

Polymerization of Fluoroacrylate and Guar Gum Copolymer as a New Pretreatment Paste for Ink-Jet Printing of Polyester

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ABSTRACT: A novel pretreatment paste containing fluoroacrylate copolymer and modified Guar Gum was carried out on the polyester fabric to provide partial water repellency and printability after inkjet printed with water-based disperse dye inks. The stable fluorinated pastes were prepared via miniemulsion polymerization of fluoroalkyl acrylates, styrene, 2-ethylhexyl acrylate, and modified guar gum in the presence of AIBN as initiator, CTAB and polyoxyethylene polyaryl ether as surfactants under suitable reaction conditions. In the analysis of monomer conversion and particle size, the highest polymerization rate with smallest particle size was obtained with increasing concentration of surfactants and initiator but the decreasing degree of substitution of guar gum to imply stronger inter-

actions between fluoroacrylate monomers, hydroxyl groups of modified guar gum and EO units of nonionic surfactants. The 30% of stock fluorinated paste with urea concentration of 6% provided the prints with highest K/S value, satisfactory edge acuity and least color difference between front and back sides of the fabric to show more transparency. The rating 80 of water repellency tested on the best treated polyester fabric demonstrated stain proof properties after sprayed with water and dried. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 705–712, 2009

Key words: fluoroacrylate; modified guar gum; polyoxyethylene polyaryl ether; miniemulsion; print transparency; water repellency; stain proof

INTRODUCTION

Unlike color paste preparation of conventional textile printing, the fabric is pretreated with thickening agents to demonstrate good print definition and optical density without bleeding when printed via inkjet method. The substrate pretreatment for inkjet printing either by surface coating or padding is low in formation viscosity, film thickness, and paste waste, which exists great opportunity in formulation design to be jetted for personalization demand.¹ Sublimation inkjet printing on polyester fabric is most widely applied in sign and advertisement industries due to quick color fixation with only heat and immediate product realization, e.g., flags, banners, display graphics, and etc. Usually, the inkjet printed polyester fabric is pretreated with commercially modified guar gum and remaining unsatisfactory color fastness to water or suffering from water-stain without wash-off.² The degree of substitution (DS) is utilized theoretically to characterize chemically modified guar gums to imply the number of hydroxyl group that were substituted with different derivatives in

order to alter their solubility and other characteristics. For example, hydroxypropylguar (HPG) provides the paste with nonionic charge while carboxymethylguar (CMG) and carboxymethylhydroxypropylguar (CMHPG) with anionic one.³

Accordingly, this work envisions the pretreatment paste or ink accepting film with lower surface energy to impart the property of water resistance by incorporating perfluoro alkyl moieties into the guar gum. Miniemulsion polymerization is preferred to prepare stable fluorinated acrylate copolymers due to complete particle nucleation and propagation in separate nanoreactor and improving the solubility of extremely hydrophobic fluoroacrylate in water.⁴ To prepare a water repellence treated polyester fabric that is ink jet printable, the paste formulation should be well optimized to permit ink droplets rapidly absorbed into the polyester fibers and retain colorants on the fabric surface without bleeding and mottle of the print pattern. The disperse dye inks have been applied according to the previous work with qualified water- and light-fastness as well as good jetting performance.⁵

The task of synthesizing fluoroacrylate and guar gum copolymer was done by miniemulsion polymerization of concentrated aqueous solution of fluorinated monomers with modified guar gum in the presence of 2,2'-azobisisobutyronitrile (AIBN), polyoxyethylene polyaryl ether and cetyltrimethylammonium bromide

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(CTAB) as surfactants through homogenizer. The stable fluorinated guar gum was determined by constant average particle size of 130 nm and maximum monomer conversion percentage of 99% as function of the reaction time, which was enhanced with increased concentration (below CMC) and HLB value of the emulsifier (below HLB value = 17.0). The degree of substituted or modified guar gum (DS) and concentration of stock paste preparation impart changes in paste viscosity to ascribe the rheological interactions between polymer chains and surfactants. The excess amount of fluorinated paste resulted in lower surface tension and mottle printing on the fabric, which was water and ink repellent to retain ink droplets on the surface without penetration into fibers. The measurement of K/S values and water repellence rates also revealed best modulation of printing pastes' rheological properties to provide the polyester fabric with best ratios of hydrophilicity to hydrophobicity, i.e., presenting good affinity to dyestuff inks and certain water resistance after sublimation process.

EXPERIMENTAL

Materials

The fluorinated monomer, heptadecafluorodecyl acrylate (FA, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{10}\text{C}_8\text{F}_{17}$, Aldrich) was used without further purification. The protonated monomers, styrene (Aldrich), and 2-ethylhexyl acrylate (BASF) were freshly distilled under reduced pressure and stored at -10°C . The initiator, 2,2'-Azobisisobutyronitrile (AIBN, Otsuka), was recrystallized in ethanol. The nonionic surfactants, Sinopol 608 and Sinopol 723 (Sino Japan Chemical Co., Ltd., Taiwan), were polyoxyethylene polyaryl ether with HLB values of 12.9 and 16.6, respectively. The Cetyltrimethylammonium bromide (CTAB, Lachema) was used as-received for phase transition and stabilization of the miniemulsion. Two kinds of modified guar gums were obtained from Cognis Deutschland GmbH, MG-C1 (DS= 1.0, nonionic, 8% paste preparation), and Amar Impex, MG-A8 (DS=0.1, nonionic, 8% paste preparation). Citric acid and urea were added in the paste formation for pH regulation and dye penetration, respectively. The polyester fabric of 75 denier was treated for all experiment and inkjet printed with disperse dye inks in cyan, magenta, yellow, and black which were formulated via microemulsion.⁵

Preparation of fluorinated guar gum via miniemulsion copolymerization

The miniemulsion started with the dissolution of CTAB (0.8 g), Sinopol 608 or Sinopol 723 (0.5 g), and modified guar gums (MG-C1 or MG-A8, 1.0 g) in

TABLE I
The Recipe for Polyester Fabric Pretreatment Paste

Formula	Amount (percentage of total weight)
Stock paste	10%–50%
Urea	2%–8%
Citric acid	0.05%–0.2%
Fungicide	0.05%
DI-water	41%–88%
Pick-up rate	95%–100%

deionized water (20 g). The monomer mixtures (5g, including FA, Styrene, and 2-ethylhexyl acrylate with appropriate ratio) containing AIBN (0.08 g) were well mixed with the aqueous solution and homogenized for 10 min at 0°C to prevent polymerization. Then the resulted miniemulsion mixture was charged into a 100-mL four necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet with N_2 purging for 30 min. The miniemulsion copolymerization started by raising reaction temperature to 70°C and completed after stirring at 600 rpm for 8 h.

Preparation of pretreatment paste and the padding process

The pretreatment paste containing fluorinated guar gum was prepared by the recipe in Table I, where the stock paste attained the viscosity in the range between 740 cps and 780 cps and fabric pick-up rate of more than 95%. The percentage of urea and citric acid amounts were determined by the optimization for the printing quality characterized as follows. Laboratory pad-mangle machine (LABTEC Co.) was used to apply the paste to the polyester fabric at squeegee pressure of 3 Kg/cm^2 . The pretreated polyester samples were then fixed and dried in oven at 100°C for 5 min.

Analysis and characterization

The conversion of the miniemulsion polymerization was measured with gas chromatography (Shimadzu GC-14B) by injecting each synthesized emulsion into the capillary column. The characteristics of the fluoroacrylate-modified guar gum (FA-MG) copolymer were determined using a MP-6100 pH meter for pH measurement, Du Noüy Tensionmeter for surface tension measurement, Brookfield DV-I+ Viscometer for viscosity measurement and Zeta PlusTM particle analyzer for particle size evaluation. Particle precipitation was detected by visual observation. The inkjet printing was realized on Lexmark Z43 printer charged with previously studied disperse dye inks⁵ to evaluate the edge acuity and mottle effect of pretreated fabrics. The color of printed samples was

TABLE II
Effects of Monomer Weight Ratio and Reaction Temperature on the Monomer Conversion, Particle Size and Viscosity after Polymerization in 120 min

Sample no.	Monomer ratio (wt %) (FA : Styrene : 2-EHA : MG-C1/MG-A8)	Reaction temperature (°C)	Monomer conversion (%)	Particle size (nm)	Viscosity (25°C, cps)
FGC7-a/FGA7-a	1: 49 : 49 : 1	65	95.5/95.7	135/133	757/744
		70	95.6/95.9	137/130	
		75	95.8/95.9	137/131	
		80	95.9/96.0	136/130	
		85	95.9/96.0	135/130	
FGC7-b/FFA7-b	3: 48 : 48 : 1	65	95.6/95.7	136/133	755/743
		70	96.8/96.9	138/130	
		75	97.0/97.0	137/132	
		80	97.0/97.0	135/131	
		85	97.0/97.1	136/132	
FGC7-c/FGA7-c	5: 47 : 47 : 1	65	95.9/96.0	140/135	752/740
		70	97.0/97.0	138/134	
		75	97.0/97.0	139/133	
		80	97.0/97.0	135/130	
		85	97.0/97.1	139/132	
FGC7-d/FGA7-d	1: 48.5 : 48.5 : 2	65	97.5/98.0	133/129	768/760
		70	98.5/98.6	132/128	
		75	98.6/99.0	132/125	
		80	98.7/99.1	130/125	
		85	98.7/99.1	131/122	
FGC7-e/FGA7-e	3: 47.5 : 47.5 : 2	65	98.3/99.0	138/125	765/753
		70	98.9/99.0	134/121	
		75	99.3/99.6	128/113	
		80	99.4/99.6	128/116	
		85	99.4/99.6	130/117	
FGC7-f/FGA7-f	5: 46.5 : 46.5 : 2	65	98.3/98.0	140/133	760/752
		70	98.3/98.5	139/130	
		75	98.5/99.1	139/131	
		80	98.8/99.2	138/130	
		85	98.9/99.2	137/129	
FGC7-g/FGA7-g	1: 48 : 48 : 3	65	98.5/98.9	134/127	778/770
		70	98.5/99.0	130/123	
		75	98.8/99.1	129/120	
		80	99.0/99.2	128/119	
		85	99.1/99.2	128/120	
FGC7-h/FGA7-h	3: 47 : 47 : 3	65	98.5/99.0	135/132	774/769
		70	98.8/99.1	133/129	
		75	98.8/99.2	132/127	
		80	99.0/99.2	129/125	
		85	99.1/99.2	129/124	
FGC7-i/FGA7-i	5: 46 : 46 : 3	65	98.5/99.0	136/132	772/766
		70	98.8/99.0	135/129	
		75	98.8/99.2	133/127	
		80	99.1/99.2	133/125	
		85	99.1/99.2	130/125	

[AIBN] = 0.5% wt; [Sinopol 723] = 5% wt, [CTAB] = 8% wt.

then fixed via sublimation by thermo trans-printing machine at 200°C for 30 seconds. Color strength and transparency of the prints were determined by reflectance measurement using the spectrophotometer (Spectraflash 600, DataColor). The print transparency was calculated as the color difference between the front and back sides of the printed sample. The water repellency was assessed by the standard spray test of AATCC 22-1977, where six ratings describe

different wetting extents: 0 (complete wetting of whole upper and lower surfaces), 50 (complete wetting of whole of upper surface), 70 (partial wetting of whole of upper surface), 80 (wetting of upper surface at spray points), 90 (slight random sticking or wetting of upper surface), 100 (No sticking or wetting of upper surface). After the water stray tested fabric was dried, the stain proof property was ascertained by visual observation.

TABLE III
The Influence of Surfactant Concentration on the Properties of FA-MG Miniemulsion

Sample no.	Surfactants	Surface tension (dyne/cm)	Particle size (nm)	Particle size (70°C × 7 days)
FGAS-e3	SDS 3%	41.0	208	232 ^P
FGAS-e5	SDS 5%	37.5	198	212
FGAS-e8	SDS 8%	36.0	186	194
FGAN-e3	NP-40 3%	47.5	203	239 ^P
FGAN-e5	NP-40 5%	44.0	185	224 ^P
FGAN-e8	NP-40 8%	42.0	169	178
FGA7-e3	Sinopol 723 3%	37.5	125	131
FGA7-e5	Sinopol 723 5%	35.5	113	118
FGA7-e8	Sinopol 723 8% ^a	35.0	128	136
FGA6-e3	Sinopol 608 3%	40.0	157	160
FGA6-e5	Sinopol 608 5%	38.5	142	146
FGA6-e9	Sinopol 608 9% ^a	36.5	160	170

Monomer ratio (wt %), FA : Styrene : 2-EHA : MG-A8 = 3 : 49 : 49 : 2; [AIBN] = 0.5% wt; [CTAB] = 8% wt; Reaction temperature = 75°C.

^a Means critical micelle concentration (CMC); P means precipitation.

RESULTS AND DISCUSSION

In the system of miniemulsion polymerization, the monomer and initiator do not transport through the water phase but initiate and propagate in the micelle droplet formed by surfactants at reaction temperature. Therefore, the stability and conversion of monomers in miniemulsion copolymerization are expected higher and more controllable.⁶ In our set of experiment, the fluoroacrylate monomer, heptadecafluorodecyl acrylate, was used for commercial availability.⁷ The hydrocarbon monomers, styrene and 2-ethylhexyl acrylate, were utilized to provide ideal hardness, penetrating, and binding to the fiber. The polymerization should be started with the hydrophobic initiator, AIBN, which we performed at a reaction temperature between 65°C and 80°C. The use of polyoxyethylene polyaryl ether was rather preferred than commonly applied SDS and nonylphenol typed surfactants^{8,9} in the combination with

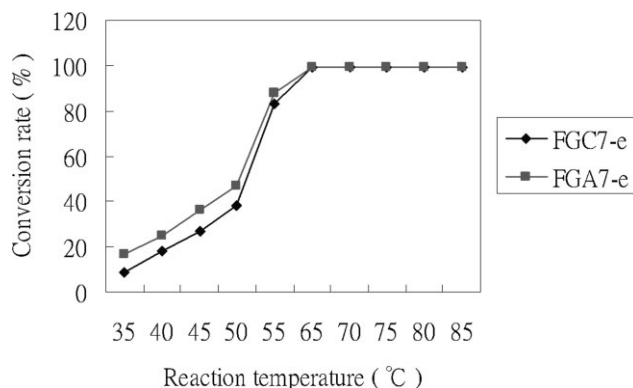


Figure 1 Effects of reaction temperature and DS values (MG-C1 = 1.0, MG-A8 = 0.1) on the monomer conversion of sample FGC7-e and FGA7-e.

CTAB due to smallest and more stabilized particle size under CMC characterized in Table III.

Effects of monomer weight ratio, reaction temperature and the DS value of guar gums on miniemulsion polymerization

As the initiation and propagation of monomer droplets occur synchronously in the miniemulsion polymerization, the completion of reaction could be determined by the monomer conversion rate which much correlates with temperature, time and the contents. Table II, III, and Figures 1–4 illustrated the effects of weight ratios of monomers and guar gums, concentration of initiator, and surfactants on the time history of overall monomer conversion at five different temperatures. From the results of Table II, the increased amounts of fluoroacrylate (FA) and two modified guar gum, MG-C1 and MG-A8, with

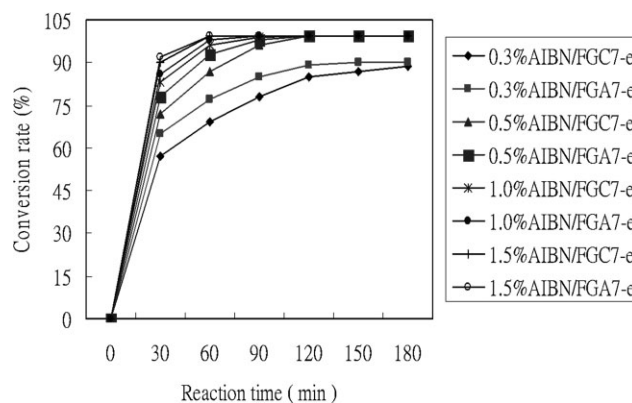


Figure 2 Effect of initiator concentration on monomer conversion as a function of the reaction time at 75°C (Samples FGC7-e vs. FGA7-e; AIBN concentration = 0.3%, 0.5%, 1.0%, and 1.5%).

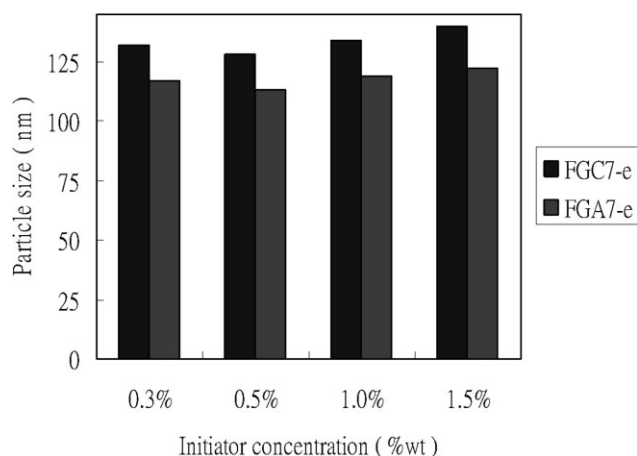


Figure 3 Effect of initiator concentration on emulsion particle size (Samples FGC7-e vs. FGA7-e; reaction time = 120 min, temperature = 75°C).

decreased styrene and 2-ethylhexyl acrylate (2-EHA) would slightly upgrade the conversion rate and enlarged particle size. The smallest particle size (113 nm) of FA-MG copolymer was obtained in sample: FGC7-e/FGA7-e at 75°C. The conversion averaged around 99% after polymerization in 120 min to imply tiny effect of reaction temperature and predominant polymerization in individual minidroplets without monomer transport or diffusion in water. It was the modified guar gum of MG-A8 to attain 99.0% conversion especially in the amount of 2% wt or more at 75°C. Moreover, the polymerization rate of FGA7-e was accelerated more than FGC7-e at higher temperature in Figure 2. It could be the higher DS value of MG-C1 (DS = 1), i.e., more substitution of hydroxyl groups of guar gums, than MG-A8 (DS = 0.1) to reduce polymerization or chemical crosslinking. The results of particle size analysis would agree with the experimental observation of Chern et al.,¹⁰ who found that styrene rich latex reduced particle size by limiting particle coagulation and adsorption of the steric stabilizer. By comparing the samples with equal styrene and 2-EHA ratios above 75°C, FGC7-b/FGA7-b vs. FGC7-g/FGA7-g, and FGC7-c/FGA7-c vs. FGC7-h/FGA7-h, the particle size was reduced with higher ratio of modified guar gums, lower DS value and higher temperature. Similar effect of higher contents of gums, styrene and 2-EHA was noted on the higher viscosity value of obtained polymers. Smaller particle observed at higher temperature probably resulted from better solubilization of the monomer mixture.

Effects of initiator concentration and reaction time on monomer conversion

The effect of the initiator, AIBN, concentration on the time evolution of overall monomer conversion at

75°C was shown in Figure 2, where sample FGC7-e and FGA7-e were represented with highest conversion rate and smallest particle size. When the amount of AIBN was lower than 0.5%, both final monomer conversion of the two samples couldn't attain 90% within 90 min whereas the amount above 1.0% approached maximum conversion of 99%. Obviously, the rates of conversion and polymerization increased as the concentration of AIBN increased. When the conversion rates reached above 99% in 120 min, the particle sizes of samples FGC7-e and FGA7-e at initiator concentration of 0.5% were smallest by comparing with other concentrations, illustrated in Figure 3. In the droplets of microemulsion, the termination of biradicals occurred immediately once the initiator decomposed and monomers captured free radicals. Therefore, the conversion rate approached above 99% easily in the appropriate ratio of monomers. Over weighted initiator (1.5% AIBN) and less hydroxyl groups of guar gums (FGC7-e) tended to influence the polymerization performance by increasing particle size and reducing conversion rate.

Effects of surfactant concentration and HLB value on polymerization rate

Based on former conditions for highest monomer conversion, the final content of surfactant was investigated as one important effect. The cationic surfactant has been studied to provide superior stability for the polymerization of fluoroacrylate miniemulsion.^{6,11} In Table I, polyoxyethylene polyaryl ether (Sinopol 608 and 723) was well compatible with CTAB to produce smallest miniemulsion droplet size with lowest variation of particle size and no precipitation observed in the accelerating test (70°C for 7 days). The critical micelle concentration of the two nonionic surfactants was found in sample

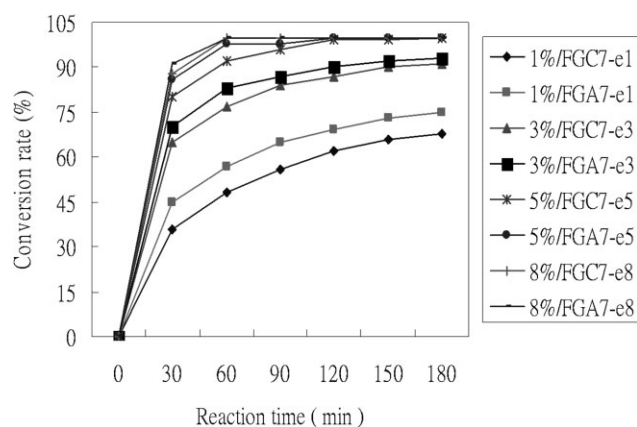


Figure 4 Effects of surfactant HLB value and concentration on the overall monomer conversion at 75°C (Samples FGC7-e vs. FGA7-e; AIBN concentration = 0.5%).

TABLE IV
The Properties of Pastes FGC7-e (75°C), FGA7-e5 and FGA6-e5 (Urea Concentration = 4%)

Sample no.	Stock paste	Surface tension (dyne/cm)	Viscosity (cps) ^a	K/S (C,M,Y,K)	Mottle effect	Water repellency/stain
FGC7-e1	10%	40.0	90.3	8.7, 8.3, 8.5, 7.0	No	70/yes
FGC7-e3	30%	39.5	233.7	9.3, 8.8, 8.6, 9.8	No	70/no
FGC7-e5	50%	39.0	380.6	5.3, 6.8, 5.1, 4.2	Yes	90/no
FGA7-e51	10%	36.5	82.3	9.6, 9.4, 9.2, 9.4	No	70/yes
FGA7-e53	30%	36.0	218.8	9.8, 9.9, 9.8, 1 0.2	No	80/no
FGA7-e55	50%	35.5	371.2	8.3, 7.4, 5.7, 4.5	Yes	90/no
FGA6-e51	10%	41.0	85.5	8.9, 7.5, 6.1, 5.3	No	70/no
FGA6-e53	30%	40.5	226.4	9.0, 8.4, 8.7, 7.4	Yes (bleeding)	80/no
FGA6-e55	50%	39.5	377.9	7.6, 6.6, 7.5, 6.3	Yes (bleeding)	90/no

^a Means the share rate at 28.1 S⁻¹.

numbers of FGA7-e8 and FGA6-e9 with larger particle size. Before reaching the CMC, the surface tension and particle size decreased with higher concentration of the four surfactants although the CMC of either SDS or NP-40 was not 8% on total weight. Such lower surface tension of smaller droplets would be the result of higher coverage of particle surface by micelles in the miniemulsion.¹² When the surfactant concentration was increased from the below CMC to above, both conversion rate and polymerization rate raised obviously in Figure 4. The rates of FGA7-e with lower DS value were accelerated more with higher surfactant concentration. Meanwhile, Sinopol 723 with the HLB value of 16.6 attained highest rate than Sinopol 608 with 12.9 and NP-40 with 13.1 as well as 17.0. The results implied stronger interaction between the hydroxyl groups of guar gum polymer and the hydrophilic EO units of nonionic surfactants.

Rheological properties and ink-jet printing performance of FA-MG printing pastes

The rheological properties of the printing paste correlate with the amount of the printing paste on the fabric surface and consequently affect the printing

quality. The earlier results provided the emulsion of fluoroacrylate and guar gum copolymer that was stabilized by the polyoxyethylene polyaryl ether surfactants and ready for paste preparation. To optimize application conditions of FA-MG paste on woven polyester fabrics of 75 denier, the amount of stock paste and urea were investigated for samples FGC7-e (75°C), FGA7-e5, and FGA6-e5 with smallest and stabilized particle size. The pH value of paste was adjusted to 4.5 with citric acid and the fabric pick-up rate was fixed at 98%. The concentration of stock paste was determined with properties of surface tension and viscosity, also with printing qualities of K/S value, mottle effect and water repellency in Table IV.

When the three kinds of stock pastes were increased in concentration, each viscosity was raised nearly two folds. However, the surface tension of higher stock paste was reduced with 0.5 extent due to more copolymer emulsion with higher surfactant content. After the polyester fabrics were treated with each paste sample, the mottle effect was observed in each sample with 50% of stock paste during inkjet printing. It was much fluorine on the fabric surface to retain ink droplets and prevent them from penetrating into fibers. After dried and sublimation, the

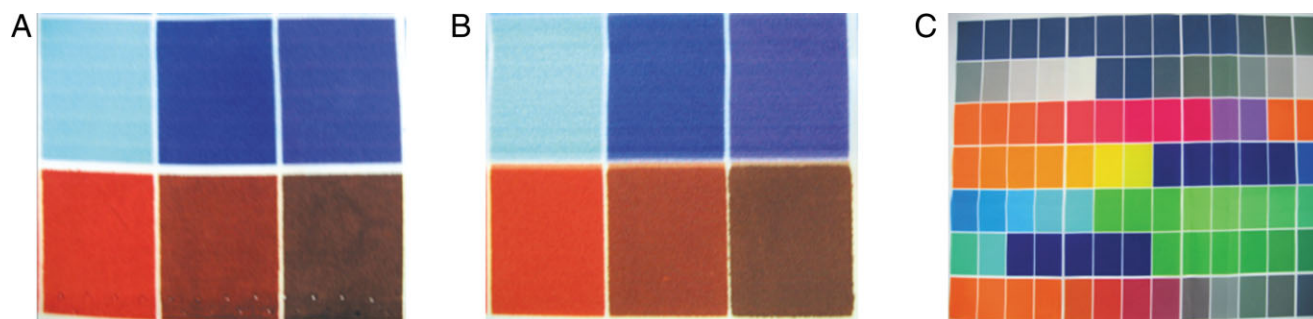


Figure 5 The three fluorinated guar gum treated polyester fabrics presented different effects after ink jet printed with disperse dye inks and sublimation. (A) FGA7-e55: mottle effect vs. (B) FGA6-e53: bleeding vs. (C) FGA7-e53: good edge acuity and even color [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

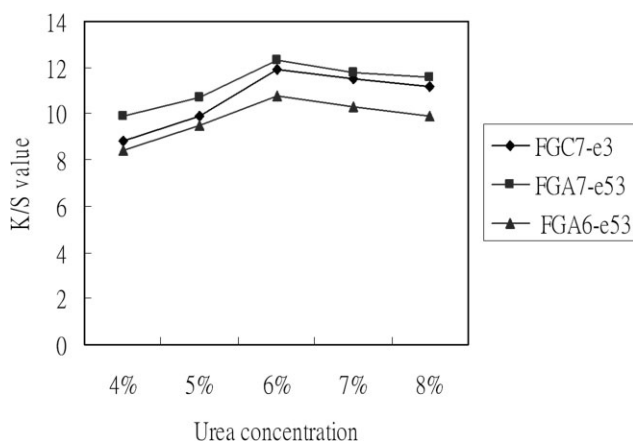


Figure 6 Effect of urea concentration on K/S value of polyester fabrics pretreated with pastes of FGC7-e3, FGA7-e53 and FGA6-e53. The color patch evaluated was inkjet printed in brown.

droplets accumulated as incompatible dots to cause less even color as shown in Figure 5. The prints with good edge acuity were also observed at higher paste concentration during inkjet printing and sublimation. The water repellency attained highest rating of 90 to present slight random wetting on the polyester fabric surface. With the same stock paste content of 30% but different guar gum copolymer and surfactant, the fluoroacrylate copolymerized with MG-A8 (FGA7-e53 and FGA6-e53) presented higher water repellency of rating 80 than with MG-C1 (FGC7-e3) of rating 70 and the surfactant Sinopol 723 made ink droplets absorbed more evenly into polyester fiber than Sinopol 608 to demonstrate the print pattern without bleeding and mottle effects.

As the concentration of stock pastes increased from 10% up to 30%, a significant improvement in color strength expressed as K/S value was obtained.

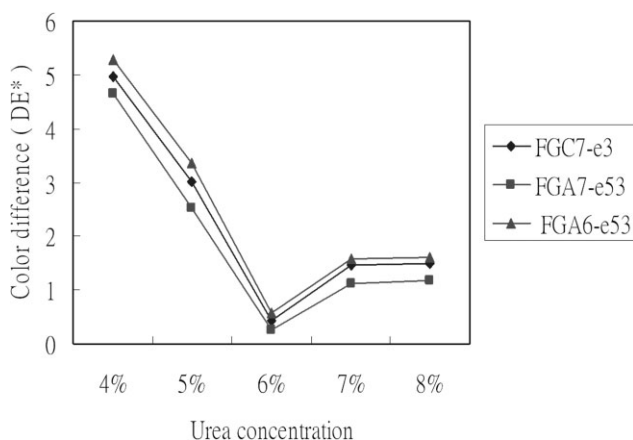


Figure 7 Effect of urea concentration on print transparency of polyester fabrics pretreated with pastes of FGC7-e3, FGA7-e53 and FGA6-e53, evaluated by color difference between front and back sides of the inkjet printed sample in brown.

The reduced strength by 50% stock paste was associated with higher water repellency and apparent mottle effect to imply the result of less dyes absorbed and concentrated into the fiber. Therefore, the 30% stock paste of FGA7-e53 provided the polyester fabric with best ratios of hydrophilicity to hydrophobicity to present best affinity to disperse dye inks and water resistance after sublimation process. The color strength and print transparency were found enhanced remarkably by increasing the urea concentration regardless of applied pastes, revealed in Figures 6 and 7. The higher print transparency was illustrated by smaller color difference between front and back sides of the printed fabric. However, the urea concentration of 6% constituted the optimal concentration to obtain deepest shades and more transparent prints since further increase in the concentration didn't take effect practically. Probably this was positive impact of urea by promoting polyester fiber swelling and facilitating disperse dye penetration during sublimation.

In Figure 8, the viscosity of three FA-MG pastes declined with increasing share rate to imply better orientation of polymer particle in the direction of rotation at higher share rate with less flow resistance. At the same share rate, the order of paste viscosity values may be drawn: FGC7 > FGA6 > FGA7. The polymerization of fluoroacrylate with higher DS value of guar gums (MG-C1) and lower HLB value of surfactant (Sinopol 608) produced the copolymer of higher viscosity. It was more incorporation of associated substitution groups into the guar gum intermolecular chains to increase the density of the primary FA-MG crosslinking structure. The pseudoplastic behavior of FGA (FA and MG-A8 copolymer) pastes was slightly reduced with more EO units or hydrophilicity in surfactant Sinopol 723.

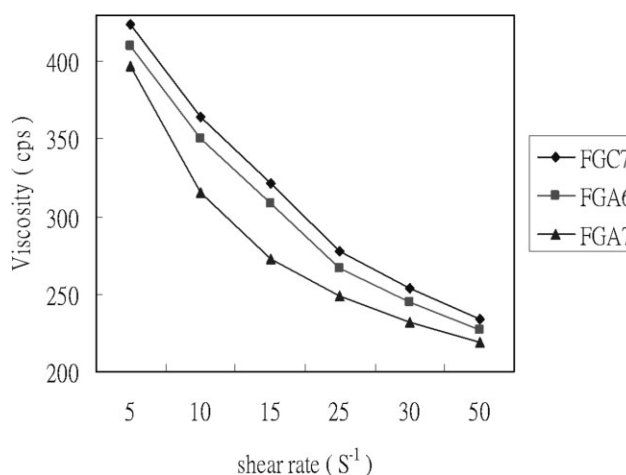


Figure 8 Effect of share rate on the viscosity of pastes, FGC7, FGA7 and FGA6 at 25°C.

CONCLUSIONS

Fluoroacrylate and modified guar gums (FA-MG) can be copolymerized via optimized miniemulsion polymerization to form stable pastes with average particle size of 113–145 nm, surface tension of 35–41 dyne/cm, and viscosity of 218–380 cps in the 30–50% of stock paste preparation. In our investigated system of miniemulsion polymerization, the monomer conversion rate attained around 99% after reacted in 120 min at 75°C to prove the initiation and propagation in the micelle droplets formed by surfactants and CTAB without monomer transport or diffusion in water. The factors influencing monomer conversion, particle size and viscosity of FA-MG could be concluded as follows.

- When the amounts of fluoroacrylate and modified guar gums increased, i.e., decreased amounts of styrene and 2-EHA, the conversion rate slightly increased with enlarged particle size. However, the particle size decreased much more when the styrene and 2-EHA ratios were equally increased to 48% at 80°C.
- Comparing pastes FGC7 formed with higher DS value, the pastes FGA7 with lower one had smaller particle size and more accelerated polymerization rate at higher temperature due to more hydroxyl groups of guar gums for the chemical crosslinking.
- The initiator concentration of 0.5% with appropriate ratio of monomers provided optimal performance with highest conversion rate of 99% and smallest particle size of 113 nm. The final monomer conversion with concentration of 0.3% couldn't attain 90% within 90 min whereas 1.5% with less hydroxyl groups of FGC7-e reduced the rate and increased particle size.
- Polyoxyethylene polyaryl ether combined with CTAB produced smallest and most stable particle size without precipitation in the accelerating test. When the surfactant concentration increased within CMC, the polymerization rate of FGA7-e was enhanced mostly with decreased surface

tension and particle size. The HLB value of 16.6 contributed appropriate hydrophilic EO units to the strongest interaction with the hydroxyl groups of guar gum polymer.

- The polymerization of fluoroacrylate with higher contents of gums, styrene and 2-EHA produced pastes with higher viscosity, which declined with increasing share rate to perform less flow resistance during rotation. The shear thinning of pastes formed by MG-A8 tended to minimize with the higher HLB value of surfactant.

The optimum fluorinated paste formulation of FGA7-e53 treated on the 75 denier polyester fabric presented the print pattern with best sharpness, highest color strength, and more transparency. The water repellence was graded at 80 to not only permit disperse dye ink droplets rapidly and evenly absorbed into polyester fiber, i.e., even color without mottle effect, but also to prevent water stain after sublimation.

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References

1. Lin, L.; Bai, X. *Pigment Resin Technol* 2004, 33, 238.
2. Katsuki, T. U.S. Pat. 6,698,874 B2, 2002.
3. Moorhouse, R.; Harry, D. N.; Merchant, U. *Soc Pet Eng* 1998, 39531, 235.
4. Guo, T. Y.; Tang, D.; Song, M.; Zhang, B. *J Polym Sci Part A: Polym Chem* 2007, 45, 5067.
5. Chang, S. Y.; Chao, Y. C. *J Image Sci Technol* 2007, 51, 413.
6. Guo, T. Y.; Tang, D. L.; Zhu, J. W.; Song, M. D.; Zhang, B. H. *China Chem Lett* 2006, 17, 1247.
7. Zhang, Q.; Zhan, X.; Chen, F. *J Appl Polym Sci* 2007, 104, 641.
8. Landiester, K.; Rothe, R.; Antonietti, M. *Macromolecules* 2002, 35, 1658.
9. Kammona, O.; Pladis, P.; Frantzikinakis, C. E.; Kiparissides, C. *Macromol Chem Phys* 2003, 204, 983.
10. Chern, C. S.; Lin, S. Y.; Chang, S. C.; Lin, J. Y.; Lin, Y. F. *Polymer* 1998, 39, 2281.
11. Bechthold, N.; Tarks, F.; Willert, M.; Landfester, K.; Antonietti, M. *Macromol Symp* 2000, 151, 549.
12. Baeurle, S. A.; Kroener, J. *J Math Chem* 2004, 36, 409.