

Water Repellency of Water-Base-Pigment Inkjet Ink Containing Amphiphilic Copolymers

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Emulsions of comb-like copolymers having hydrophilic and hydrophobic sidechain were used as a binder and water-repellency modifier in waterbase-pigmented inkjet inks. Methyl methacrylate (MMA) and styrene (St) were copolymerized with polyethyleneglycol methacrylate (MPEGMA) as a hydrophilic sidechain, and polydimethylsiloxane methacrylate (PDMSMA), perfluorooctylethyl methacrylate (PFOM), or polypropyleneglycol methacrylate (MPPGMA) as a hydrophobic sidechain. The inkjet inks mixed with these polymeric emulsions could be printed by a piezo-driving inkjet printer. Water repellency of the printed images was tested via static and dynamic contact angle measurement. The results showed that the water repellency of the inks could be significantly improved by the introduction of the copolymer having high hydrophobic segment of PDMS or perfluoroalkyl group, which they adsorbed and oriented to the surface of the printed images.

Keywords: comb-like copolymer, hydrophobic/hydrophilic sidechain, dynamic contact angle, static contact angle, water repellency

1. INTRODUCTION

Inkjet, a digital printing system is being used widely e.g. home user, general business, and graphic art. The ink used in inkjet technology is water-based, which poses certain problems, so there have been enormous improvements in ink chemistry. Because the limitation of the ink component which the ink contains not only much of water, and water-like solvent, but also very small amount of other ink agent, therefore the ink properties tend to be near that of the water and the inkjet-print matter has poor waterfastness [1]. By the early 2000s most inkjets used dye-based color inks and pigment-based black, pigment-based color inks are also developing for inkjet, especially in graphic art technology, because the pigment-ink type provides superior advantage in waterfastness, lightfastness, and overall fastness. For pigmented ink, any pigments need the additional use of polymeric materials, known as binders, to encapsulate the pigment particle and form ink film adhered on the surface. Unfortunately, an inkjet system has seriously limitation of ink particle size (0.1 to 0.5 μm , preferably) and viscosity (1 to 15 mPa s, depending on jet system), because all inks must pass through a jet nozzle without nozzle clogging. Polymeric emulsion is used mostly as a binder because it achieves low viscosity and good adhesion on printing substrate. Vehicle of inkjet ink is made up of large amount of water mixed with polyhydric alcohols such as glycol compounds, glycerol, and so on. From the reason as mentioned above, the ink film of inkjet print has low water resistance when compared to other printing systems. Water repellency of print image means that the image has poor water wetting when it contacts to water, for providing a durable print image.

In our prior works [2-7], we have studied on the surface molecular mobility of the copolymers composed of hydrophilic and hydrophobic sidechains, or so called

amphiphilic copolymer, used as a functional polymer, and applied them in some applications such as a surface-active agent, a biocompatibility material, an adhesive agent, and so on.

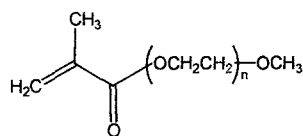
In this work, we aimed to apply the amphiphilic comblike copolymers as emulsions added into aqueous inkjet ink, which were used as a binder of the ink, in order to improve water repellency of an inkjet image. The emulsions were copolymerized by changing hydrophobic sidechains of polydimethylsiloxane methacrylate (PDMSMA), perfluorooctylethyl methacrylate (PFOM), and polypropyleneglycol methacrylate (MPPGMA), including a hydrophilic sidechain of methoxy (polyethylene glycol) methacrylate (MPEGMA), and polymer backbones of methyl methacrylate (MMA), or styrene (St). These polymeric emulsions were mixed into aqueous-pigment-based inkjet ink, and then printed on a commercial-grade paper. Since the hydrophobic segment of the copolymers orient towards the print surface when the ink film was completely dried, providing water repellency to the print surface. Water repellency of the printed images was determined via water contact angle measurement by Wilhelmy plate method (surface dynamic, DCA) [8], and drop method (the static contact angle measurement).

2. EXPERIMENTAL

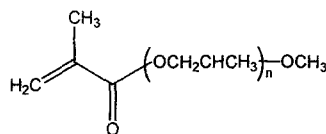
2.1 Materials

Chemicals: Methyl methacrylate (MMA), and styrene (St) [Wako Pure Chemical Industries Ltd. Japan] were purified according to a general rule before using. Macromonomers of methoxypolyethyleneglycol methacrylate (MPEGMA, $n = 20$) [Aldrich Chemical Co., Inc., USA] was used as received. Macromonomer of methoxy (polypropylene glycol) methacrylate (MPPGMA, $n = 16$) was prepared by esterification of

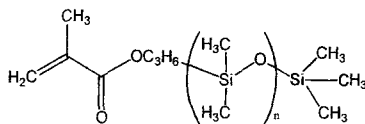
methoxy (polypropyleneglycol) [Nihon Nyukazai Corporation, Japan], and methacrylic acid (Aldrich Chemical Co., Inc., USA). Polydimethylsiloxane methacrylate (PDMSMA, repeating unit of siloxane; $n = 24$) was supplied by Shin-Etsu Chemical & Industry Co., Japan, and perfluorooctylethyl methacrylate (PFOM) was supplied by Dainippon Ink and Chemical Corporate, Japan. Chemical structure and surface tension of the macromonomers were shown in Figure 1. The monomers and macromonomers mentioned above were emulsified prior to emulsion polymerization via anionic and nonionic emulsifiers of poly (oxyethylene) polycyclic phenyl ether sulfuric acid ester salt (Newcol-707SF supplied by Nippon Nyukazai Co.), and ethylene oxide/propylene oxide/ ethylene oxide triblock copolymer (Pruronic-F68, MW=8350; Asahi Denka Kogyo Co.), respectively.



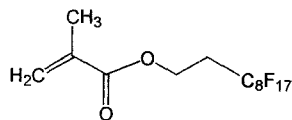
(a) Methoxy (polyethyleneglycol) methacrylate,
Surface tension, γ^a at 25 °C = 43 mN/m



(b) Methoxy (polypropyleneglycol) methacrylate,
Surface tension, γ^b at 25 °C = 31 mN/m



(c) Polydimethylsiloxane methacrylate,
Surface tension, γ^c , at 25 °C = 22 mN/m



(d) Perfluorooctylethyl methacrylate,
Surface tension, γ^d at 25 °C = 14.1 mN/m

Figure 1 Chemical structure and surface tensions of (a) MPEGMA: γ^a [9], (b) MPPGMA: γ^b [9], (c) PDMSMA: γ^c [9], and (d) PFOM: γ^d [10]

Pigment: The pigment used in this study was SP Blue 6447 (Fuji Pigment Co., Japan), which blue pigment dispersed with a low molecular weight surfactant in the aqueous medium containing 7 wt% of glycerin. Mean particle size of the pigment dispersion was approximately 0.1 μm .

2.2 Methodology

Emulsion Polymerization: Polymeric emulsions synthesized in this study were MMA/ MPEGMA/

MPPGMA, MMA/ MPEGMA/ PDMSMA, MMA/ MPEGMA/ PFOM, St/ MPEGMA/ PFOM, and St/ MPEGMA/ PDMSMA. Feeds of the co-monomers were adjusted until getting fine particles and low viscosity emulsions, which suited for applying to inkjet inks. Emulsion polymerization was carried out with a polymerization recipe (see Table I) by the dropping method according to our previous work [9]. Ammonium peroxodisulfate, and 1-dodecanethiol were used as an initiator, and a chain-transfer agent, respectively. The synthesized emulsions were measured the plain properties as follows; non-volatile content according to JIS K6828, mean particle size using a laser light scattering analysis instrument (SALAD-2000), and compositions by $^1\text{H-NMR}$ (Varian 400 NMR, frequency 400 MHz).

Table I Emulsion polymerization recipe

Chemical	Amount (g)
Ion exchange water	120
Monomer mixture	100
Emulsifier	1.5
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	1.0
$\text{C}_{12}\text{H}_{25}\text{SH}$	1.0

Purification of emulsions: To determine the composition by $^1\text{H-NMR}$ and surface property (DCA), the polymeric emulsions were purified by salting out process. Step of the salting out process were, first, pouring a saturated NaCl aqueous solution into the emulsions, and then stirring at 100 °C for 2 hours or until emulsion coagulation occurred completely, rinsing the coagulated polymer product by non-ionic water, and then drying it in vacuum for 2 days.

Composition by $^1\text{H-NMR}$: The purified emulsions from the above procedure were dissolved up to 1 wt% in a CDCl_3 solution with TMS standard (Chloroform-D, D99.8%, Cambridge Isotope Laboratories, Inc.), and then were brought to record $^1\text{H-NMR}$ spectra. The compositions were determined by using ester methylene signal (approximately 4.32 ppm) assigned to MPEGMA, ester methine signal (approximately 4.46 ppm) assigned to MPPGMA, ester methyl signal (approximately 0.14 ppm) assigned to PDMSMA, and ester methine signal (approximately 4.67 ppm) assigned to PFOM.

Preparation of emulsion inks: Inkjet inks were prepared by mixing SP Blue 6447, 2 wt%, and the synthesized emulsions, 4 wt%, together with the other ingredients, i.e., deionized water, ethylene glycol (EG), 20 wt%, and polyethyleneglycol monocytlether ($n=23$), 0.5wt%. The inks were adjusted to pH ~8 by NaOH, 0.1 M, and stirred by a magnetic stirrer for 30 min. The inks were filtered through a syringes filter (pore size = 0.8 μm .) before printing.

Inkjet printing: The inkjet printer used in this study was PM-740DU, a piezoelectric drop-on-demand machine (Epson Corp., Japan), printing on a kind of two-sidedness bond paper (business multipurpose paper,

Xerox co.) with a resolution of 1440 dpi. After printing, the printed papers were baked at 150°C for 1 hour for removing high boiling point cosolvents: GLY in SP Blue 6447, and EG, from printed ink film in order to determine contact angle of the printed image without any effect of GLY, and EG.

Surface dynamic (DCA): The synthesized copolymers and the printed papers were measured by the Willhelmy plate method [8] using DCA20 (Orientec). Standard liquid was deionized water and the dipping velocity was 20 mm/min in both advancing, and receding contact angle. Specimens for the DCA were prepared as follows: glass plates (20 mm wide, 50 mm length, 1.3 mm thickness) were dipped into 15wt% of benzene solutions of the copolymers, (using acetone or chloroform in some cases), and then the glass plates were dried in a vacuum oven at 90 °C for 3 days. Specimens of the printed papers for the DCA were prepared by making the printed papers into a size of 20 mm wide, 50 mm length, and 0.35 mm thickness, with two-printed sides.

Static contact angle of water on printed images: The water was dropped onto the image through a tiny needle at R.T. (20°C). The contact angles were determined by measuring the dimensions of the water drop. The contact angle (θ) was calculated by following equation:

$$\theta = 2 \tan^{-1} (h/r) \quad (1)$$

where h represents the height of the water drop, and r represents the radius of the drop base

Time dependence of water contact angle on printed images: The contact angle of water drops as function of times on the printed images was determined. Change in the static contact angle (θ) of a water drop on a printed image was measured every 10 min until the drop was completely absorbed into the paper.

X-ray photoelectroscopy (XPS) measurement: Surface of the printed images was analyzed C_{1s} , O_{1s} , Si_{2p} , and F_{1s} by X-ray photoelectron spectrometer (Shimadzu ESCA 3400) using Mg $K\alpha$ X-ray source and operated at 10kV, and 20mA. A take off angle of photoelectron was 90 deg allowing the depth of 10nm, approximately, for analyzing.

3. RESULTS AND DISCUSSION

3.1 Emulsion polymerizations of the copolymers and ink property

The copolymer emulsions, which were synthesized for mixing into the inks as a binder and modifier of water repellency of them, are shown in Table II. The copolymers of MMA/ MPEGMA/ MPPGMA, MMA/ MPEGMA/ PDMSMA, MMA/ MPEGMA/ PFOM, St/ MPEGMA/ PFOM, and St/ MPEGMA/ PDMSMA were denoted as MP, MS, MF, SF, and SS, respectively. The group of copolymers having MMA as a polymer backbone had the composition close to the feed contents. Since styrene was difficult to copolymerize with MPEGMA, and PFOM, therefore SF, and SS copolymers (see Table II) had low content of MPEGMA, PFOM or PDMSMA. The emulsion products

copolymerized without the hydrophilic MPEGMA sidechain as MS 50, MF50, and SF 50 emulsions had a relatively large median particle size approximately 5 μ m. The presence of MPEGMA at the contents about 5 to 15 wt% in the copolymer formulation of emulsions resulted in small size emulsions approximately 0.2 μ m. The interfacial free energy is defined as the minimum amount of work required to create unit area of the interface: $W_{\min} = \text{interfacial tension} \times \text{area of the interface}$ [11]. Since in the process of emulsion copolymerization, the synthesized copolymers having hydrophilic MPEGMA segment could be adsorbed to the interface between the emulsion particles and the aqueous media so as to minimize its interfacial free energy, resulting in small particle size. Consequently, the emulsions having MPEGMA had smaller size than those of the emulsions without MPEGMA. However, since the addition of exceed amount of MPEGMA caused particle coagulation (the data does not be shown in Table II), the synthesized emulsion could not be applied to the inkjet ink.

The cyan inks mixed with the polymeric emulsions had viscosity at 25°C in the range of 2 to 2.5 mN/m, and surface tension in the range of 57-59 mN/m, which are suitable for a piezoelectric drop-on-demand inkjet printer, and for ink drop formation, respectively. The emulsion inks made of the small size emulsions (smaller than 0.2 μ m as shown in Table II) could be easily ejected through an inkjet nozzle. The ink coverage of the images printed using these inks on paper surface observed by naked eyes was about 97 to 100%, except MS 50, MF50, and SF 50 inks, which could not be printed through an inkjet printhead due to containing large particles.

3.2 Dynamic contact angle (DCA) of the copolymers

The copolymers casts on the glass plates were measured dynamic contact angle (DCA) in order to determine their own surface property. On DCA measurement, the advancing contact angle (θ_a), receding contact angle (θ_r), and the contact angle hysteresis ($\theta_a - \theta_r$) were determined. θ_a could be obtained in the process of immersing the sample plate into the liquid (water) in order to measured wet ability of the surface and θ_r could be obtained in the emersion out process.

Figure 2 shows a plot of dynamic contact angles (DCA) of water on the different copolymers against the hydrophobic sidechain content of the copolymers. The data of the SS copolymers were not plotted on the figure because they were undissolved in any solvents used in casting process. The values of the hydrophobic sidechain contents plotted on the figure were the data of polymer contents calculated from $^1\text{H-NMR}$ spectra shown in Table II except the SF copolymers, which the PFOM contents plotted on the graph were the feed monomer contents as shown in Table II. Figure 2 shows that the advancing contact angles (θ_a) for the MS, MF, and SF copolymers having low surface free energy segment of PDMSMA or PFOM were independent of the sidechain content, and the surfaces of these copolymers exhibit a large advancing contact angle even if they had a low content of them. Because the hydrophobic segments of the perfluoroalkyl group, which had surface tension of

Table II Composition, non-volatile contents, and particle size of the polymeric emulsions

Polymeric emulsions	Feed content		Composition*		Non-volatile	Median
(Series names)	(wt%)		(wt%)		content** (%)	Particle Size***
						(micrometer)
MMA/MPEGMA/PDMSMA	MPEGMA	PDMSMA	MPEGMA	PDMSMA		
MS40	5	40	5	35	45	0.077
MS15	15	15	14	16	39	0.118
MS10	10	10	10	10	37	0.171
MS5	5	5	8	6	50	0.167
MS50	0	50	57	43	45	5.197
MMA/MPEGMA/PFOM	MPEGMA	PFOM	MPEGMA	PFOM		
MF40	5	40	4	49	45	0.173
MF15	15	15	11	24	41	0.182
MF10	10	10	12	14	42	0.179
MF5	5	5	9	7	45	0.167
MF50	0	50	62	38	45.5	6.078
MMA/MPEGMA/MPPGMA	MPEGMA	MPPGMA	MPEGMA	MPPGMA		
MP40	5	40	9	35	55	0.184
MP15	15	15	7	14	37	0.173
MP10	10	10	4	11	38	0.088
MP5	5	5	30	23	50	0.179
St/MPEGMA/PFOM	MPEGMA	PFOM	MPEGMA	PFOM		
SF40	5	40	3	2	53	0.105
SF20	5	20	-	-	55	0.195
SF10	5	10	-	-	45	0.194
SF50	0	50	-	-	41	6.062
St/MPEGMA/PDMSMA	MPEGMA	PDMSMA	MPEGMA	PDMSMA		
SS40	5	40	-	-	47	0.122
SS20	5	20	0	12	48	0.161
SS10	5	10	-	-	44	0.143

- is for ‘not determined’ because they were not dissolved in CDCl₃

* Calculated based on ¹H-NMR ** Determined according to JIS K6828

*** Determined by laser light scattering analysis

14.1mN/m [10] for the surface completely covered with it, and the poly (dimethylsiloxane) segment (surface tension: 22 mN/m [9]) were predominated at the surface of these polymers even if those contents were not so much. Therefore, these segments were mainly contributed to the observed relatively large θ_a around 110 degrees. For the MP copolymers having MPPGMA sidechain, the θ_a increased with an increase in MPPGMA content in the region where the content was more than 20 wt%. Since surface tension of polypropylene glycol (PPG, surface tension: 31mN/m [9]) was not so low, it could not be predominated at the surface in its low content region. The surfaces of this polymer were constituted by the competitive adsorption of the segments.

Receding contact angles for all copolymers used showed very low value than advancing one. Generally, for multi-component polymeric system, θ_r showed lower value than θ_a , because the hydrophobic component adsorbed and oriented to water/polymer interface so as to minimize interfacial free energy. θ_r of the MF and MS copolymers increased with an increase of the PFOM, and PDMSMA contents, respectively. For the MF copolymers, θ_r increased from its initial value and reached a maximum value at 25 wt%, and θ_r of the MS

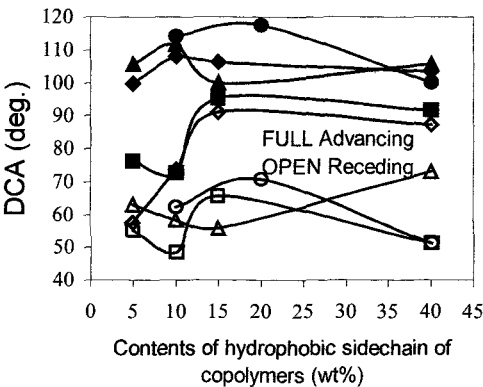


Figure 2 Plots of dynamic contact angles of water for the copolymers against contents of the hydrophobic sidechain of the copolymers: The circles, diamonds, triangles, and sqaures are for the SF, MF, MS, and MP copolymers, respectively.

copolymers increased with an increase in PDMSMA content in a region where the content was approximately more than 15 wt%. Considering on the SF and MP copolymers, the receding angles against the hydrophobic sidechain contents did not differ significantly. All of the copolymers exhibited large contact angle hysteresis

because of the hydrophilic PEG (polyethelene glycol) segments, which was adsorb and reorient into the copolymer/water interface as to minimize the interfacial free energy [2]. Other results of DCA for MMA/MPEGMA/ PDMSMA copolymer have been reported in our previous works.

3.3 X-ray photoelectron spectroscopy measurement on surfaces of the printed images

The inks mixed with the polymeric emulsions were denoted according to the name of the emulsion as follow; MP, MF, MS, SS, and SF inks represented the inks containing MP, MF, MS, SS, and SF emulsions, respectively. Table III shows atomic ratios of O_{1s} , F_{1s} , and Si_{2p} to C_{1s} in the ink bulk, and on the printed surfaces

and Si_{2p} to C_{1s} in the bulk and on the surface of the printed images. The depth of about 10nm of the printed image was measured via XPS. The values of atomic ratios of F_{1s} or Si_{2p} to C_{1s} on the printed images increased with an increase of PFOM or PDMSMA content (wt%) in the copolymers. For the printed images of SF40 and MF40 inks, atomic ratios of F_{1s} to C_{1s} were 0.49 and 0.47, respectively, and for SF10, and MF5, the values were 0.28, and 0.21, respectively. These values were very lager than that of bulk calculated with the formulation of the ink. It was clear that perfluoroalkyl group having extremely low surface free energy adsorbed and reoriented to the surface of the printed image. However, since the values must be 2.0

Table III Atomic ratios of O_{1s} , F_{1s} , and Si_{2p} to C_{1s} in the ink bulk, and on the printed surfaces

Samples and compositions	In bulk of the inks*			On surface of the printed images**			
	Atomic ratios to C_{1s}			Atomic ratios to C_{1s}			
	O_{1s}	F_{1s}	Si_{2p}		O_{1s}	F_{1s}	Si_{2p}
SF40 (95/3/2)	0.33	0.01	-	Baked print	0.19	0.49	-
SF10 (85/5/10)	0.34 [#]	0.02 [#]	-	Unbaked print	0.27	0.29	-
				Baked print	0.10	0.28	-
MF40 (47/4/49)	0.36	0.13	-	Baked print	0.35	0.47	-
MF5 (84/9/7)	0.42	0.01	-	Unbaked print	0.35	0.07	-
				Baked print	0.37	0.21	-
SS40 (52/5/40 and AA3wt%)	0.39 [#]	-	0.12 [#]	Baked print	0.31	-	0.14
SS20 (72/5/20 and AA 3wt%)	0.37 [#]	-	0.07 [#]	Unbaked print	0.31	-	0.12
				Baked print	0.26	-	0.10
MS40 (60/5/35)	0.40	-	0.09	Baked print	0.36	-	0.16
MS5 (86/8/6)	0.39	-	0.02	Unbaked print	0.45	-	0.12
				Baked print	0.37	-	0.11
MP40 (56/9/35)	0.12	-	-	Baked print	0.34	-	-
MP5 (47/30/23)	0.14	-	-	Unbaked print	0.34	-	-
				Baked print	0.35	-	-

*Calculated from the copolymer composition obtained by $^1\text{H-NMR}$ (see TableII), and the ink formulation

[#] Calculated from the copolymer feed content (see Table II), and the ink formulation

** Determined by XPS

if surface was completely covered with perfluoroalkyl group, about 25% and 12% of surface area were covered with it for SF40, and MF40 inks and SF10, and MF5 inks, respectively. On the other hand, for the printed images of SS40, and MS40, the atomic ratios of Si_{2p} to C_{1s} were 0.14, and 0.16, respectively, and for SS20, and MS5, the values were 0.10, and 0.11, respectively. These values were also very lager than that of the bulk calculated with the ink formulation. It was also clear that PDMS segemnt having very low surface free energy, adsorbed and oriented to the surface of the printed image. However, since the values must be 0.5 if surface was completely covered with PDMS segment, 20%, and 22% of surface area were covered with it for SS40 and MS40 inks, and SS20 and MS5 inks, respectively. From the results, it was shown that some hydrophobic segments, having low surface free energy, adsorbed and oriented to the image surfaces printed with the inks prepared in this

study. However, these surfaces could not completely covered with hydrophobic segments and other relatively hydrophobic hydrocarbon segments coexisted in them.

3.4 Dynamic contact angle (DCA) of the printed images

Figure 3 shows the plots of DCA of water on the images printed by the emulsion inks against contents of the hydrophobic sidechain of the copolymers. The advancing contact angle (θ_a) for the printed image of each emulsion ink: SS, SF, MS, MF, and MP ink, was independent of the hydrophobic sidechain content, but the different emulsions exhibited different θ_a . This was due to the adsorption of the hydrophobic segment that had very low surface free energy to surface as shown via XPS measurement. Johnson and Dettre [12] reported that hydrophobic component contributed to θ_a and hydrophilic one to θ_r . The images printed with the ink of

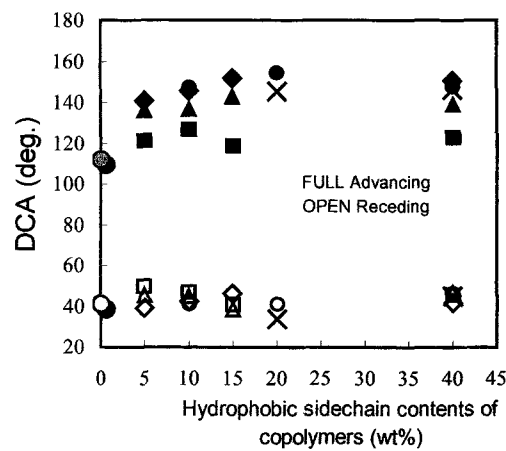


Figure 3 Plots of dynamic contact angles of water for the images printed with the emulsion inks against contents of the hydrophobic sidechain of the copolymers: The circles, diamonds, triangles, cross, and squares are for the SF, MF, MS, SS, and MP copolymers, respectively.

the emulsions having PFOM (SF and MF inks) showed the very high values of θ_a around 150 degree. This result suggested that the roughness of the paper surface effected to increase in θ_a . The MP inks showed the relatively low θ_a around 120 degree. Surface tension of 31 mN/m for hydrophobic segment (PPG) of MP copolymers was significantly higher than that of SF and MF copolymers. The ink without emulsion (see at 0 wt% on Figure 3) showed the lowest θ_a approximately 110 degree. It was shown that when these emulsions mixed into the inkjet ink formulation, the hydrophobicity of the printed surface was largely enhanced, and the copolymers having the more hydrophobicity provided the more water repellency to the printed surface. The receding contact angle (θ_r) of all printed images showed an approximately constant value, and very low values than θ_a . If the surface was entirely covered with PDMS or perfluoroalkyl group, not only θ_a showed high value but also θ_r showed relatively high value. As shown XPS measurement, the coverage of surface with hydrophobic segments was less than 25%. Therefore, the hydrophilic PEG segment easily oriented to water/printed image interface to reduce θ_a . It should be noted that, since a paper is a heterogeneous material composed of many chemical additives and its surface character is non-uniform, rough, and porous, so that the exact base area was difficult to measure and there was some variance in the data. In addition, as mentioned above, the contact angle measurement is sensitive to surface roughness, which the roughness factor (r) induced to enhance apparent contact angle (θ) from true contact angle (θ_o), thus it is well known that the roughness of a hydrophobic solid enhances its hydrophobicity [13]. However, in this case, it must be considered that the rough and porous structure on paper surface. Since when advancing the water over the printed paper to measure θ_a , the porous on paper surface was filled with the water, therefore the water- filled porous on paper surface caused low receding contact angle.

The hysteresis of contact angle was very large, which was affected by roughness of paper surface. It was well

known that the contact angle measurement is sensitive to surface roughness. The basic conclusion is that as roughness increases, the hysteresis increases; the advancing angle ($\theta > 90^\circ$) increases with increasing roughness and the receding angle ($\theta < 90^\circ$) decreases with increasing roughness. Since a paper surface has roughness therefore it caused high advancing angle, and very low receding angle, resulting in very large hysteresis. Generally, it was required for complete water repellency that not only high θ_a , but also θ_r must be showed the higher value than, at least, 100 degree. However, as these inks had very high θ_a higher than 130 degree in spite of low θ_r , it was expected to have the significant water repellency. Therefore, we tried to examine the durability of water repellency for these inks by the sessile contact angle measurement.

3.5 Static contact angle of water on the printed images

The emulsion inks were printed on papers. And then the static contact angles of water on the unbaked and baked printed surfaces were measured to examine water wetting, complementary to the matter of water repellency of the printed images. The contact angles of water for the different emulsion inks printed on papers showed some significant difference as shown in Table IV.

Table IV Static contact angles of water on the images printed by the emulsion inks

Emulsion inks	Contact angle (deg)	
	Unbakes print	Baked print
Paper base	104	123
Ink without emulsion	87	97
MS40	118	129
MS15	122	130
MS10	120	126
MS5	120	126
MF40	114	133
MF15	105	129
MF10	113	140
MF5	98	121
MP40	103	112
MP15	102	114
MP10	98	101
MP5	81	101
SF40	117	140
SF20	117	134
SF10	112	128
SS40	126	131
SS20	112	127
SS10	113	125

Table IV shows the contact angle of water drops on the printed images printed by the emulsion inks. The water contact angles tend to increase with increasing of hydrophobic sidechain from the content of 5wt% to the content of 40wt% especially the MP ink, except the values of the MS ink shows a approximately constant value. All image printed by the emulsion inks show larger water contact angle than those of the image printed by the ink without emulsion, it means that the

emulsion inks has capability to improve water repellency of the printed image. The MP inks provided relatively low water contact angles, in other words, the images printed with the MP ink had poor water repellency, which was worse than that of the paper base. On the contrary, the inks having the low surface free energy segment of PDMSMA or PFOM as MS, MF, SF, and SS inks exhibited relatively large water contact angles. The water contact angles of the baked print images were larger than those of the unbaked print images, since the unbaked print image still had hydrophilic agents of EG and GLY remaining in the ink film, causing reduction of the water contact angle. For the ink film without the water-soluble cosolvents of EG and GLY, the emulsion inks could provide a high water repellent image with the water contact angle about 130 to 140 degree.

3.6 Dependence of static water contact angle on the printed images on emulsion contents

MS40 inks were made up by changing the contents of MS40 emulsion as follows: 0%(ink without emulsion), 2%, 6%, 8%, 14%, and 20% based on total weight of the ink, the inks were printed on a paper, and contact angles of water drops on these printed images were measured. The water contact angles on the printed images plotted against the contents of the emulsion in inks is shown in Figure 4. The water contact angle increases from the contents of 0wt% and reached a maximum value at 2 wt%, and then shows a constant value from 2 wt% to 20 wt%. Since the PDMSMA has low surface free energy (high hydrophobicity), therefore it exhibits high water contact angle even if the ink contains low content of MS emulsion. We suppose that the result for other inks containing PFOM, having low surface free energy than PDMS of MS copolymers, might show as same as the result of MS40 ink. For the printed image of MP ink,

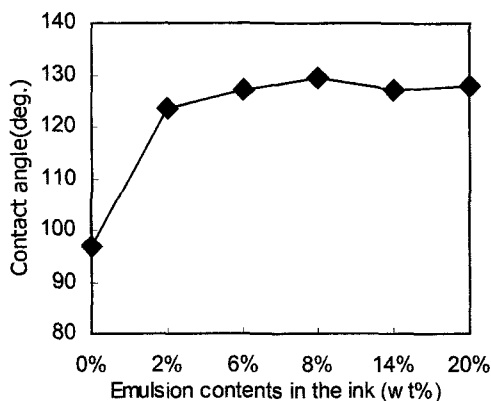
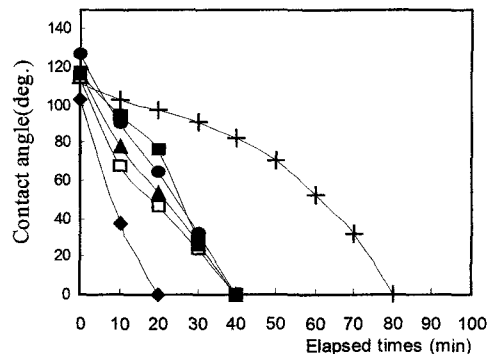


Figure 4 Dependence of static contact angles of water on the printed images on emulsion contents in the ink (testing by MS40)

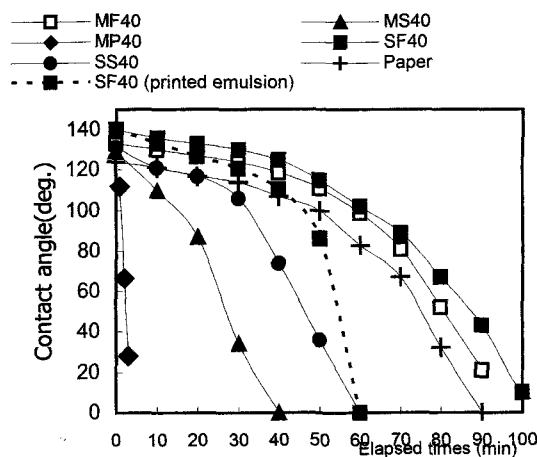
the water contact angle might increase when contents of the MP emulsion in the ink increase. From this result, it was suggested that water repellency of the pigment ink could be significant improved by the introduction of these copolymer emulsions.

3.7 Static water contact angles as function of time on the printed images

In order to examine the durability of water repellency for the printed image, we tried to measure the variance of contact angle with time after putting water on it. Figure 5 (a) and (b) show the plots of the contact angle of water as function of times on the printed images unbaked and baked, respectively. Degree of water repellency of a printed image was shown by characteristic of the curves. For water repellency, it was required to maintain the contact angle larger than 100 degree.



(a) unbaked print images



(b) baked print images

Figure 5 Plots of static contact angles of water on the printed images against elapsed time

Figure 5 (a) shows that the water contact angle on the printed images decrease immediately after putting water on the surface and reach to a 0 angle within 40 min. The durations of water repellency of the unbaked print images could not be observed and were less than that of the paper base. Generally, in drying process of water-borne system, surface was constructed by two factors. That is; (1) the lowest surface free energy component selectively adsorbed and oriented to surface and (2) the hydrophilic component could be migrated to surface with evaporating water and remained near the surface layer. Since EG and GLY remained in the unbaked ink film surface layer, attracted water molecules, it caused rapid spreading for a water drop on the image. Figure 5 (b) shows that the printed image of SF40, and MF40

inks provided a long duration of water repellency and the contact angles were maintained the values larger than 100 degree for more than 60 min, which was longer than those of the paper base and the printed images of SS40, MS40, and MP40 ink. The sequence of the water repellency of the printed images is SF40 > MF40 > SS40 > MS40 > MP40.

In order to determine water repellency of the polymeric emulsion without any effect of the pigment of the ink, the polymeric emulsions of SF40, SS40, MF40, MS40, and MP40 were diluted with deionized water at 2wt% and were printed on a paper by the inkjet printer. And then the printed emulsions were tested water contact angles as function of time as the result was shown in Figure 6. Figure 6 represents the plots of static contact angles of water on the printed emulsions against elapses time, which the sequence of water repellency of the printed emulsion is SF40 > MF40 > SS40 > MS40 > MP40. For SF and MF copolymers, the contact angles larger than 100 degree were maintained for 40 min.

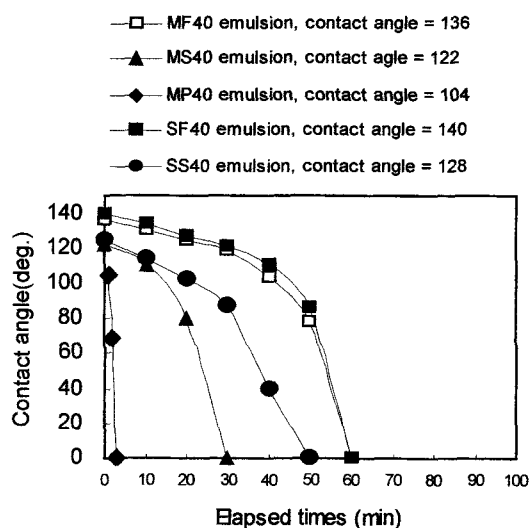


Figure 6 Plots of static contact angles of water on the printed emulsions against elapsed time

The water repellency duration of the images printed with the pigmented inks as shown in Figure 5 (b) was longer than that of the printed emulsions as shown in Figure 6. As these copolymers were very soft and had high molecular mobility, their durability of water repellency was not so long in spite of their high hydrophobicity. For SF and MF inks, the hydrophilic segments such as PDMS and perfluoroalkyl group could be adsorbed and oriented to surface by the baking, resulting in very hydrophobic surface. In emulsion inks, copolymers, including added emulsion, also acted as the binder for the pigment. The particles of pigments, which were rigid and hydrophobic, could be bound each other by the binder copolymer in the mixture of ink to make the rigid hydrophobic surface. The pigment particles restricted the mobility of copolymer and reinforced the ink composite. That is: the particles also act as the filler. It was clear that the copolymer emulsions synthesized, containing the low surface free energy side chain such as PDMS and perfluoroalkyl group, could give the water repellency of the printed image effectively. Whereas the

copolymer composed of hydrophobic sidechain of MPPGMA affected the less water repellency to the printed image because surface free energy of PPG segment was not so low as PDMS and perfluoroalkyl group.

4. CONCLUSION

The emulsions of the amphiphilic copolymers composed of the low surface free energy segment of PDMS or perfluoroalkyl group introduced into the aqueous-pigment inkjet ink could provide good water repellency to a printed image which it had a high water contact angle, more than 100 degree for 1 hour, although they were added at a small amount in the ink formulation. The hydrophobic segments were absorbed and oriented to the printed-image surfaces, however these surfaces could not be completely covered with them. The introduction of emulsion into the pigmented ink, which the pigment particles restricted the mobility of copolymer and reinforced the ink composite, enhances water repellency to the printed image of an inkjet printing system.

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