ISSN(Print) 1229-0033
ISSN(Online) 2234-036X
http://dx.doi.org/10.5764/TCF.2012.24.3.173
Textile Coloration and Finishing Vol.24,No.3

〈Research Paper〉

Effect of Washing and Subsequent Heat Treatment on Water Repellency of Silk Fabric Treated with Fluorocarbon Resins

Hyeiran Park and Muncheul Lee†

Department of Organic Material Science and Engineering, Pusan National University, Busan, Korea

(Received: August 7, 2012 / Revised: September 4, 2012 / Accepted: September 21, 2012)

Abstract: Silk fabric treated with fluorocarbon resins (Asahi Guard AG-7005 and AG-E061) were washed and subsequently heat treated varying the washing cycles and the temperature. After the processing, the water and oil repellencies, and contact angle to water were evaluated. The water and oil repellencies decreased by the washing and recovered by following heat treatment. Also ESCA measurement was carried out to investigate the surface chemical composition of the treated fiber. The F_{1s} intensity of the treated fabric decreased by the washing and recovered by the subsequent heat treatment. On the other hand, the O_{1s} intensity increased by the washing and decreased by following heat treatment. From the results, it is clear that change of the water and oil repellencies of the silk fabric treated with fluorocarbon resin occurred by the washing and subsequent heat treatment. Considering a change of the water repellency of the silk fabric treated with fluorocarbon resin, it seems likely that the fluoroalkyl group of the fluorocarbon resin rotates from surface to inside of the fiber by the washing to adapt to the hydrophilic circumstance, and the orientation of the fluoroalkyl groups of the resin disturbed by the washing recovers the orientation to the fiber surface after the subsequent heat treatment.

Keywords: *repellency, perfluorocarbon resin, silk fabric, washing and heat treatment, ESCA analysis*

1. Introduction

Surface of the textile fiber plays an important role for the fabric characteristics such as the water and oil repellency, soil resistance, fabric hand and luster. Water repellency is one of the most practical textile property, and also it has been investigated that the water repellency of the textile fabric treated with fluorocarbon resin decreased by the washing and recovered by the subsequent heat treatment remarkably[1)].

The effect has been explained by the following consideration; 1) rotation of the fluoroalkyl group of the fluorocarbon resin from surface to inside of the fiber by the washing to adapt to the hydrophilic circumstance, 2) deposition of the water which bonded or clustered on the fiber surface by the washing and release of the water by subsequent heat treatment, 3) disturbance of orientation of the fluoroalkyl groups of the resin by washing and recovery after the heat treatment. Above explanation is all speculation.

Detail of the phenomenon is not clear at present[1-10)]. Fluorocarbon water repellent agents contain perfluoroalkyl group ($CF_3(CF_2)_n$-) in its molecular structure, and it shows water and oil repellency coincidently, for it has low surface energy, and have been used a lot as the water resistant agent. While fluorochemicals fulfill water and oil repellent requirements, some have expressed concerns about the persistence and widespread presence in the environment of some of them. PFOS (perfluorooctane sulfonates) and longer chain PFCAs (perfluorocarboxylic acid with more numbers of carbons than PFOA) are thought to bioaccumilate. It has been shown that as the number of carbons in the perfluoroalkyl group of the chemical compound increases, bioaccumulation (and toxicity) increase. When there are the same numbers of carbons in fluorinated chemical compounds, sulfonic acid has higher toxicity and bioaccumulation than carbon acid. Conventional fluorinated water and oil repellent agents have more than seven carbons in the Rf base (such as PFOA or PDFA). Asahi Guard AG-E061 has 5 carbons in Rf base; PFHxA (perfluorohexanoic acid), and it doesn't

†Corresponding author: Muncheul Lee (leemc@pusan.ac.kr)
Tel.: +82-51-510-2408 Fax.: +82-51-512-8175

contain any PFOA (at or above detection limit), PFOS, longer-chain PFCAs or their precursors.

Wakida et. al. investigated on the water repellency of the film and fabric by the treatment of the low temperature plasma with carbon tetrafluoride (CF_4) gas[2] and of the fluorocarbon resin[8]. The water and oil repellencies increased by the treatment considerably. The contact angle, critical surface tension and ESCA analysis were measured in relation to the water repellency during the washing and subsequent heat treatment. The water repellency decreased by the washing and recovered considerably by the heat treatment. The behavior was considered on the basis of the critical surface tension by the Zisman plots and the extended Fowkes equation[8,9], and by the ESCA analysis[4].

To improve the water and oil repellency, especially oil repellency, fluorocarbon resin has been used in silk fabric, especially silk neck-tie.

In this article, silk fabric was treated with two commercial fluorocarbon resins, AG-7005 and AG-E061, and cross-linking agent, Meikanate Neo, for the textile finishing. Then, the fluorocarbon resin treated fabrics by the pad / dry / cure procedure were washed and heated varying the washing cycles and the temperature.

The effect of the cross-linking agent was also examined by adding it or not with resin. The effect of the treatment on the water and oil repellency after the washing and heat processings was evaluated by the spray test method, and contact angle measurement. Furthermore, in order to investigate the surface characteristic of the treated fabric, ESCA analysis was carried out. Change of the F_{1s}, O_{1s} and other chemical components during the processing were measured in relation to a parameter of the water and oil repellencies of the treated fabric.

2. Experimental

2.1 Materials

As a fabric material, refined silk fabric (Habutae, 58 g/m^2) was used. The fabric was treated with two commercial fluorocarbon resins, Asahi Guard AG-7005 (copolymer of fluoroalkyl acrylate and alkyl acrylate) and E-061 (eco-friendly type, alkylphenolethoxylate (APEO) free, and no containing PFCS, PFOA, longer chain PFCAs or their precursors) (Asahi Glass Co., Ltd.) for water and oil repellency. Meikanate Neo (Meisel Chemical Works, Japan) was used for cross-linking agent. Fluorocarbon repellent agent on the fiber was illustrated in Figure 1.

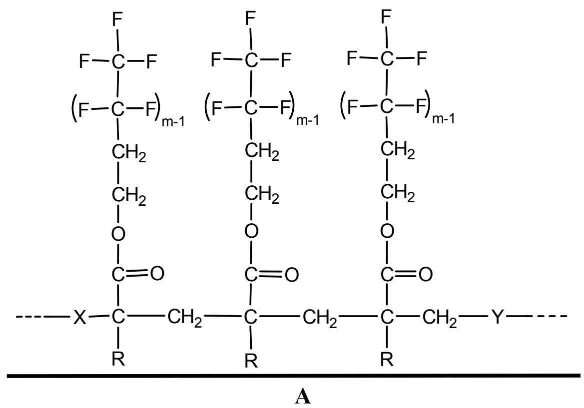

Figure 1. Fluorocarbon repellent agent on fiber surface.
M = 8~10, X and Y are comonomers, mainly stearylacrylates.
R = H and CH_3(polyacrylic or polymethacrylic acid esters).
A is the fiber surface.

2.2 Water and Oil repellency treatment

The fabrics were padded with 1 dip-1 nip in aqueous solutions containing 8% of the resins, AG-7005 and AG-E061 each, with or without cross-linking agent, and the dried (110^{o}C / 90 s) and cured (170^{o}C / 60 s).

2.3 Washing durability and heat treatment

To measure water and oil repellency, the treated fabrics were laundered one (HL-1) or twenty cycles (HL-20) at 50℃ for 30 min using Launder-O-Meter (Hanwon, Korea), and subsequently heat treated (80^{o}C / 3 min and 120^{o}C / 3 min) in a pintenter.

2.4 ESCA analysis

To investigate the surface chemical composition, ESCA analysis was carried out with a VG Scientific ESCA LAB 50 Spectrometer (England).

The relative intensity of the C_{1s}, O_{1s}, N_{1s}, and F_{1s} were determined with regard to the water and oil repellency of the silk fabric treated with fluorocarbon resin.

2.5 Water repellency test

2.5.1 Spray method

Water repellency of the treated fabrics was evaluated by the five steps ofthe KS K0590 spray method according to following method[7], 250 mL water sprayed onto fabric fitted on a 20 cm diameter circular frame rotating in a plane at 45^o to the horizontal. The effect was evaluated with a pattern of the index between 1 and 5, where 1 represents complete wetting out and 5 total water repellency.

To evaluate humidity resistibility contact angle was measured using contact angle meter (Contact angle meter. ERMA INC. G-1). 10 μm of distilled water was fallen from the syringe onto the silk fabric treated with resins, and the evaluation was done after 1 min.

2.6 Oil repellency test

Oil repellency test was carried out using the liquids shown in Table 1 approximately on the basis of the AATCC-118 method[11].

Beginning with the lowest-numbered test liquid, carefully place small drop (ca 0.05 mL) on the test fabric. If no wetting of the liquid-fabric interface, place of the next higher-numbered test liquid. Observe the drop for 30 seconds. Wetting of the fabric is normally evidenced by a darkening of the fabric at the liquid-fabric interface or by loss of sparkle within the drop.

The oil repellency was obtained with the rating between 0 and 8 of the liquid which takes place the wetting.

Table 1. Liquids for oil repellency test by AATCC-118 method

Liquid	Surface tension (N/m x 10^3)	Rating of oil repellency
n-Heptane	20.0	8
n-Octane	21.7	7
n-Decane	23.9	6
n-Dodecane	25.4	5
n-Tetradecane	26.5	4
n-Hexadecane	27.7	3
n-Hexadecane/Nujor, 35/65	29.5	2
Nujor	32.8	1
Salada oil	33.0	0

*The oil repellency improves with an increase of the rating.

3. Results and Discussion

3.1 Water repellency

Table 2 shows the water repellency of the fabrics treated with AG-7005 and AG-E061 with or without cross-linking agent. Untreated silk fabric is considerably wettable. Although the water repellency was improved remarkably by the treatment with AG-7005 and AG-E061, the effect decreased apparently by the washing. We suppose that a little water molecules were bonded on the fabric surface by the washing and leads to a decrease of the water repellency, and the water was released from the surface by the heat treatment. As a result, water repellency was partly recovered. The more laundry was carried out, the worse the water repellency was obtained. Water repellency increased gradually by the subsequent heat treatment for both resins.

Table 3 shows contact angle of the silk fabric treated with resins during washing and heat treatment.

Table 2. Water repellency of silk fabric treated with fluorocarbon resin during washing and heat treatment

Treatment	Water repellency	
	Resin	Resin / Meikanate Neo
Untreated	1	1
AG-7005 treated washed after resin treatment	5	5
HL-1	3-4	4
HL-20	1	1
Heat treated after HL-20 120^{o}C/3 min	2	2
AG-E061 treated washed after resin treatment	5	4-5
HL-1	3	3-4
HL-20	1	1
Heat treated after HL-20 120^{o}C/3 min	2	2

*HL-1: one cycle washing, HL-20: twenty cycles washing.

Table 3. Water contact angle of silk fabric treated with fluorocarbon resin during washing and heat treatment

Treatment	Water contact angle (degree)	
	Resin	Resin / Meikanate Neo
Untreated	-	-
AG-7005 treated washed	131	136
after resin treatment		
HL-1	114	124
HL-20	58	57
Heat treated after HL-20		
120°C/3 min	102	105
AG-E061 treated washed	136	136
after resin treatment		
HL-1	124	112
HL-20	57	64
Heat treated after HL-20		
120°C/3 min	105	71

Table 4. Oil repellency of silk fabric treated with fluorocarbon resin during washing and heat treatment

Treatment	Oil repellency	
	Resin	Resin / Meikanate Neo
Untreated	0.5	0.5
AG-7005 treated washed	7.5	7.5
after resin treatment		
HL-1	5.5	6.5
HL-20	0.5	1.5
Heat treated after HL-20		
120°C/3 min	7.5	7.5
AG-E061 treated washed	7.5	7.5
after resin treatment		
HL-1	6.5	6.5
HL-20	2.0	2.5
Heat treated after HL-20		
120°C/3 min	6.5	5.5

The contact angle obviously decreased by washing and recovered by subsequent heat treatment.

3.2 Oil repellency

In order to obtain a soil resistance, it is necessary to improve not only the water repellency but also the oil repellency. For that purpose, fluorocarbon resin has been used widely in the textile finishing.

Table 4 shows the oil repellency of the silk fabrics treated with AG-7005 and AG-E061.

The effect of the treatment is almost the same as that of the water repellency.

Although the oil repellency obtained by the treatment decreased greatly by the washing and recovered with an increase of the heat treatment, it seems that effect of the washing and subsequent heat treatment on the oil repellency of the fabric is much more greater comparing with that of the water repellency.

3.3 ESCA analysis

So as to determine the relative intensity of the C_{1s}, O_{1s}, N_{1s} and F_{1s}, ESCA analysis was carried out.

It is expected that change of the surface behavior during washing and following heat processing of the fluorocarbon resin treated fabric is related to the surface chemical composition.

Tables 5, 6 and Figure 2 show the surface relative intensities during the process. The F_{1s} intensity increased considerably by the resin treatment and decreased with an elevation of the temperature of the heat treatment, whereas the O_{1s} intensity decreased by the resin treatment and increased by the washing and decreased by the heat treatment. So, we supposed that an increase of the O_{1s} intensity of the treated fabric by washing is attributed to the bound or clustered water on the fabric surface, especially on the resin surface. On the other hand, an increase of the F_{1s} intensity and a decrease of the O_{1s} intensity are result of a release of the water by subsequent heat treatment.

From the above results, it is clear that change of the water and oil repellencies of the resin treated silk fabric by the washing and subsequent heat treatment takes place on the resin surface of the treated silk fiber regardless of the substrate chemical composition.

With regard to the change of the water and oil repellency the silk fabric treated with fluorocarbon resin, it seems likely that the fluoroalkyl group of the fluorocarbon resin rotates from surface to inside of the fiber by the washing to adapt to the hydrophilic circumstance, and the orientation of the fluoroalkyl groups of the resin disturbed by the washing recovers after subsequent heat treatment.

As the result, water and oil repellency are recovered.

Table 5. Relative chemical composition of silk fabric treated with AG-7005 resin during washing and heat treatment

Treatment	Relative intensity (%)			
	C_{1s}	O_{1s}	N_{1s}	F_{1s}
Untreated	66.2	21.5	12.3	-
AG-7005 treated washed	42.1	5.3	-	52.6
after resin treatment				
HL-1	51.6	7.5	0.9	40.0
HL-20	64.9	17.4	6.3	11.4
Heat treated after washing				
120°C/3 min (HL-20)	51.7	9.3	3.2	35.8
AG-7005 / Meikanate Neo treated washed	44.5	4.9	-	50.6
after resin treatment				
HL-1	48.3	6,4	1.6	43.7
HL-20	59.3	20.3	7.3	13.1
Heat treated after washings				
80°C/3 min (HL-1)	47.7	6.5	1.3	44.5
120°C/3 min (HL-1)	39.9	6.8	1.8	51.5
120°C/3 min (HL-20)	49.7	14.3	3.9	32.0

Table 6. Relative chemical composition of silk fabric treated with AG-E061 resin during washing and heat treatment

Treatment	Relative intensity (%)			
	C_{1s}	O_{1s}	N_{1s}	F_{1s}
Untreated	66.2	21.5	12.3	-
AG-E061 treated washed	48.0	7.5	1.3	43.2
after resin treatment				
HL-1	47.6	11.0	3.1	38.3
HL-20	60.0	16.9	4.7	18.4
Heat treated after washing				
120°C/3 min (HL-20)	54.2	12.9	2.1	30.8
AG-E061 / Meikanate Neo treated washed	49.5	7.8	0.6	42.1
after resin treatment				
HL-1	55.8	8,4	2.3	33.5
HL-20	63.2	16.6	4.5	15.7
Heat treated after washings				
80°C/3 min (HL-1)	50.8	9.8	2.2	37.2
120°C/3 min (HL-1)	51.9	7.7	2.6	37.8
120°C/3 min (HL-20)	56.8	13.5	5.9	23.8

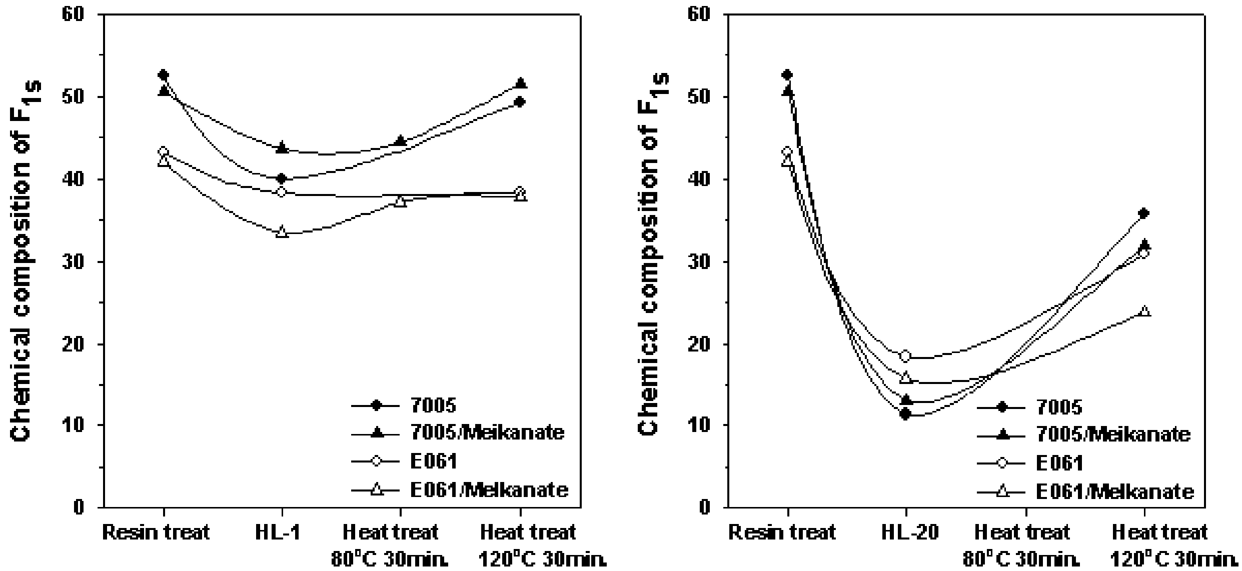

Figure 2. Change in chemical composition of F_{1s} of fluorocarbon resin (AG)-treated silk fabrics after washing and heat treatment.

4. Conclusions

Silk fabric was treated with commercial fluorocarbon resins, AG-7005 and AG-E061, and cross-linking agent, Meikanate Neo, for the textile finishing. Then, the treated fabrics were washed and heated varying the washing cycles and the temperature.

The fluorocarbon resin treated silk fabric showed excellent water and oil repellency.

AG-7005 treated-silk fabric showed higher water repellency than AG-E061 treated one. Furthermore, as evident from the surface chemical composition by the ESCA analysis, the F_{1s} intensity increased considerably by the both resin treatments, and decreased by the washing. The intensity increased again by subsequent heat treatment. On the other hand, the O_{1s} intensity increased by the washing and decreased by the heat treatment. The behavior coincided well with the water and oil repellencies during the washing and subsequent heat treatment.

After treating the fluorocarbon resins onto silk fiber, F_{1s} intensity increased. Water and oil repellency of the resin treated silk fabric decreased by washing and recovered by subsequent heat treatment.

It is expected that fluoroalkyl group of the fluorocarbon resin rotated from surface to inside of the fabric by the washing, and get it back to the surface of the fabric by subsequent heat treatment. After washing, F_{1s} intensity of the AG-7005 treated silk fabric showed a much more decrease than that of the AG-E061 treated one.

Yet it showed that the recovery of the water repellency of the AG-7005 treated silk fabric was higher rather than that of the AG-E061 treated one. When it comes to washing cycle, 20 cycles washing made water repellency more decreased than when 1 cycle washing was carried out.

The effect of cross-linking agent was not much after washing and subsequent heat treatment, even though it showed a little higher water repellency when applying it before washing. In particular, the AG-7005 treated-silk fabric with 20 cycles washing and heat treatment at 120℃ showed the best water and oil repellency than any of the resin treated fabric. Considering a change of the water repellency of the silk fabric treated with fluorocarbon resin, it seems likely that the fluoroalkyl group of the fluorocarbon resin rotates from surface to inside of the fiber by the washing to adapt to the hydrophilic circumstance, and the orientation of the fluoroalkyl groups of the resin disturbed by the washing recovers the orientation to the fiber surface after the subsequent heat treatment. As the result, water and oil repellency are recovered.

Acknowledgement

This work was supported by a 2-Year Research Grant of Pusan National University.

References

1. Y. Ono, Characteristics of Water Repellent and Oil Repellent Agent, *Dyeing Industry*, **30**(9), 460(1982).
2. T. Wakida, T. Goto, H. Li, T. Sato, M. Lee, and J. Chen, Effect of Washing and Subsequent Heat Treatment on the Water Repellency of Poly(ethylene terephthalate) Fabrics and Film Treated with Carbon Tetrachloride and Trifluoromethane Low Temperature Plasma, *Sen'i Gakkaishi*, **50**(11), 533(1994).
3. F. Ide, "Surface Modification of Polymer", Kindai Henshusha, Tokyo, Japan, p.162, 1987.
4. T. Wakida, H. Li, Y. Sato, H. Kawmura, M. Ueda, H. Mizushima, and S. Takekoshi, The Effect of Washing and Heat Treatment on the Surface Characteristics of Fluorocarbon Resin Treated Polyester, *Journal of Society of Dyers and Colourists*, **109**(9), 292(1993).
5. Y. Sato, T. Wakida, S. Tokino, S. Niu, and M. Ueda, Effect of Crossling Agents on Water Repellency of Cotton Fabrics Treated with Fluorocarbon Resin, *Textile Research Journal*, **64**(6), 316(1994).
6. Y. Ikada, "Fundamental and Application of Polymer Surface", Kagaku Donin, Tokyo, Japan, p.A69, 1986.
7. T. Wakida, T. Mori, M. Saito, and C. Doi, A Change of Surface Characteristics of Commercial Water Repellent Fabrics by Washing and Subsequent Ironing, *Japan Research Association Textile End-Uses*, **42**(2), 113(2001).
8. T. Wakida, H. Kawamura, J. C. Song, T. Goto, and T. Takagishi, Surface Free Energy of Poly (ethylene terephthalate) and Nylon 6 Films Treated with Low Temperature Plasma, *Sen'i Gakkaishi*, **43**(7), 384(1987).
9. Y. Kiatazaki and T. Hata, "Kobunshi Jikkengaku (Vol. 12)", Maruzen, Tokyo, Japan, p.173, 1983.
10. M. Lee, K. Nishi, M. Miyazaki, M. S. Lee, T. Tokuyama, and T. Wakida, Effect of Washing and Heat Treatment on Surface Characteristic of Glass Fabric Treated with Fluorocarbon Resin, *Sen'i Gakkaishi*, **61**(12), 330(2005).
11. AATCC Test Method 118-1992, AATCC Technical Manual 196, 1994.