AN IMPROVEMENT IN FLUOROCARBON CHAIN RE-ORIENTATION BY REACTIVE DYES

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Abstract Nowadays, there is an increasing demand for air-dry performance of fluorocarbon finished materials. Therefore, using different types of reactive, mono, bi, and multi-functional dyes were evaluated as a novel treatment to create correct surface interface to maintain fluorocarbon performance without ironing or tumble drying. The effects of pre-treatment on fluorocarbon finishing of cotton fabric, a cellulosic polymer, was investigated by measuring wash fastness as well as 3M water repellency test and samples hot pressing. The tensile strengths of the fabrics were compared. Also, effect of finishing on colour of the samples was examined. The results indicated that dyeing with proper reactive dye not only improve the fastness and repellency properties, but also the molecular re-orientation of fluorocarbon polymers for water repellency may reach to fulfilment level at ambient temperature. Furthermore, no negative effect on tensile properties and samples colour was observed.

Keywords Fluorocarbon, Chain Re-orientation, Reactive Dyes, Cellulosic Substrate, Multi-functional Reactive Dyes.

چکیده امروزه تقاضای زیادی برای کالاهای تکمیل شده با ترکیبات فلوئورو کربنی که کیفیت اولیه دافعیت خود را در مرحله خشک شدن بازیابند وجود دارد. بهمین علت استفاده از رنگهای راکتیو تک ، دو، و چند عامله مورد ارزیابی قرارگرفت تا سطح مرزی ویژه ای بوجود آورند تا ترکیبات فلوئورو کربنی بدون هیچ عملیات حرارتی کارایی اولیه خود را حفظ کنند. تاثیر این عملیات مقدماتی بر خصوصیات پارچه پنبه ای، پلیمر سلولزی، با اندازه گیری ثبات شستشویی، آزمون ۳-ام و بررسی اثر عملیات گرمایی ارزیابی گردید .تغییر خواص مکانیکی کالا نیز با اندازه گیری استحکام کالا برسی شد. همچنین تاثیر عملیات تکمیلی بر ویژگیهای رنگی نمونه ها مطالعه گردید. نتایج مشخص می سازند که با رنگرزی نمونه ها با رنگ راکتیو مناسب نه تنها خواص ثباتی و دافعیت کالا بهبود میابد بلکه تغییر آرایش یافتگی پلیمر فلوئورو کربنی به حدی خواهد رسید که کالای خشک شده در دمای محیط آبگریزی خود را حفظ میکند. همچنین مشخص گردید که این عملیات تاثیر منفی بر استحکام و خواص رنگی کالا ندارد.

1. INTRODUCTION

Dual Action/Total Action of fluorochemicals, alternating surface configuration states are dominantly governed by the polarity of environment, is necessary to produce a fabric with high level of stain repellency in air and satisfactory performance in oily soil releasing in washing [1-3]. However, the process of molecular re-orientation may be imperfect if the fabric is dried at low temperature in air. Thus, it has generally recommended that after washing, fabric should be tumble dried or hot ironed in order to use high temperature to activate the molecular re-orientation of the perfluoroalkyl residues [4, 5]. Clothing made from wool can mainly be cleaned by dry cleaning or laundering. However, in many cases like manufacturing machine-washable products, it is essential to keep a good protection level without additional heating, tumble drying or ironing. Other cases which in ironing would not be possible without damaging the garment (coated fabric with a breathable, polyurethane (PU) coating or a hydrophilic coating) and accomplishing recent market requirement for rainwear and sportswear for air-dry performance also require a appropriate protection [4,5].

Therefore, it is indispensable to use fluorochemicals in a way that they could regenerate their performance at ambient temperature.

In this research, fluorocarbon finishing of the cotton fabric by conventional pad-dry-cure (PDC) method to construct easy-care textile materials was investigated. The present research also evaluates the new treatment process for dyeing with mono and multi-functional reactive dyes to enhance fluorocarbon performance without ironing or tumble drying.

2. EXPERIMENTAL

Desized, scoured, and bleached cotton with plain weave (100%, $125 g/m^2$) was supplied by Borojerd Textile Company. The used fluorochemical (Rucostar EEE) was supplied by Rudolf, Germany. Reactive dyes including: Remazol Deep Black B with one vinyl sulfon group, Remazol Black B with two vinyl sulfon groups, and Remazol Carbon RGB with one vinyl sulfon and two dichlorotriazin groups were utilized as mono, bi, and multi-functional reactive dyes, respectively. ECE non phosphate reference detergent without O.B.A. was used in washing process.

The cotton fabric was washed with 0.5 g/l detergent, pH 8-9 (sodium carbonate) at 80 ºC for 60 min to remove any impurities which may adversely affect the treatment. Then, it rinsed completely with minimum mechanical action and finally air dried without any tension.

The scoured sample was finished by the fluorocarbon before or after dyeing. Effects of treatment on fabrics performance and properties have been studied by measuring wash fastness, as well as 3M water repellency tests [6], and samples hot pressing. The tensile strengths of the fabrics were compared.

The samples were treated by pad-dry-cure method with Rucostar EEE. The pad bath contained 40 g/l fluorochemical, at pH 6-7. Wet pick up was 70%. The padded fabrics were dried at 100ºC for 2 min, and then cured for 1 min at 160ºC.

A group of samples before being fluorocarbon finished were dyed by reactive dyes with different structural properties to create correct surface interface (possibly cross linking) to maintain fluorocarbon performance without ironing. So, the samples dyeing carried out according to the recommended conditions with pad-dry-pad steam method. The dyeing pad bath contained 80 g/l dye with 5-10 g/l ludigol as an oxidative agent. Wet pick up was 70%. The padded fabrics were dried at 50-60ºC, and then chemical pad was prepared with 250g/l sodium chloride, 20g/l sodium carbonate, and 6 ml/l sodium hydroxide. Saturated steam for 90 s was the next step. Finally, the dyed samples were washed with 0.5 g/l detergent at 60ºC for 15 minute.

In 3M water repellency tests [6], test drops of liquids consisting of specified proportion of water and Propane -2-ol (isopropyl alcohol) are placed on the surface of samples and the wetting behaviour was observed. If the sample does not absorb the liquid, it will have adequate repellency to pass the test.

Dyed and undyed fluorocarbon finished samples were washed with 0.5 g/l detergent, boiled for 60 min, then completely rinsed and air dried.

In addition, the samples were hot-pressed using an Elnapress/SDL with the temperature set for cotton fabrics after laundering to evaluate the effect of re-orientation of fluorocarbon polymer chains and consequently on the water and oil repellency of the finished samples.

Determination of fabrics tensile properties were studied according to BS 13934-1:1999 test method on an Instron model 5564, with gauge length of 100 mm, crosshead speed of 50mm/min, and 10 tests for each sample which conditioned at 20˚C and 65% RH prior the tests.

The samples colour changes were investigated by reflectance factor measurement using Spectraflash model 600 from DataColor.

3. RESULTS AND DISCUSSIONS

The results of undyed sample are shown in Table 1. According to this Table, by applying a block copolymer, Rucosatr EEE, containing both highly fluorinated and highly hydrophilic polymer segments within a single chain molecule, the required surface energy in air or in an aqueous environment can be attained. Thus the hybrid fluorochemical functions effectively as a stain repellent in air and also as an effective oily soil release finish in washing. However, the re-orientation of Rucosatr EEE during air drying is incomplete; consequently they need to be hot pressed to retrieve their original repellency performances. Also, the results indicate that the treated sample by PDC method have no fastness problems. So, they show high level of water and oil repellency after activation the fluorocarbons molecules by high temperature. Similar behaviour of the finished fabrics with fluorochemicals has already reported [7].

Furthermore; studying the repellency properties after washing revealed that re-orientation is so sensitive to aqueous medium. They lost their entire repellency due to the surface movement of the fluorocarbon segments which may be resulted from the effects of polarity and surface tension of the environments on polymer chains [8]. This effect, retrieving original configuration, is the drawback of finishing. Considering fluorocarbon finishing as only method for produce polymer surface with minimum surface energy to repel oily stains forced end user to iron the goods after washing or dry cleaning. Nonetheless, there are some cases which ironing will not be possible without damaging the garment. Subsequently, it is essential to find out new pre-treatment in order to manufacture air-dry performance products. It was reported that particular types of reactive dyes are able to cross link between cellulosic polymer chains [9]. Therefore, in this research we attempted to investigate the effect of possible cross link to limit fluorocarbon surface chain movement to keep better level of protection.

Mono-functional reactive dye, Remazol Deep Black N 150, showed the same behaviour as the undyed sample did, while the dyed finished fluorocarbon before and after treatment show maximum repellency (3M=10). Comparing the obtained value with white sample (3M=9) clarifies the necessity of high-quality preparation processes to achieve superior performance.

Bi-functional reactive dyes show the similar results to the mono-functional dye, Remazol Black B, before washing and after hot-pressing. It maintains its water repellency at washed condition (3M=1) which is enough to repel water. Further improvement was obtained with the multi-functional dye, Remazol Carbon RGB, which showed enhancement after washing with 3M=1-2.

TABLE 1. 3M water repellency analysis of fluorocarbon treated samples (All samples 3M water repellency before fluorocarbon finishing was 0)

Sample (Dye)	Dye Structure	With no after-treatment	After washing	After washing and hot-pressing
Undyed	-------	9	0	8-9
Remazol Deep Black N150	Mono-functional	10	0	9
Remazol Black B	Bi-functional	10	1	9-10
Remazol Carbon Black RGB	Multi-functional	10	1-2	10

The precise chemical moieties arrangement at the surface is described by “surface configuration” to find out why some reactive dyes can improve the decay of hydrophobicity of fluorocarbon treated samples. The surface configuration is strongly dependent on the surrounding medium so its variation could be usually described by “surface dynamics”. Surface dynamics contends with effect of variations in the environmental conditions on the surface characteristics [10].

It was stated that the concentration of functional groups on the polymer surface is being optimized to reach the minimum boundary free energy between the polymer surface and the surrounding medium [11]. Subsequently, the fluorocarbon hydrophobic groups on the substrate surface would not decay in air. In contrast, according to Table 1,

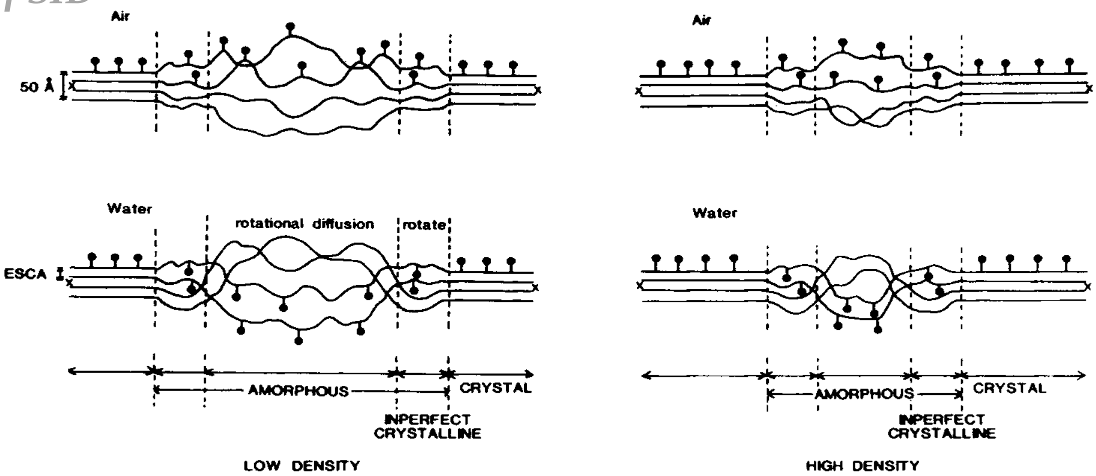

Figure 1. Schematic representations of the migration modes of fluorine-containing moieties from the surface in crystalline, amorphous, and transitional regions for films of low and high degrees of crystallinity [10].

TABLE 2. CIE 1976 color scale of samples.

Sample		L*	a*	b*	c*	Hue angle	ΔE
Remazol Black B	Before Finishing	19.75	-0.27	-12.28	12.28	88.74	0.69
	Fluorocarbon Finished	19.17	-0.49	-11.97	11.98	88.65	
Remazol Carbon Black RGB	Before Finishing	16.44	0.82	-2.30	2.44	-70.37	0.514
	Fluorocarbon Finished	16.02	0.83	-2.02	2.183	-67.66	

TABLE 3. Tensile Properties of the cotton fabric after finishing with water repellent agent.

Sample (Dye)	Dye Structure		Tensile Strength (kN/m)	Strain (%)
Undyed	-------	Before Finishing	10.3±0.46	21.0±0.39
		Fluorocarbon Finished	10.1±0.48	19.5±0.66
Remazol Deep Black N150	Mono- functional	Before Finishing	10.2±0.35	20.3±0.58
		Fluorocarbon Finished	9.9±0.30	19.7±0.53
Remazol Black B	Bi-functional	Before Finishing	9.8±0.28	20.8±0.38
		Fluorocarbon Finished	9.7±0.38	19.5±0.41
Remazol Carbon Black RGB	Multi-functional	Before Finishing	9.7±0.32	21.2±0.56
		Fluorocarbon Finished	9.6±0.63	19.0±0.69

it is evident that immersing the samples in water during washing resulted in the decay of hydrophobicity as it is compatible with the other findings [10].

This decay of the hydrophobicity is closely related to the rotational and diffusional movement of the polymer chains near the surfaces, the fluorine-containing moieties from the air/polymer interface into the bulk phase of the polymers. Therefore, decay of the water and oil repellency after wet treatment as already discussed is primarily due to surface dynamic changes of the treated samples but not due to washing off the hydrophobic moieties formed by the finishing process, the applied Pad-Dry-Cure method. Such migration processes are anticipated to be hindered by the presence of crystalline phases in the samples because by considering Figure 1, the highly crystalline polymers show slower decay of the hydrophobicity than low-crystalline polymers. Thus, the durable hydrophobic surface may be accomplished by the restriction of the polymer chain movement (cross linking). In other words, variation in surface-configuration may be considered to be minimal for polymer molecules in the crystalline phase or it can be said that the higher the crystallinity, the more difficulty the migration [10, 12, 13]. The effect of bi, and multi-functional reactive dyes could be related to the possible cellulose cross linking of adjacent polymer chain which limited the surface dynamic change. In addition, the comparison of bi and multi-functional reactive dyes reveals the direct relation between the number of cross links and air-dry performance. This is the reason why the black shade dyes were preferred due to the high required concentration to reach the appropriate shade. From Table 2, the effect of fluorocarbon finishing on samples colour is negligible. However, finishing which increased the bi and multi functional dyed samples lightness (L*) and chroma (C*) caused samples appear less black.

4. CONCLUSIONS

The decay of hydrophobicity of fluorocarbon finishing is due to the re-orientation of Rucosatr EEE during wet processing. The treated samples by PDC method have no fastness problems, so after activation the fluorocarbons molecules by high temperature they show high level of water and oil repellency.

The results also indicate that by cross linking adjacent cellulose polymer chain using proper reactive dyes, fluorocarbons re-orientation is at reasonable level during air drying to repel water. So there is no necessity to tumble dry or hot-pressing the samples. Therefore, the direct relation between the number of cross links and enhancement in repellent properties after wet processing paves the way to construct air dry performance products. This process does not have any negative effect on tensile properties and colour of dyed cotton fabric.

This effect could be due to the thin layer of fluorocarbon on the fibres surface [14]. Tensile properties of the fluorocarbon finished samples did not show any statistically significant difference.

5. ACKNOWLEDGMENTS

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