# Enhancement of the Water Repellency Durability of the Fabrics Treated by Fluorinated Nanocopolymer Emulsions

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Received 4 October 2005; accepted 30 March 2006
DOI 10.1002/app.24736

**ABSTRACT:** The fluorinated copolymer emulsions containing different monomers with the reactive groups were successfully prepared at our lab, using emulsion polymerization technique. The water repellency and the durability for the fabrics treated by fluorinated water repellents after 30 and 50 washes were measured and compared. Actually, the combination of the comonomers containing blocked isocyanate or other reactive groups after copolymerization would increase the durability of the water repellency. In addition, the blocked isocyanate crosslinking agent (Jintexguard FCN) does, indeed, substantially increase the durability also. It clearly indicates that the copolymer emulsion prepared by the reaction of fluorinated acrylate, cyclohexyl methacrylate, and 3-chloro-2-hydroxy-propyl methacrylate(Topolene M) with monomers containing blocked isocyanate group(Jintexan BIA) showed very good durability. More importantly, the combination of this copolymer and Jintexguard FCN will significantly provide excellent water repellency and durability after 50 washes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2451–2457, 2007

**Key words:** emulsion polymerization; crosslinking; monomers; FTIR; surfactants

## INTRODUCTION

Fluorine-containing copolymer latex, having the fluorinated surface able to reduce the surface-free energy on the numerous systems,[1–8] are prepared using emulsion polymerization technique. The incorporation of the perfluoro alkyl moieties ($-(CF_2)_nF$) into the backbone of the polymers significantly changes the properties of the polymeric materials, such as wettability. To deal with the wettability, one can use Young's equation,[9] as follows:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}$$

where $\gamma_L$, $\gamma_S$, and $\gamma_{SL}$ refer to interfacial tension at the liquid/air interface ($\gamma_L$), solid/air interface ($\gamma_S$), and solid/liquid ($\gamma_{SL}$) interface, respectively. $\theta$ Denotes the contact angle of a liquid droplet spreading on the solid surface. Fluorochemical surfaces on commonly available materials, because of their low surface free energy (surface tension), yield a large contact angle. The successful application of perfluoro alkyl-containing polymers in thermostable materials coatings has been reported.[10,11] Fluorine-containing coatings make textile, paper and leather surfaces water, oil, and soil repellent because of their low surface tension.

In the textile industry, many fabrics have been commercially treated with fluorine-contained polymers which were manufactured using emulsion polymerization method. Because of the high price of fluorinated acrylate, the water repellent fabric is quite expensive. We had prepared a fluoroacrylated-based nanocopolymer by using miniemulsion polymerization,[12–19] in the previous article.[20] Because of the higher surface area of nanoparticles when compared to that of the traditional 300 nm particles of fluoroacrylate copolymer, the fabrics treated with this nanocopolymer emulsion containing fluoroacrylate have better water repellency, thus are able to decrease the dosage of the water repelling agent and decrease the finishing cost. In recent days, water repellent fabrics with high durability are requested by customers. However, the durability of the treated fabrics after 50 washes cannot meet the commercial requirements (the water repellency after 50 washes should be higher than 80 according to AATCC 22-2001 evaluation method). Basically, this research was attempted to improve the durability of the fabrics treated by fluorinated copolymer emulsions containing monomers with blocked reactive functional group. The combination of blending with crosslinking agent to enhance the durability was also studied.

## EXPERIMENTAL

### Materials

Perfluoro-octyl ethyl acrylate (TAN) was supplied by Du Pont (Wilmington, DE). 3-chloro-2-hydroxy-propyl

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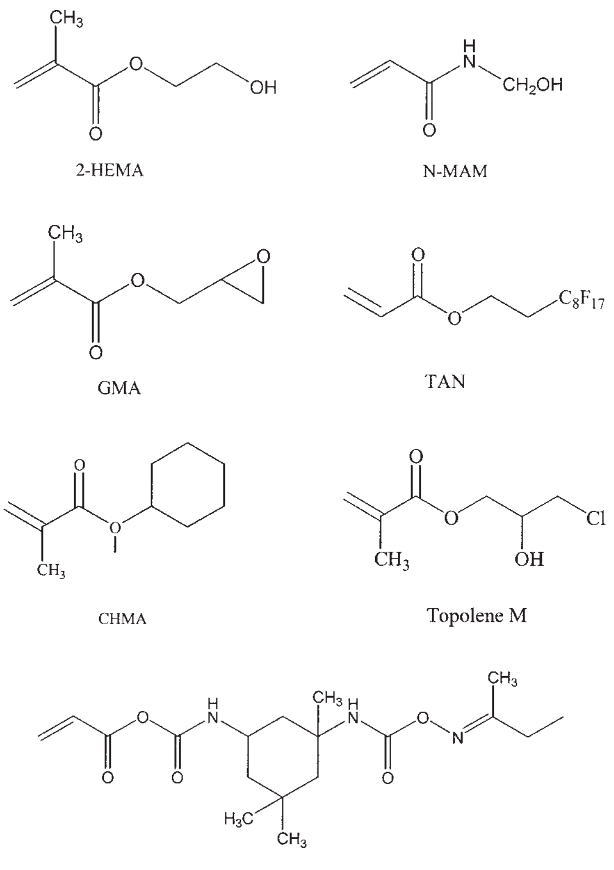
Contract grant sponsor: Jintex Corp.

Journal of Applied Polymer Science, Vol. 104, 2451–2457 (2007)

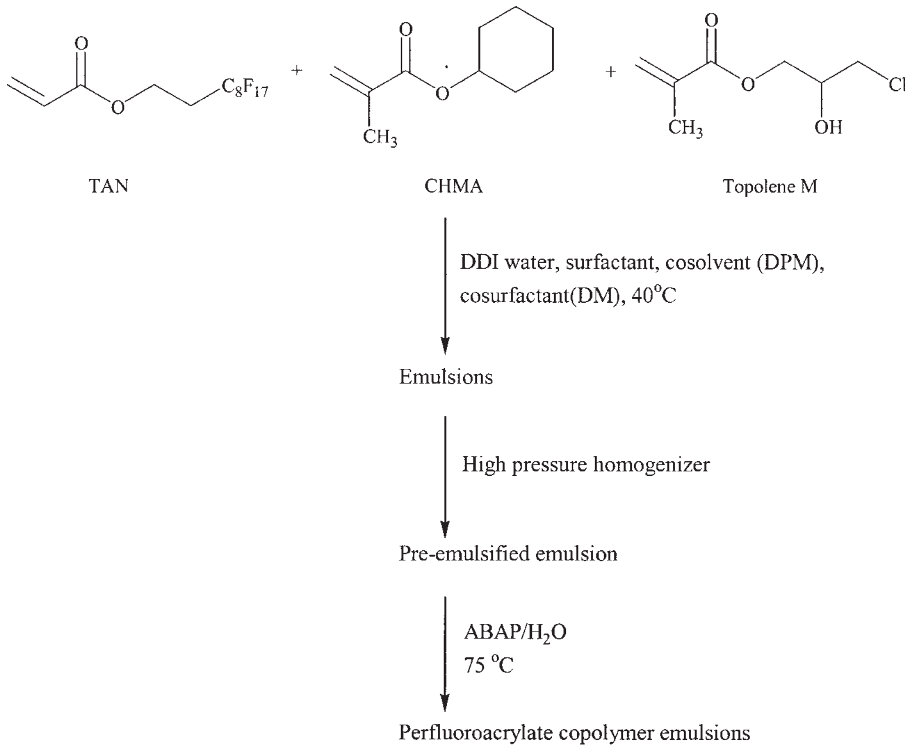


**Scheme 1**

methacrylate (Topolene M), 2-hydroxyethyl methacrylate (2-HEMA), *N*-methylol acryl amide (*N*-MAM), glycidyl methacrylate (GMA) and cyclohexyl methacrylate (CHMA) were purchased from Shin-Nakamura Chemical (Japan). 2,2′-azo bis(2-amidinpropane) dihydrochloride (ABAP) and dodecyl mercaptan (DM) were received from Nippoh Chemical (Japan) and Pennwalt Chemical (Wyandotte, MI) respectively. Stearyl trimethyl ammonium chloride (STAC) was supplied by Kao (Japan). Crosslinking agent (Jintexguard FCN) and monomer Jintexan BIA were received from Jintex (Taiwan). Double deionized water (DDI water) was used for all experiments. All of the chemicals were used without further purification.

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 the conventional procedures were used.

Scheme 1 shows the chemical structures of the monomers having a reactive functional group, except TAN and CHMA, used in this study. Scheme 2 summarizes a typical procedure[20] for preparing the emulsion of fluorinated acrylate copolymers. The premelted 20 g TAN, 320 g DDI water, 20 g CHMA, 0.6 g DM (chain transferring agent), and 10 g STAC (cationic surfactant) were added into a 500 c.c. beaker and heated to 40°C under magnetic stirring. After 30 min of mixing, the emulsion was passed through a high pressure homogenizer (Rannie and Gaulin Homogeneizers APV 1000) under the pres-



**Scheme 2**

sure of 200 kg/cm$^2$. The homogenized emulsion was then transferred to a four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and condenser under $N_2$ 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 then stirred vigorously at 75°C for 12 h of reaction to complete the polymerization. The polymer N-301 emulsion obtained was cooled down to room temperature, and then poured out. The average particle size of the polymer N-301 emulsion was measured to be 60 ± 10 nm, and the number average molecular weight ($M_n$) and the melting point ($T_m$) of this emulsion were 42,000 and 45.12 ± 0.05°C, respectively.

**TABLE I**
**Evaluation of the 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 |

Polymer N-413 was prepared as N-301 except 20 g CHMA was substituted with 14 g CHMA, 4 g Jintexan BIA and 2 g Topolene M. The average particle size of the polymer N-413 was measured to be 65 ± 10 nm, and the number average molecular weight ($M_n$) and the melting point ($T_m$) of this emulsion were 43,000 and 43.17 ± 0.05°C, respectively.

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

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 water was 27°C) and evaluated the water repellency grades, as shown in Table I. Evaluation of the durability was carried out using the washing test of AATCC 135-2001.

The mixed emulsion was twice passed through a high-pressure homogenizer (Rannie and Gaulin Homogenizers APV 1000) at 200 kg/cm$^2$.

The average particle size was measured using a light scattering instrument (Malvern Zetasizer 3000HS). All measurements were carried out at Chung-Shan Institute of Science and Technology, Taiwan.

The molecular weight of the prepared polymer was determined by gel permeation chromatography (GPC) using a Waters 410 Instrument. HPLC-grade tetrahydrofuran (THF) served as the eluent.

Fourier-transform infrared spectroscopic (FTIR) measurements of the prepared emulsions were carried out on Perkin–Elmer FTIR Spectrum One. The samples were dried under vacuum at room temperature to make a thin film which was measured from 4000 to 400 cm$^{-1}$.

## RESULTS AND DISCUSSION

There are several ways[21–24] to improve the durability of the fabrics treated with the emulsions made from fluoroacrylate copolymer. The most important thing is to enhance the bonding between polymer chains and fabrics. One can prepare a copolymer emulsion containing different monomers with the reactive groups which can react with the function group of the fabrics after the curing process; one can also use the crosslinking agent to make a bonding between the polymer chains and the fabrics. The first part of this work is to examine the influence of these different monomers on the water repellency grade after 30 and 50 washes; the second part of this work is to compare the water repellency durability of treated fabrics by blending of the fluorinated copolymer emulsions with different crosslinking agents, and the third part of this work combines the first and second parts to achieve the best water repellency durability which can meet the requirements of the customers.

**TABLE II**
**Different Monomer Ratios of the Polymerization Recipes**

| | | | Percentage of monomers that contain reactive group after polymerization | |
|---|---|---|---|---|
| Test no. | TAN | CHMA | Topolene M | Others |
| N-301 | 50 | 50 | – | – |
| N-302 | 50 | 45 | 5 | – |
| N-303 | 50 | 40 | 10 | – |
| N-304 | 50 | 35 | 15 | – |
| N-305 | 50 | 45 | – | N-MAM 5 |
| N-306 | 50 | 45 | – | 2-HEMA 5 |
| N-307 | 50 | 45 | – | GMA 5 |
| N-308 | 50 | 40 | 5 | N-MAM 5 |
| N-309 | 50 | 40 | 5 | 2-HEMA 5 |
| N-310 | 50 | 40 | 5 | GMA 5 |
| N-311 | 60 | 30 | 5 | N-MAM 5 |
| N-312 | 70 | 20 | 5 | N-MAM 5 |
| N-313 | 50 | 30 | 10 | N-MAM 10 |
| N-410 | 50 | 45 | – | Jintexan BIA 5 |
| N-411 | 50 | 40 | – | Jintexan BIA 10 |
| N-412 | 50 | 35 | – | Jintexan BIA 15 |
| N-413 | 50 | 35 | 5 | Jintexan BIA 10 |
| N-414 | 50 | 30 | 5 | Jintexan BIA 10<br>N-MAM 5 |
| N-415 | 50 | 35 | 2.5 | Jintexan BIA 10<br>N-MAM 2.5 |

**TABLE III**
**Water Repellency Test Results of N-301 to N-313**

| Polymer | Water repellency grade<br>0 wash | 30 washes | 50 washes |
|---|---|---|---|
| Jintexguard FPL | 100 | 0 | 0 |
| N-301 | 100 | 0–50 | 0 |
| N-302 | 100 | $70^{-}$ | $50^{-}$ |
| N-303 | 100 | 70 | 50 |
| N-304 | 100 | $70^{-}$ | $50^{-}$ |
| N-305 | 100 | 50 | 0–50 |
| N-306 | 100 | 50 | 0–50 |
| N-307 | 100 | 50 | 0–50 |
| N-308 | 100 | $80^{-}$ | $70^{-}$ |
| N-309 | 100 | 70 | 50 |
| N-310 | 100 | 70 | 50 |
| N-311 | 100 | 80 | 70 |
| N-312 | 100 | $80^{+}$ | $70^{+}$ |
| N-313 | 100 | 70 | 50 |

Table II lists the different ratios of monomers with the same recipe and reaction conditions as mentioned in the experimental part. According to the spray test of AATCC 22 and the durability test of AATCC 135, the water repellency performances were tested by treating fabrics with these different fluorinated copolymer emulsions, and the results were shown on Table III. Fabrics treated with the commercial product, Jintexguard FPL, possesses very good water repellency, but the water repellency decreased remarkably to zero after 30 and 50 washes. This implied that the bonding between the polymer chains of Jintexguard FPL and the fabrics was very weak, thus leading to the poor durability. Fabric treated with the polymer N-302, a nanocopolymer emulsion, showed slightly better water repellency after 30 washes than that of Jintexguard FPL whose particle size was 300 nm. The reason for this may be due to the better penetration of the nanocopolymer particle into the polyester fiber than that of the bigger polymer particle of Jintexguard FPL.

**TABLE IV**
**Water Repellency Test Results of N-302 Blended with Crosslinking Agents**

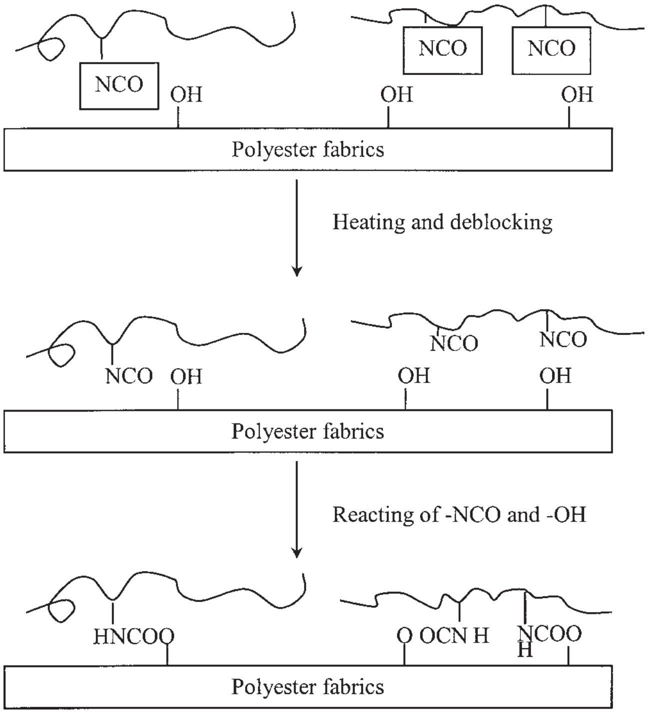
| Crosslinking agent addition (%) | Water repellency grade<br>0 wash | 30 washes | 50 washes |
|---|---|---|---|
| Blank | 100 | $70^{-}$ | $50^{-}$ |
| Melamine (1%) | 100 | 80 | 70 |
| Melamine (2%) | 100 | 80 | 70 |
| Jintexguard FCN (1%) | 100 | $80^{+}$ | $70^{+}$ |
| Jintexguard FCN (2%) | 100 | $80^{+}$ | $70^{+}$ |
| Jintexguard FCN (3%) | 100 | 80 | 70 |

**TABLE V**
**Water Repellency Test Results of N-410 to N-415**

| Polymer | Contact angle | Water repellency grade<br>0 wash | 30 washes | 50 washes |
|---|---|---|---|---|
| N-410 | 119 ± 0.5 | 100 | 80 | $70^{+}$ |
| N-411 | 120 ± 0.5 | 100 | 90 | 80 |
| N-412 | 118 ± 0.5 | 100 | 90 | $80^{-}$ |
| N-413 | 120 ± 0.5 | 100 | $90^{+}$ | $80^{+}$ |
| N-414 | 119 ± 0.5 | 100 | $90^{-}$ | $80^{-}$ |
| N-415 | 118 ± 0.5 | 100 | 90 | 80 |

Table II showed the recipes of the different monomers with the reactive groups after polymerization, such as, 2-HEMA, GMA, *N*-MAM, and Topolene M. It was clearly indicated that the water repellency of the fabrics treated with the copolymer emulsion containing 5% addition of these monomers, and their durabilities after washes were better than that with the copolymer emulsion without addition of these monomers However, Topolene M was considered to be slightly better than the others. Increasing the content of Topolene M from 5 to 10% did slightly increase the durability of the water repellency, but 15% Topolene M did not show better durability than that of 10% Topolene M. Experimental results indicated that the combination of 5% Topolene M and 5% *N*-MAM achieved a better performance than that of the other combinations. Increasing the fluorine content could also slightly increase the durability, but due to the high price of the fluorinated monomer-TAN, it was not a good idea. The durability of the water repellency was improved as described in our previous article, but it still could not meet the requirements of the customers.

In this study, two different types of crosslinking agents were used to blend with fluorinated polymer. The first type of the crosslinking agent, melamine



**Scheme 3**

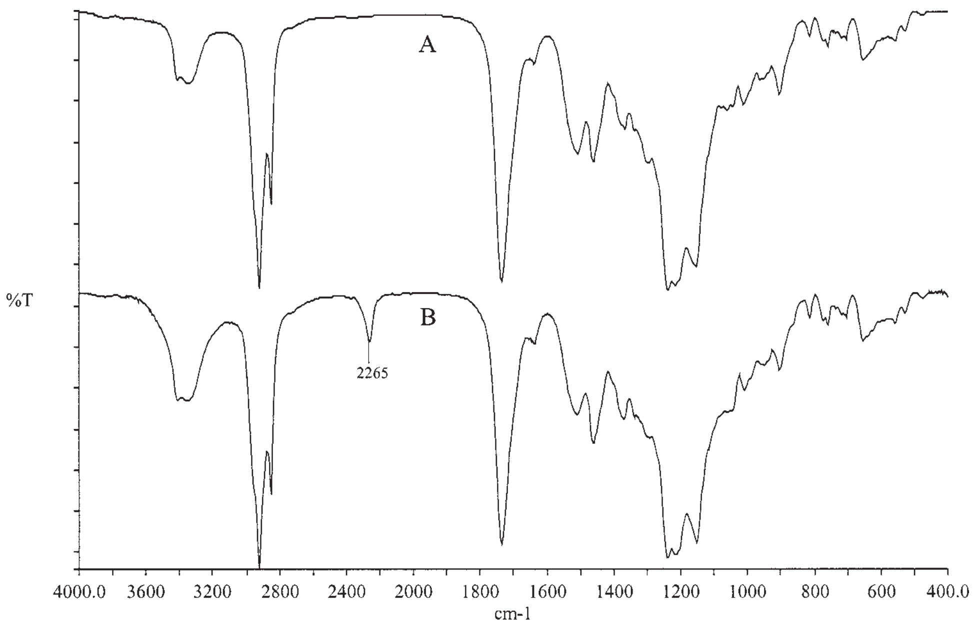


**Figure 1** IR spectra of N-413 blocked (designed A) and N-413 deblocked (designed B) at (170 ± 0.05)°C, respectively.

resin, has many hydroxyl group in their chemical structure, which may react with the functional groups of the polymer chains and polyester fabrics to form chemical bonding, thus possibly improving the durability of the fabrics treated with fluorinated polymer emulsions. Table IV shows that the addition of 1% melamine resin could slightly increase the durability of the fabrics, but the increased dosage of melamine resin could not further increase the durability. The second type of the crosslinking agent, Jintexguard FCN, containing trifunctional blocked isocyanate chemical structure, would be deblocked and react with the functional groups of the polymer chains and polyester fabrics to form chemical bonding during the curing process. The water repellency of the treated fabrics blended with 1% Jintexguard FCN is slightly better than that of the treated fabrics blended with melamine resin. This could be due to the higher reactivity of the isocyanate groups than that of the hydroxyl groups of the polymer chains to react with the hydroxyl groups attached to the polyester fabrics.

There was no commercial acrylic type monomer which contained blocked isocyanate group. Fortu-

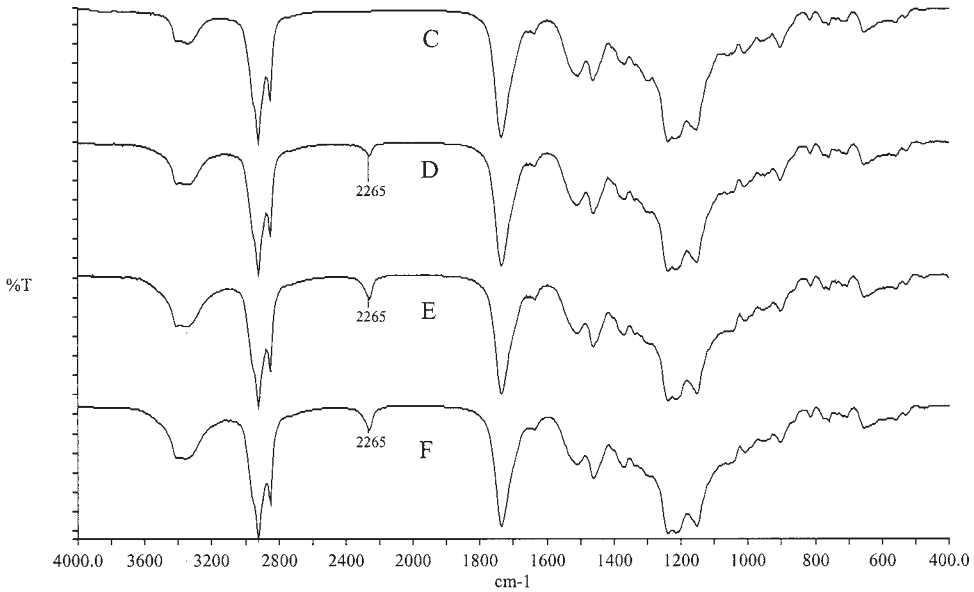


**Figure 2** IR spectra of N-413 deblocked at 110°C (C), 130°C (D), 150°C (E), and 170°C (F) ±0.05°C, respectively.

nately, Jintex supplied a blocked isocyanate monomer, Jintexan BIA, which was formed from 2-HEMA reacting with IPDI (isophorone diisocyanate) and then blocked with methyl ethyl ketoxime. We had successfully prepared some fluorinated copolymer emulsions from the combination of Jintexan BIA and other monomers as shown in Table II (N-410 to N-415). The water repellency durabilities of the fabrics treated by these copolymer emulsions had been tested, as shown in Table V. N-413 was prepared by using the combination of TAN 50%, CHMA 35%, Jintexan BIA 10% and Topolene M 5% as the monomers and it was a nanocopolymer emulsion as mentioned in the experimental part. The durability of the water repellency of the polyester fabrics treated by 10% N-413 solution with the higher contact angle was the best and could achieve $80^{+}$ after 50 washes. This high durability could be due to the strong reaction between the deblocked isocyanate groups on the polymer chains and the hydroxyl groups on the polyester fabrics or the polymer chains, thus a strong bonding between the polymer chain and fabric making the polymer chain not easy to be washed off the fabric. The possible mechanism between the fluorinated nanocopolymer and polyester fabrics is given in Scheme 3.

Figure 1 indicates the IR spectra of N-413 blocked (designed A) and N-413 deblocked (designed B) at 170°C for 1 min. The absorption peak at around 2265 $\text{cm}^{-1}$ (NCO) indicated the presence of the isocyanate group after the curing process. Decreasing the curing temperature would decrease the absorption intensity for NCO functional group at 2265 $\text{cm}^{-1}$ peak as shown in Figure 2. The peak intensity of E (curing temperature was 150°C) at 2265 $\text{cm}^{-1}$ was similar to that of F (curing temperature was 170°C). However, the peak intensity of D (curing temperature was 130°C) decreased remarkably and the peak intensity of C (curing temperature was 110°C) was zero. The lower curing temperature could decrease the amount of the deblocked isocyanate group, thus substantially decrease the durability of the water repellency, as shown in Table VI.

As mentioned in the previous section, Jintexguard FCN, a trifunctional crosslinking agent, could react with the hydroxyl groups linked to the fabrics or the polymer chains after it had been deblocked and could form the strong bonding between the polymer chains and the fabrics. More importantly, the blending of 10% polymer N-413 with 1% Jintexguard FCN could slightly increase the durability of the water repellency as shown in Table VII. However, increased concentration of Jintexguard FCN up to 2% did not increase its durability. Our experiment results showed that the best water repellency could achieve $90^{-}$ after 50 washes and meet the requirements of the customers.

**TABLE VI**
**Water Repellency Test Results of N-413 at Different Curing Temperatures**

| Curing temperature (°C) | Water repellency grade | | |
|---|---|---|---|
| | 0 wash | 30 washes | 50 washes |
| 170 | 100 | $90^{+}$ | $80^{+}$ |
| 150 | 100 | $90^{+}$ | 80 |
| 130 | 100 | 80 | $70^{+}$ |
| 110 | 100 | $70^{-}$ | $50^{-}$ |

**TABLE VII**
**Water Repellency Test Results of N-413 10% Blended with Jintexguard FCN**

| Crosslinking agent addition | Water repellency grade | | |
|---|---|---|---|
| | 0 wash | 30 washes | 50 washes |
| 0 | 100 | $90^{+}$ | $80^{+}$ |
| Jintexguard FCN (1%) | 100 | $90^{+}$ | $90^{-}$ |
| Jintexguard FCN (2%) | 100 | $90^{+}$ | $90^{-}$ |

## CONCLUSIONS

Miniemulsion polymerization technique could afford stable and nanosized latex with fluorinated acrylate copolymer which provides good water repellency, but poor durability of the water repellency after 50 washes. It clearly indicated that the copolymer emulsions prepared by the monomers with reactive functional groups after polymerization could enhance the durability of the water repellency. Apparently, Jintexan BIA is a monomer containing blocked isocyanate group, which enables the isocyanate group, after curing process, to deblock and to form a bonding between the polymer chains and the fabrics. This copolymer emulsions possibly form a strong bonding between the polymer chains and the fabrics could remarkably enhance the durability of the water repellency for the fabrics. Importantly, this copolymer emulsion blended with crosslinking agent, Jintexguard FCN, could achieve the best durability or water repellency—$90^{-}$ after 50 washes. This result could definitely meet the requirements of the customers.

The authors thank Chun-Shan Institute of Science and Technology for supporting the average particle size measurements and Professor D. Y. Chao at Chinese Culture University for stimulating discussions.

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