

# Enhancement of Hydrostatic Pressure for Water Repellent Treated Fabrics

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**ABSTRACT:** The aqueous dispersions based on perfluorinated acrylate and other comonomers were prepared by means of emulsion polymerization in the presence of stearyl trimethyl ammonium chloride (STAC) and 2,2'-azobis(2-amidinopropane) dihydrochloride (ABAP) as water-soluble initiators. Several different types of resins and additives were added with the water-repellent polymers. Hydrostatic pressure and water repellency of fabrics that were treated by fluorinated water repellents with different recipes were measured and compared. In addition, the nano clay and the blocked isocyanate crosslinking agent (Jintexguard FCN) do,

indeed, substantially increase the hydrostatic pressure. Actually, increased hydrostatic pressure for the water repellent treated fabrics is our objective of this study. However, our recipes containing the fluorinated-acrylate copolymer, nano clay, and Jintexguard FCN will successfully provide excellent hydrostatic pressure, excellent water repellency, and excellent soft hand. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4711–4715, 2006

**Key words:** emulsion polymerization; initiator; crosslinking; surfactant; fluoropolymer

## INTRODUCTION

In the textile industry, many resins were used for durable press (DP) finishing, for example melamine resins, glyoxal resins, polyacrylate resins, and water-based polyurethane (PU) resins. For the water based PU resins with strong hydrophilic properties, they were not suitable for water repellent finishing. In this study, glyoxal, melamine, and polyacrylate resins were added into the fluorinated-acrylate copolymer dispersion prepared for water repellent treatment.

Fluorine-containing copolymer latices with fluorinated surface were prepared by emulsion polymerization technique to reduce the surface free energy on numerous systems.<sup>1–8</sup> The incorporation of perfluoroalkyl moieties ( $-(CF_2)_nF$ ) into organic polymers significantly changes the properties of polymeric materials, such as wettability, surface tension, and hydrophilicity.

Fluorochemical surfaces, because of their low surface free energy (tension), have a large contact angle on commonly available materials. The successful application of perfluoroalkyl-containing polymers in thermostable materials has already been reported.<sup>9–11</sup> The coatings made by the fluorinated-acrylate copol-

ymers are able to make the surfaces of fabrics, papers, and leathers have water-repellent, oil-repellent, and soil-repellent properties because their surface tensions can be greatly reduced.

Some commercially-available fabrics, which have been treated with these fluorine-containing polymers, were manufactured using emulsion polymerization technique.<sup>12–14</sup> The treated fabrics were mostly used for sports wear. Lately, fabrics with good water repellency, soft hand, and high hydrostatic pressure are necessary for the sports wear in the heavy rain. However, the hydrostatic pressures of treated fabrics can not meet the commercial requirements when the fluorinated water repellent was used alone. Basically, this study was attempted to improve the hydrostatic pressure of the fabrics treated by fluorinated water repellents, containing resins used as the DP treating agent in the textile industry, colloid silica, nano clay, and crosslinking agents.

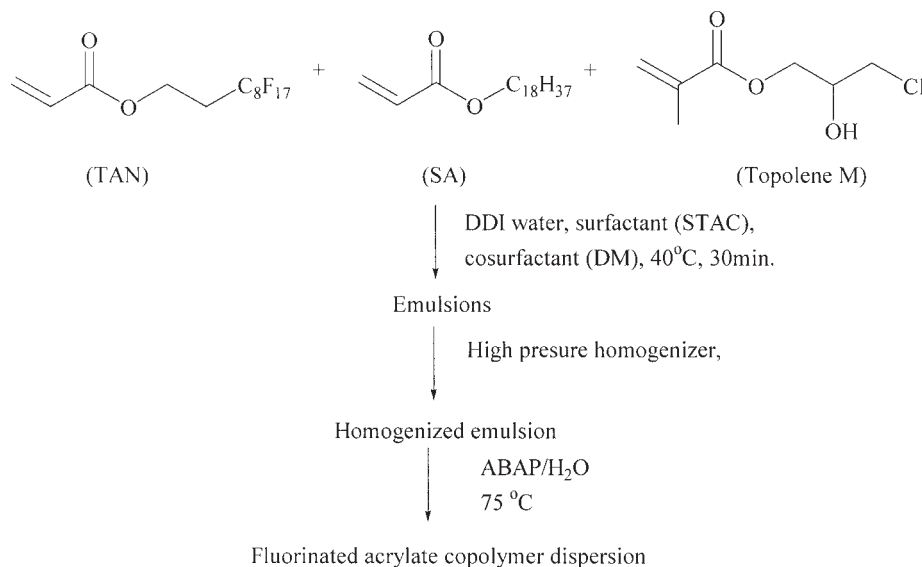
## EXPERIMENTAL

### Materials

All of the chemicals were used without further purification. Perfluoro-octyl ethyl acrylate (TAN) was supplied by Du Pont Inc. (US). 3-Chloro-2-hydroxy-propyl methacrylate (Topolene M), stearyl acrylate (SA), and cyclohexyl methacrylate (CHMA) were purchased from Shin-Nakamura Chemical Co., Ltd. (Japan). 2,2'-Azobis(2-amidinopropane) dihydrochloride

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**Scheme 1** Preparation of fluorinated-acrylate copolymer dispersion.

(ABAP) and dodecyl mercaptan were received from Nippon Chemical, Co., Ltd. (Japan) and Pennwalt Chemical Ltd. (USA), respectively. Stearyl trimethyl ammonium chloride (STAC) and crosslinking agent CX-100 were supplied by Kao Co., Ltd. (Japan) and Everpure Co., Ltd. (Taiwan), respectively. Crosslinking agent (Jintexguard FCN) was received from Jintex Co., Ltd. (Taiwan). Double deionized water (DDI water) was used for all experiments.

The 202 × 144 (40D × 40D) and 97 g/yard Polyester fabrics were used throughout this research. The fabrics after scouring, dyeing, and reduction clearing by conventional procedures were used.

#### Preparation of fluorinated-acrylate copolymer dispersion (polymer A)

Scheme 1 summarizes a typical procedure for preparing fluorinated-acrylate copolymer dispersions. The premelted 16 g TAN, 320 g DDI water, 4 g Topolene M, 24 g SA, 0.6 g DM, and 10 g STAC (cationic surfactant) were added into a 500 cc beaker and heated to 40°C under magnetic stirring. After 30 min mixing, the emulsion was passed through a high pressure homogenizer (Rannie and Gaulin Homogenizers APV 1000) under the pressure of 200 kg/cm<sup>2</sup>. The homogenized emulsion was then transferred to a four-neck flask fitted with a mechanical stirrer, thermometer, nitrogen inlet, and condenser under N<sub>2</sub> purging. The reaction temperature was raised to 75°C, followed by adding 0.6 g ABAP (initiator) and 10.0 g DDI water to the pre-emulsified solution, and stirred vigorously at 75°C for 12 h reaction to complete the polymerization. The polymer A dispersion obtained was cooled down to room temperature, and then poured out. The average

particle size of the polymer A dispersion was measured to be 250 ± 10 nm, and the number average molecular weight ( $M_n$ ) and the melting point ( $T_m$ ) of this dispersion were 42,000 and 45.12 ± 0.05°C, respectively.

#### Preparation of the fluorinated-acrylate copolymer nanoemulsion (polymer B)

The procedures of preparing polymer A dispersions were repeated, except SA was replaced by CHMA, and 0.6 g DM was replaced by 20 g DPM and 1 g DM. Importantly, the average particle size of the polymer B dispersion was measured to be 60 ± 10 nm. The number molecular weight ( $M_n$ ) and the melting point ( $T_m$ ) of the polymer B dispersion were measured to be 57,000 and 43.17 ± 0.05°C, respectively.

#### Preparation of the treated fabrics

A treating solution was prepared by adding 270 g DDI water and other additives (i.e., resins, colloid silica, nanoclay, and crosslinking agent) to 30 g of fluorinated copolymer emulsion. A 200 mm × 200 mm fabrics was cut and dipped into the prepared treating solution, and squeezed by a pair of rubber rollers to reach wet pick up of 60 wt %. It was then dried in oven at 110°C for 90 s and subjected to further cure at 170°C for 60 s.

#### Evaluation of the water repellency

Evaluation was carried out using the spray test of AATCC 22-2001 (provided that the amount of water sprayed was 0.25 L or 1 L, and the temperature of

**TABLE I**  
Evaluation of Water Repellency

Water repellency grade	State
100	No wetting observed on the surface
90	Slight wetting observed on the surface
80	Partial wetting observed on the surface
70	Substantial wetting observed on the surface
50	Wetting observed over the entire surface
0	Complete wetting observed over both surfaces

water was 27°C) and evaluated the water repellency grades, as shown in Table I.

#### Evaluation of the hydrostatic pressure

A 200 mm × 200 mm treated fabrics was conditioned at 21 ± 2°C and (65 ± 2)% RH (Relative Humidity) for 4 h. The hydrostatic pressure of the fabrics was then tested by a Hydrostatic Pressure Tester (i.e., AATCC 127-1998). Five readings were taken from each sample and the mean value was reported.

#### Average particle size measurement

The average particle size for both polymer A and polymer B dispersions was measured using a laser light scattering apparatus (Malvern Zetasizer 3000HS). All measurements were carried out at Chung-Shan Institute of Science and Technology, Taiwan.

## RESULTS AND DISCUSSION

#### Effect of the added resins

Table II lists the hydrostatic pressure and water repellency of fabrics treated with polymer A, polymer B, and resin-added polymer A, respectively. For more accuracy, the data for blank fabrics were also included for comparison. It clearly indicated that the hydrostatic pressure of polymer B-treated fabrics was obviously lower than that of polymer A-treated fabrics. However, the hydrostatic pressure increased slightly with increasing the dosage of polymer B dispersion. This result showed that the polymer B dispersion had weak film strength and high penetrating capability. Interestingly, the addition of polyacrylate resin and glyoxal resin did increase the hydrostatic pressure slightly, but on the other hand the addition of melamine resin significantly increased the hydrostatic pressure. This film strength could be due to increased crosslinking capability that results from the addition of melamine resin. Melamine resin, because of its impairing water repellency and hard hand feeling, was

not appropriate for use in added resin. In addition, melamine resin is facile to decompose even at room temperature to release formaldehyde,<sup>15</sup> which is not acceptable to the customers and is not allowed under the regulations of many nations.

#### Effect of colloid silica and nano clay

Colloid silica and nano clay have been widely used as the antilubricating agent in the textile industry. It is well known that the colloid silica can significantly increase the static coefficient of the friction of fabrics. On the other hand, nano clay, due to its possibility in enhancing the film strength made by the fluorinated-acrylate copolymer, is considered to be an alternative of the colloid silica to achieve the same purpose. Although, the nano clay is a mixture of silicon dioxide, dialuminum trioxide, and other metal oxides, its poor nonpolarity and hydrophobicity can be improved by introducing a long-chain alkyl cation, such as alkyl amine. This long chain alkyl cation is compatible with the polymer, and may be able to make the polymer chains easily diffuse into the clay layers. To improve the dimensional stability, heat distortion temperature, and the mechanical properties of polymer matrix, the rigid clay is able to inhibit the mobility of the polymer chains. More importantly, the nano clay, having more efficient surface area and more intercalation, enables the nanocomposite to have the better performance. However, the nano clay we used in this study was intercalated with the long-chain alkyl amines. As shown in Table III, the addition of colloid silica, due to

**TABLE II**  
Hydrostatic Pressure and Water Repellency Grade of Fabrics Treated by the Prepared Polymers with/without Resins

Test samples	Hydrostatic pressure (kg/cm <sup>2</sup> )	Water repellency grade
Polymer A (10%)	380	90+
Polymer A (15%)	390	100
Polymer B (10%)	190	90
Polymer B (15%)	210	100
Polymer B (20%)	230	100
Polymer A + Glyoxal resin (10 + 1)%	400	100
Polymer A + Glyoxal resin (1 + 2)%	433	100
Polymer A + Melamine resin (10 + 1)%	510	90
Polymer A + Melamine resin (10 + 2)%	530	90
Polymer A + Polyacrylate resin (10 + 1)%	400	100
Polymer A + Polyacrylate resin (10 + 2)%	414	100
Blank	0	0

**TABLE III**  
Hydrostatic Pressure and Water Repellency of the Fabrics Treated with Polymer A and Nano Clay

Test samples	Hydrostatic pressure (kg/cm <sup>2</sup> )	Water repellency grade
Polymer A + Colloid silica (10 + 2)%	380	80
Polymer A + Nano clay (10 + 0.2)%	425	90 <sup>+</sup>
Polymer A + Nano clay (10 + 0.5)%	442	90 <sup>+</sup>
Polymer A + Nano clay (10 + 1)%	492	90
Polymer A + Nano clay (10 + 2)%	464	90
Polymer A + Nano clay (10 + 4)%	437	80

its hydrophilic property, may not be able to improve the hydrostatic pressure but, on the other hand, may decrease the water repellency. However, the addition of the nano clay in the amount of about 1% by weight does significantly increase the hydrostatic pressure.

#### Effect of the crosslinking agent

To increase the strength of the textile treated with fluorinated polymer, the crosslinking agent can be used to form the direct bonding between the fluorinated polymer and the textile. Two crosslinking agents were used in this study, one was CX-100, a polyaziridine derivative and sold in the liquid form, and the other was Jintexguard FCN, a trifunctional blocked isocyanate and sold in dispersion form. As shown in Table IV, the addition of the CX-100 appeared to increase the hydrostatic pressure slightly, but the addition of Jintexguard FCN was seen to increase the hydrostatic pressure remarkably, with increasing the amount of FCN to 2% by weight, without impairing the water repellency. It could be explained that Jintexguard FCN was able to deblock and react with the hydroxyl group of the polymer to form strong crosslinking during the curing process.

#### Combination effect of the crosslinking agent and the nano clay

Because the crosslinking agent, Jintexguard FCN, is costly about five times than nano clay, the combination of the crosslinking agent and the nano clay was applied to achieve an acceptable hydrostatic pressure and price. In Table V, it shows that the mixture of 10% by weight of polymer A dispersion, 1 wt % Jintexguard FCN, and 1 wt % nano clay may give the best performance and reasonable cost.

**TABLE IV**  
Hydrostatic Pressure and Water Repellency of the Fabrics Treated with Polymer A and Crosslinking Agents (CX-100 and Jintexguard FCN)

Test samples	Hydrostatic pressure (kg/cm <sup>2</sup> )	Water repellency grade
Polymer A (10%)	380	90 <sup>+</sup>
Polymer A + CX-100 0 (10 + 0.3)%	392	90 <sup>+</sup>
Polymer A + CX-100 (10 + 1)%	390	90 <sup>+</sup>
Polymer A + Jintexguard FCN (10 + 0.25)%	477	90 <sup>+</sup>
Polymer A + Jintexguard FCN (10 + 0.5)%	531	90 <sup>+</sup>
Polymer A + Jintexguard FCN (10 + 1)%	582	90 <sup>+</sup>
Polymer A + Jintexguard FCN (10 + 2)%	630	90 <sup>+</sup>
Polymer A + Jintexguard FCN (10 + 3)%	613	90
Polymer A + Jintexguard FCN (10 + 4)%	592	90
Polymer A + Jintexguard FCN (10 + 5)%	564	90

## CONCLUSIONS

Fluorinated-acrylate copolymers dispersions were prepared by emulsion polymerization technique. To increase the hydrostatic pressure of the textile treated with fluorinated water repellent, it is an important subject in the textile industry. The experimental results indicate that the nano-sized fluorinated-acrylate copolymer has lower hydrostatic pressure, but increased dosage of polymer may

**TABLE V**  
Hydrostatic Pressure and Water Repellency of the Fabrics Treated with Polymer A, Jintexguard FCN, and Nano Clay

Test samples	Hydrostatic pressure (kg/cm <sup>2</sup> )	Water repellency grade
Polymer A + Jintexguard FCN (10 + 1)%	582	90 <sup>+</sup>
Polymer A + Jintexguard FCN + Nano clay (10 + 1 + 0.2)%	608	90 <sup>+</sup>
Polymer A + Jintexguard FCN + Nano clay (10 + 1 + 0.5)%	628	90 <sup>+</sup>
Polymer A + Jintexguard FCN + Nano clay (10 + 1 + 1)%	653	90
Polymer A + Jintexguard FCN + Nano clay (10 + 1 + 2)%	630	90
Polymer A + Jintexguard FCN + Nano clay (10 + 1 + 4)%	600	80

slightly increase the hydrostatic pressure. It is believed that the melamine resin is able to increase the hydrostatic pressure remarkably, but difficult to be accepted by the users, as a result of the formalin releasing and the hard hand feeling. However, the addition of the nano clay to the fabrics may increase the hydrostatic pressure of the fabrics due to their high surface coverage able to inhibit the mobility of the polymer chains, and thus improve the mechanical strength of the fabrics. It is interesting to point out that use of a polyaziridine-like crosslinking agent appears not to increase the hydrostatic pressure, but, on the other hand, use of the blocked isocyanate-like crosslinking agent (i.e., Jintexguard FCN) can remarkably increase the hydrostatic pressure without impairing the water repellency grade. It is important to indicate that use of the combination of crosslinking agent and nano clay not only can provide the highest hydrostatic pressure, good water repellency grade and good hand feeling, but also offer a reasonable cost to the user as well.

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