

Polymer Emulsion for Thermal Ink Jet System

T. Tsutsumi, M. Sawada and K. Azuma

*Kao Corporation, Materials Development Research Laboratories
Wakayama, Japan*

Abstract

Polymer emulsion is very useful for inkjet inks because it can treat media surface at the same time of printing and improve the print durability and then enlarge the application of inkjet printer. But for the thermal inkjet system, polymer emulsion is likely to make aggregates by heating of the ejection and make serious kogation on the heater. To avoid this thermal problem, heat stable polymer emulsion is necessary.

In this paper, several kinds of polymer emulsion are investigated for thermal inkjet inks and low molecular polyester emulsion, polyacrylamide emulsion, and acrylic polymer emulsion with silicone graft side chain are found to show good heat stability for thermal inkjet systems. Especially, the introduction of silicone graft side chain improves the heat stability of the polymer emulsion with only 10% modification and is favorable for further polymer designing.

Introduction

Polymer emulsion is a set of small particles of polymer, which disperse in a fluid stably, and has unique feature different from polymer solution; it can make a water-fast hard film when dried and show very low viscosity in spite of high molecular weight of polymer. This technology has been applied to many industrial fields, such as water-based paints, paper coating, and water-based adhesion. For ink jet application, Yao, Croucher, and we reported the usage of polymer emulsion containing dye as a colorant, which could make waterfast and sharp print on the porous media.¹⁻³ And the use of polymer emulsion for UV curable ink⁴ and textile printing⁵ were also proposed.

To eject ink droplet, there are two ink jet systems. One is piezoelectric ink jet and the other is thermal ink jet. Because the piezoelectric ink jet pen ejects ink droplets mechanically, ink requirements are not so strict as those for thermal ink jet system. Thermal ink jet inks must have enough heat stability not to make kogation on the heater. The water-soluble dye based inks had well researched about the heat stability⁶ and obtains very high ejection reliability for actual commercial usage. But the heat stability of polymer emulsion was not researched well and most of the investigated emulsion inks are designed for piezoelectric ink jet system.

The present work was undertaken to investigate the polymer emulsion for thermal ink jet system. The generation process of kogation with the acrylic polymer emulsion was studied. And several kinds of kogation free polymer emulsion were proposed.

Experiment

There are several technologies to make polymer emulsion such as emulsion polymerization technology, phase inversion emulsification technology, and mechanical emulsification technology. Among these emulsion technologies, we take the mechanical emulsification technology because it can be applied to very wide range of polymer without surfactant. Polymer emulsion with this technology was made as follows;

Polymer Synthesis

Acrylic polymers were synthesized by solution polymerization with MEK solvent. A quarter of mixed solution of monomers, mercaptoethanol, and 2,2'-Azobis(2,4-dimethylvarelonitrile) was pored into the nitrogen purged separable flask and heated to 75°C. The rest of the mixed solution and MEK was dropped into the flask with a dropping funnel over a period of three hours and polymerized at 75°C. After the droplet of all monomer solution, polymer solution was heated to 80°C and added a small amount of initiator for running out of the monomer residue. The polymer compositions used for the experiment were listed in Table 1.

Table 1. Polymer Compositions.

	Composition	Mw
Polymer 1	t-BMA/AA=85/15	12,000
Polymer 2	n-BMA/AA=85/15	12,000
Polymer 3	n-BA/AA=85/15	12,000
Polymer 4	t-BMA/AA/DAAAm*=55/15/30	12,000
Polymer 5	t-BMA/AA/M-4F*=75/15/10	12,000
Polymer 6	t-BMA/AA/FM-0711*=75/15/10	12,000
Polymer 7	Polyester	3,000

*DAAAm : Diacetone acrylamide

M-4F: tetra-Fluoroethyl methacrylate

FM-0711: Polydimethylsiloxy methacrylate (Mw=1000)

Polyester was synthesized by conventional method. 105g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl) propane, 35g of maleic acid, and 0.2g of hydroquinone were

reacted in the separable flask at 210°C under a nitrogen stream while removing produced water. The reaction was stopped when the softening point of the polymer reached 107°C. The obtained polyester had an acid value of 31 KOHmg/g.

Emulsion Preparation

Two grams of oil soluble phthalocyanine dye (C.I. Solvent Blue 70) and 18g of the synthesized polymer were dissolved to the mixed solvent of toluene (30g) and MEK (30g). Sodium hydroxide and 150g of deionized water were added into the polymer solution and emulsified with the ultra-sonic emulsifier for 15 minutes keeping the temperature under 30°C. The emulsified mixture was set to the evaporator and solvent was removed. And the mixture was condensed to 15wt% of solid. The physical properties of polymer emulsions used to this experiments were listed in table 2.

Table 2. Physical Properties of Polymer Emulsions.

Emulsions	Viscosity (mPa.s)	pH	Diameter (nm)	S.T. (mN/m)
Emulsion 1	4.54	8.19	92	33.7
Emulsion 2	4.21	8.06	94	34.2
Emulsion 3	4.67	8.09	96	34.1
Emulsion 4	6.04	7.69	88	33.7
Emulsion 5	4.23	8.09	99	33.4
Emulsion 6	3.71	8.26	91	34.5
Emulsion 7	3.93	8.63	82	36.2

Heat Stability Test and Analyses

The thermal heater, which was separated from BJ-10Vlite ink cartridge (Canon Inc.), was dipped into 10% polymer emulsion and put 10,000 electronic pulses to the heat resistor. After the kogation test was ended, the thermal heater was washed with water and made further analysis. Three-dimensional microscopic analysis of the heater surface was made with the laser microscopic analyzer VK-8500 (Keyence Corp.). The kogation residue on the heater was corrected by dissolving into DMF (dimethylformamide) solvent and used for GPC analysis.

ESCA analysis of the polymer film surface was examined with PHI-5400 (Ulvac-phi.Inc.).

Results and Discussion

Kogation of Polymer Emulsion

Heat stability is the indispensable property of inks for thermal ink jet system. So the kogation tests of the polymer emulsion were carried out. Figure 1 shows the photographs of the ink jet heater before and after the kogation test. As shown in the photograph, Polymer Emulsion 1 made serious kogation on the heater. The thickness of the kogation was about 0.4 μm (Figure 2). A part of the kogation residue was solved into acetone but the rest was not solved even with DMF. Kogation residue was observed in less than 10 firing counts and its height was almost no change through the

kogation test except for the irregular partial exfoliation. The height of the acetone insoluble kogation residue was gradually increased after 1,000 firing counts and decreased to make a flat glossy surface after 100,000 firing counts. The acetone soluble part of kogation residue at 1,000 firing counts was collected (by repeating 50 times) and a GPC analysis of that residue was made. Small amount of very high molecular weight portion was found (Figure 3).

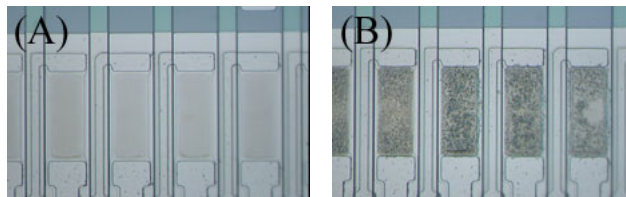


Figure 1. Photographs of the heater surface (A) before and (B) after kogation test of Polymer Emulsion 1.

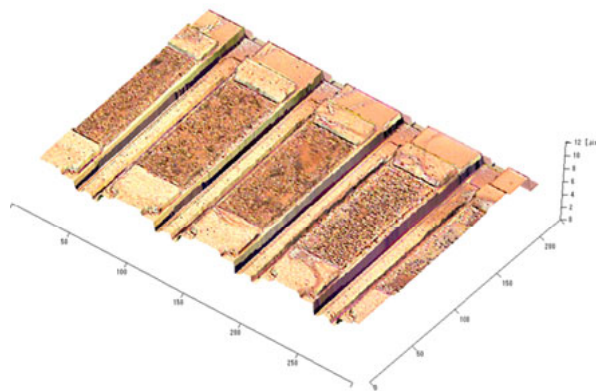


Figure 2. 3-D analysis of the heater surface.

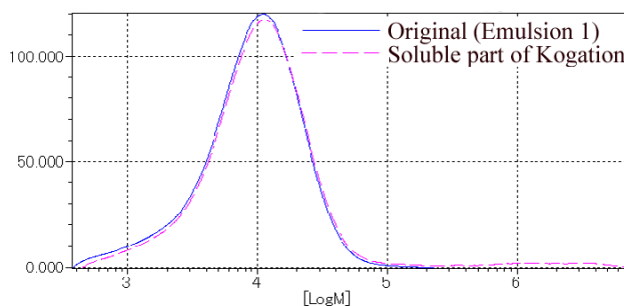


Figure 3. GPC analysis of soluble part of kogation residue.

From these results, the polymer emulsion was suggested to make aggregates on the heater surface by superheating or cavitation of the bubble from the beginning of the firing. The aggregated polymer emulsion repeated the exfoliation and generation for some period, and the deposit of the heater surface became cross-linked by further heating.

The thermal decomposition of acrylic polymer is known very complicated because several kinds of primary reaction occur simultaneously. But almost of the reaction was known to occur with radical intermediates. In the reaction of the polymer kogation on thermal ink jet heater, these radical intermediates would be the cause of the highly cross-linked polymer deposit. The control of the cross-linking reaction of the polymer would be important to prevent the polymer kogation.

Tg of Emulsion Polymer

Methacrylic polymer is known to decompose at lower temperature than acrylic polymer because of the presence of α -methyl unit. The kind of alcohol in the ester unit of acrylic polymer was also known to differ the decomposition temperature.⁷ The physical property of the polymer at high temperature depends on the glass transition temperature (Tg). Then the kogation test of three kinds of analogous polymer emulsion with different Tg was examined (Emulsion 1,2,3). The heights of the kogation residue of these polymer emulsions were almost the same (Figure 4). In the range of this experiment, the increase of polymer Tg could not improve the heat stability of the polymer emulsion. The fluid on the heater surface was thought to be heated over 300°C,⁸ if the polymer emulsion had Tg over 300°C, the heat stability might have been improved.

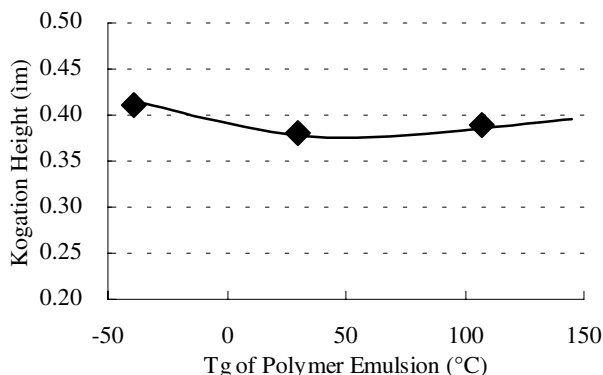


Figure 4. Kogation height of the Polymer Emulsion 1,2,3.

Less Cross-Linking Polymer Emulsion

To improve the heat stability of the polymer emulsion, we examined the polymer emulsion having less cross-linking property. Comparing with (meth)acrylic polymer, polyacrylamide derivatives were thought thermally stable because they had not α -methyl unit and easily degradable ester unit. So the polyacrylamide emulsion (Emulsion 4) was investigated. As shown in Figure 5, Emulsion 4 made almost no kogation on the heater.

Calculated Tg of the Emulsion 4 was 101°C, which was between Tg of Emulsion 1 and that of Emulsion 3. Though the mechanism of heat stability of polyacrylamide was not clear, the replacement ester unit with amide unit would reduce the probability of cross-linking reaction and consequently the exfoliation, which was caused by the

bubble cavitations, became superior. Polyacrylamide derivatives seemed to be one solution for applying polymer emulsion to thermal ink jet system.

Decomposable Polymer Emulsion

Polyester has the ester bond in the polymer main chain and is hydrolyzed when heated with water. Hydrolysis of polyester is a problem for applying it to water-based polymer emulsion, however decomposition with the heat was thought to be favorable for kogation problem. As we would expect, polyester emulsion showed good result on kogation test (Figure 5). The molecular weight of polyester emulsion was not changed after the ejection from the thermal ink jet pen. Therefore the amount of the hydrolyzed polyester was seemed very small.

Aggregates of polyester emulsion would be hydrolyzed on the heater surface without cross-linking and disappeared from the heater surface. Polyester emulsion was thought to be another answer for thermal inkjet printer. Actually, some polyester derivatives, not emulsion but hyper-branched oligomers, had already commercialized for the ink jet application.⁹

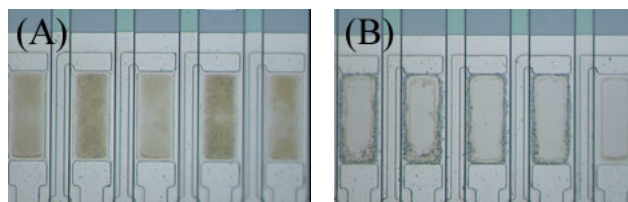


Figure 5. Photographs of the kogation residue of polyacrylamide emulsion (A) and polyester emulsion (B).

Less Adhere Polymer Emulsion

As another approach to prevent kogation of the polymer emulsion, less adhesive polymer design was tried. Generally on the design of the polymer molecule, polyfluoroalkyl and silicone unit are well used to make the polymer less adhere and easily repelled from the substrate. So fluoro polymer emulsion (Emulsion 5) and silicone grafted polymer emulsion (Emulsion 6) were investigated in expectation that these polymer emulsion come off from the heater surface before the cross-linking reaction occurs. As shown in Figure 6, introduction of alkyl fluoride into the polymer molecule was not effective for the kogation test but the silicone grafting was found to be effective.

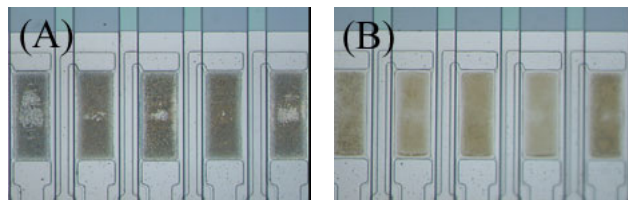


Figure 6. Kogation residue of fluoro polymer emulsion (A) and silicone grafted polymer emulsion (B).

Both the polyfluoroalkyl and silicone units are known to reduce the surface energy of the polymer surface and make the polymer less adhesive. To understand the difference of the kagation result of these polymer emulsions, ESCA analysis of the polymer films was examined. Table 3 shows the atom compositions of the film surface made at different two temperatures. Silicon ratio of silicone grafted polymer emulsion was relatively high comparing with the calculated atom ratio and became higher with the increase of the treated temperature. Fluorine ratio of fluorinated polymer emulsion was also high comparing with the calculation, but the dependence of the treated temperature was much smaller than that of silicone grafted polymer emulsion. Silicone grafted polymer emulsion would reduce the surface energy effectively at high temperature by migrating silicone side chains to the polymer surface. The ability of the polymer emulsion to come off the heater surface was thought to depend on the interfacial energy between polymer and the heater. The difference of the surface energy between these polymers at high temperature would be the results of kagation tests. And the morphology of the polymer would be important for thermal stability because the graft chain can migrate easily from the polymer matrix. Silicone grafted polymer emulsion was concluded to be suitable for thermal ink jet system.

Table 3. ESCA Analysis of the Polymer Surface.

Film sample	C%	O%	N%	Si%	F%
Emulsion 5	69.0	20.3	1.1	-	9.6
Emulsion 5 (Annealed 150°C)	67.1	19.8	0.9	-	11.2
Emulsion 6	66.5	21.8	1.2	10.6	-
Emulsion 6 (Annealed 150°C)	61.4	22.6	0.8	15.3	-

Conclusion

This paper discussed the heat stability of several kinds of polymer emulsion for the thermal ink jet system. Polymer emulsion made kagation by aggregation on the heater and cross-linking subsequently while dropping off from the heater competitively. Simple polyacrylic emulsion did make a serial kagation independent of Tg. The control of cross-linking reaction of polymer was very important to improve the heat stability of polymer emulsion. To prevent kagation, three kinds of polymer emulsion were proposed; less cross-

linking polymer emulsion, decomposable polymer emulsion, and less adhere polymer emulsion. In the concrete, polyacrylamide emulsion did not show kagation because of its less cross-linking property. Polyester emulsion did not show kagation either because of its decomposable property. And silicon grafted polyacrylic emulsion had good heat stability because it could come off the heater before cross-linking reaction occurs. These polymers were thought to be suitable for thermal ink jet system.

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Biography

Takehiro Tsutsumi received his B.S. and M.S. in Synthetic Chemistry from University of Tokyo in 1989 and 1991 respectively. In 1991, he joined Kao Corporation and has been engaged in research and development of polymer emulsions. Since 1994, he has worked on ink jet colorants and inks.