmed the formation of prepolymer of PU.

The successful synthesis of PU-2 could be substantiated by the disappearance of the absorption band of the —NCO group at 2270 cm^{-1} , indicating a complete end-capping reaction with HEMA. In the spectrum of FPUA, the absorption band at 1730 cm^{-1} was characteristic of C=O in (meth)acrylate. In addition, a series of absorption bands associated with the C—F bond were identified. For example, characteristic bands of —CF₂ in acrylates at 1243 cm^{-1} and C—C of perfluoroalkane at 1199 cm^{-1} were prominent in the spectrum of FPUA. The absorption bands at 708 cm^{-1} and 656 cm^{-1} originated from —CF₂ and —CF₃, respectively. Based on the above results from FTIR, fluorine was successfully introduced into PU by fluorinated acrylate, and the structure of fluorinated polyurethane was confirmed as expected.

Particle Size and Distribution Analysis

Figure 2 presents the particle size distribution of FPUA prepared by two different emulsifiers. The FPUA hybrid emulsion prepared by PSVNa was smaller in size and narrower in distribution than that prepared by PFOA. Therefore, PSVNa performed better as an emulsifier in emulsion polymerization in the current system of interest. These results indicated that PSVNa could perform the same as PFOA in emulsion polymerization.

To investigate the effect of the reactive surfactant on the emulsion polymerization in the presence of fluorinated monomers, a series of emulsions with conventional fluorinated surfactant

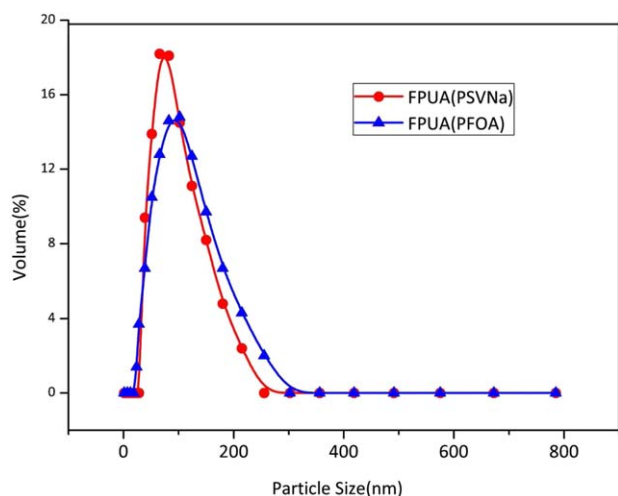


Figure 2. Particle size and distribution of FPUA emulsion with different emulsifiers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(PFOA) were compared in terms of their properties, as tabulated in Table I. The results showed that the single-component emulsifier did not contribute to a significant difference in particle size, viscosity, and storage stability of the FPUA emulsion.

Compared to the dual-component emulsifier with Sodium dodecyl sulfate (SDS), however, the viscosity and particle size of the FPUA emulsion prepared by the single-component emulsifier PSVNa were slightly larger. But this did not affect the stability of the emulsion and its application. Therefore, PSVNa was identified as a qualified substitute for PFOA.

Transmission Electron Microscopy

The morphology of PU and FPUA (containing 10 wt % FA) emulsions was visualized by TEM, as shown in Figure 3. The diameters of the PU particles were less than 100 nm. When fluorine was grafted onto the PU polymer, the microspheres exhibited a core-shell structure in bright-field TEM images, as shown in Figure 3. After negative staining with phosphotungstic acid, the cores of the FPUA particles presented the same dark color as the PU particles in Figure 3, whereas the shells of the FPUA particles were lighter in color. It has been reported that during the preparation of fluorine-containing emulsion, fluorine tended to aggregate in the cores of the latex particles due to its hydrophobicity.⁹ This phenomenon, however, indicated that a core-shell structure has been successfully prepared, and fluorine aggregated onto the surface of FPUA particles during formation of the core-shell structure. Therefore, during the subsequent formation of the FPUA latex films, a majority of fluorine could

Table I. Effect of Fluorinated Emulsifier on FPUA Emulsions

Fluoroemulsifier	MMA/FA/PU (w/w/w)	Particle size (nm)	Distribution	Viscosity (mPa s)	Storage stability (months)
PSVNa	20/10/70	80.3 ± 0.43	0.34	85.2 ± 2.95	≥6
SDS/PSVNa	20/10/70	77.8 ± 1.15	0.36	80.7 ± 1.03	≥6
PFOA	20/10/70	85.0 ± 0.84	0.36	87.9 ± 0.73	≥6
SDS/PFOA	20/10/70	74.7 ± 0.31	0.31	81.5 ± 0.37	≥6
PSVNa	20/5/75	71.1 ± 0.46	0.34	77.0 ± 1.47	≥6
SDS/PSVNa	20/5/75	68.4 ± 0.34	0.34	64.4 ± 0.31	≥6
PFOA	20/5/75	69.4 ± 0.23	0.32	65.2 ± 0.87	≥6
SDS/PFOA	20/5/75	66.7 ± 0.29	0.34	61.7 ± 1.0	≥6

All emulsions were prepared under the same conditions.

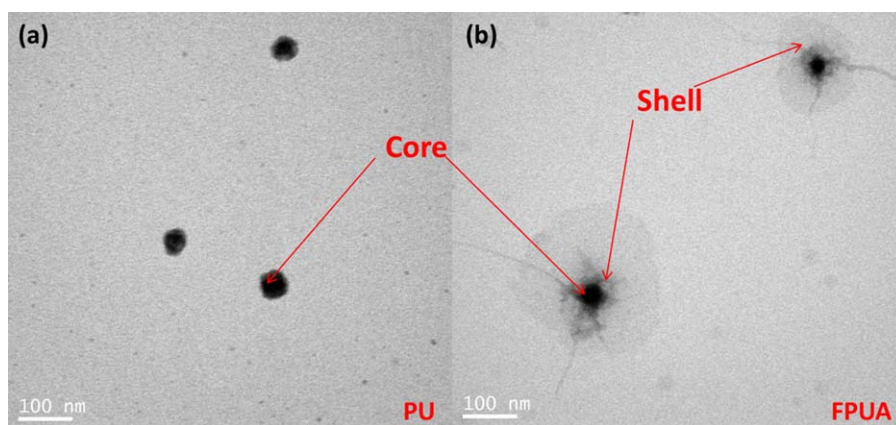


Figure 3. Bright-field TEM images of PU and FPUA emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

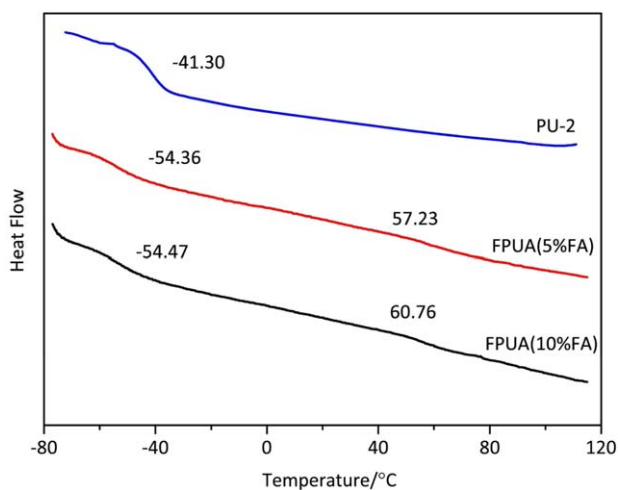


Figure 4. DSC curves of PU and FPUA with different FA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be enriched on the surface of the films, and the enrichment of fluorine could help to improve the water resistance of those films.

Differential Scanning Calorimetry

The DSC diagrams of PU and FPUA are presented in Figure 4. Glass-transition temperatures (T_g) were observed on all of the heating diagrams. In the presence of FA and MMA, the FPUA latex film experienced two glass transitions, and the T_g of the soft segment dropped from -41.30°C to -54.36°C . That could

be contributed to the micro-phase-separated structure promoted by the introduction of fluorine.

When the content of FA increased, the T_g of the soft segment of FPUA remained unaltered, while the T_g of the hard segment increased by over 3°C . That is because the increase of fluorine content lead to the enhancement of hydrogen bonding interactions between fluorine and $-\text{NH}$.

Wetting Behavior and Mechanical Properties of the Latex Films

In order to assess the performance of varied soft segments, PTMG was selected for comparison with PPG (Table II). Given that the other conditions were identical, FPUA latex films containing PPG were less hydrophilic than those containing PTMG, but their tensile strength was superior to that of PPG, although the toughness was slightly lower yet high enough to meet the requirements. These differences in properties could be attributed to the branched methyl groups on PPG, which have a great influence on the mechanical properties of the latex films.

The effect of DMPA concentration on PU emulsion and FPUA films is summarized in Table III and Table IV, respectively. With DMPA concentration increasing from 2.0 wt % to 5.0 wt %, the particle size decreased dramatically, and the storage period increased from less than 1 month to more than 6 months. The dispersion of PU in water was highly dependent on the hydrophilic carboxyl groups, which were closely associated with the concentration of DMPA. As the concentration of the hydrophilic groups increased, the average diameter decreased, and the emulsion became more stable.

Table II. Surface and Mechanical Properties of the FPUA Latex Films with Varieties of Soft Segments

Soft segment	MMA/FA/PU (w/w/w)	Contact angle ($^\circ$)	Water absorption (%)	Breaking elongation (%)	Tensile strength (MPa)
PTMG	20/10/70	93.6 ± 0.32	10.12 ± 0.61	485.3 ± 26.9	7.32 ± 0.44
PPG	20/10/70	101.7 ± 0.19	3.6 ± 0.07	450.9 ± 11.0	12.5 ± 0.32
PTMG	20/5/75	81.9 ± 0.92	15.7 ± 0.53	547.0 ± 23.6	6.84 ± 0.67
PPG	20/5/75	98.9 ± 0.57	5.3 ± 0.21	485.2 ± 18.7	10.3 ± 0.28

Table III. Effect of DMPA Concentration on PU Emulsion

DMPA (wt %)	Particle size (nm)	Distribution	Viscosity (mPa s)	Storage stability (months)
2.0	313.6 ± 16.9	0.87	89 ± 2.10	≤ 1
3.0	138.9 ± 4.5	0.16	75 ± 0.91	≤ 3
4.0	51.8 ± 0.43	0.12	63 ± 0.38	≥ 6
5.0	45.6 ± 1.32	0.10	58 ± 0.56	≥ 6

Table IV. Effect of DMPA Concentration on FPUA Films

DMPA (wt %)	MMA/FA/PU (w/w/w)	Contact angle ($^\circ$)	Water absorption (%)	Breaking elongation (%)	Tensile strength (MPa)
4.0	20/10/70	101.7 ± 0.19	3.6 ± 0.07	450.9 ± 11.0	12.5 ± 0.32
3.5	20/10/70	104.2 ± 0.61	3.1 ± 0.34	470.4 ± 14.9	10.2 ± 0.76
3.0	20/10/70	107.7 ± 0.49	2.9 ± 0.22	548.3 ± 36.5	9.5 ± 2.50

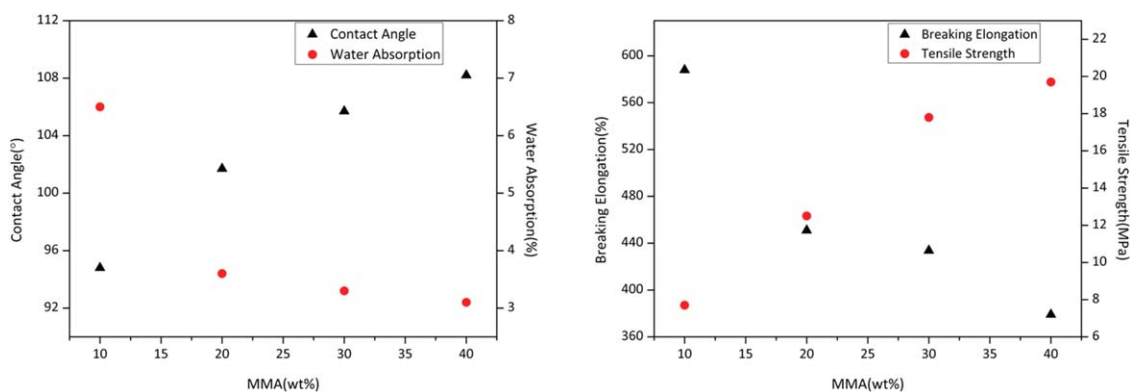


Figure 5. Surface and mechanical properties of the FPUA latex films with varied MMA concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Given that the other conditions were identical, the contact angle of FPUA films declined when the concentration of DMPA in FPUA films increased, due to the presence of an increasing amount of hydrophilic groups. The increasing concentration of DMPA also contributed to an increasing proportion of hard segments, so the tensile strength of FPUA with 4.0 wt % DMPA was the highest among all.

Considering the properties of PU emulsion and FPUA films, 4.0 wt % DMPA was an optimized option.

The effect of MMA concentration on the surface properties of FPUA films is presented in Figure 5. When the concentration of MMA increased from 10 wt % to 40 wt %, the contact angle of the film was improved from 94.8° to 108.2° . The water absorption of the film became lower. This phenomenon could be explained by the presence of more hydrophobic groups with increasing MMA concentration.

The effect of MMA concentration on the mechanical properties of FPUA films is also presented in Figure 6. The tensile strength increased from 7.7 MPa to 19.7 MPa with increasing MMA concentration. This could be explained as the improved compatibility between MMA and PU, which is due to the presence of stronger hydrogen bonding. Therefore, the introduction of MMA segments should be considered as the cause of the improved tensile strength of the FPUA films, due to the higher concentration of the hard segment.

The effect of the FA level on the surface and mechanical properties of FPUA latex films is presented in Figure 6. With increasing FA concentration from 0 wt % to 12.5 wt %, the contact angle increased from 28.7° to 105.8° , indicative of improved hydrophobicity of the films. The improved water absorption from 11.5% to 3.2% also confirmed the argument. Compared to FPUA, PUs were lower in tensile strength. However, the elongations at break were relatively higher in FPUA. The increase of fluorine concentration may promote hydrogen bonding, and the proportion of hard segments of FPUA is more than that of PU.

CONCLUSIONS

Environmentally friendly FPUA latex films with hydrophobic surface properties and improved mechanical properties were prepared by copolymerization of methyl methacrylate, FA, and PU via free-radical emulsion polymerization, and a reactive fluoro-carbon surfactant was attempted as an emulsifier. The results of FTIR and TEM performed on these systems indicated that the core-shell structure had been generated as expected, and the fluorine preferentially aggregated on the surface of the films. In addition, a micro-phase-separated structure between hard segments and soft segments to some extent was speculated from DSC.

PPG was confirmed to be an ideal soft segment compared to PTMG when side groups were considered. The mechanical

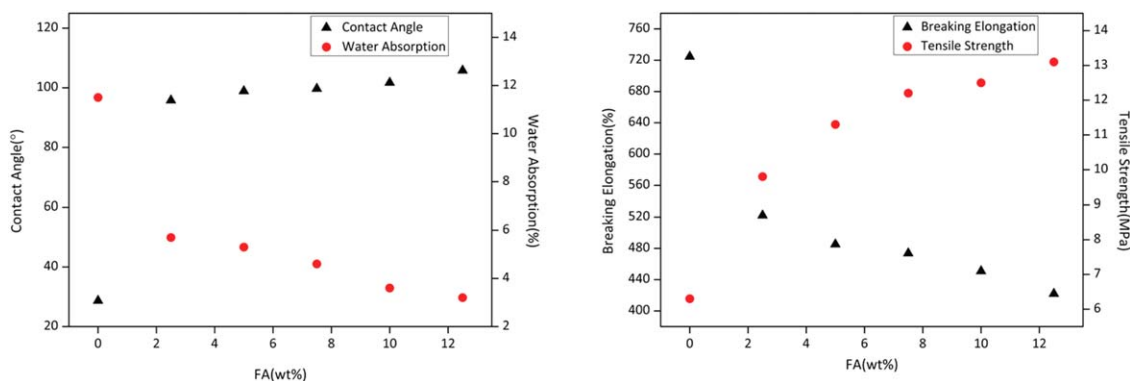


Figure 6. Surface and mechanical properties of the FPUA latex films with varied FA concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties and surface properties of FPUA latex films were improved dramatically upon the introduction of fluorine, and the concentration of DMPA was considered as the primary cause of this change. The introduction of MMA and FA performed well in improving the properties of FPUA latex films, and the films could have great potential to be commercialized in various coating applications.

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