A Qualitative Analysis of Different Types of Water Repellent Agent Used on Cotton Fabric

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Abstract

The existence of intermolecular attractive forces of polarity and hydrogen bond is imperative in providing strength, heat resistance and dry-cleaning resistance to cotton fabric. However, these forces enhance easy wetting of fiber by water offering little resistance to snow and rain for outerwear garments. This problem could be overcome by adding water repellent chemicals to the fabric either chemically or with mechanical coating which prevent penetration of water through the fabric without destroying comfort of the fabric. The aim of the work is to evaluate the effect of different types of water repellent agents used on cotton fabric and analyze different possible factors affecting the performance and quality of treated fabrics. For this purpose, three water repellent chemicals: Lurotex protector RP ECO is a product based on C6 technology, Rucostar EEE6 product consists of a hydrocarbon matrix and hyper-branched, star-shaped polymers(dendrimers) and Nuva TTC is a conventional fluorocarbon based water repellent chemicals were used in three different concentrations to find out an optimum chemical concentration. To judge the quality of the treated fabrics, spray test, air permeability test, strength test and abrasion resistance test were evaluated. The quality of treated fabrics for all three chemicals was very close to each other and if the process parameters is maintained successfully, desired results can be achieved.

Keywords: Water Repellent, Fluorocarbon, C6 Technology, Dendrimers

Introduction

Cotton is an outstanding versatile fibre with superior quality mainly comfort ability. Water repellency is one general functional property that is required for protective clothing without deteriorating the comfort ability.

Water repellent textiles have many uses such as industrial, consumer and apparel purpose. This repellency can be achieved by applying water repellent chemicals which imparts a thin surface layer of chemicals on textile fibers by the modification of surface energy of textiles without much deterioration of other mechanical and aesthetic properties like strength, flexibility, luster, breathability, softness etc. (Chowdhury & Kawser Parveen, 2018)

The formation of permanent covalent bonds between the fiber and water repellent chemicals are necessary to produce durable repellency as the bonds prevents the removal of the water repellent chemicals during laundering or dry-cleaning. Pyridinium compounds, chromium based metal complexes and N-methylol based products accomplish the durable chemical bond formation. Unfortunately, these compounds are hazardous and toxic to the environment limiting their production. Polysiloxanes can also be applied to textile fabrics based on hydrogen bonding and mechanical interactions between the fabric and the –Si-O-Si- bonds of the silocone compound along with the network cross link formation within the polysiloxane compound itself. This finish gives semi-durable repellency. Fabric treated with fluorocarbon chemicals exhibit excellent durable repellency. (Kissa E., 2001)

Materials and Methods

Table 1. Specification of Cotton fabric (Knit)

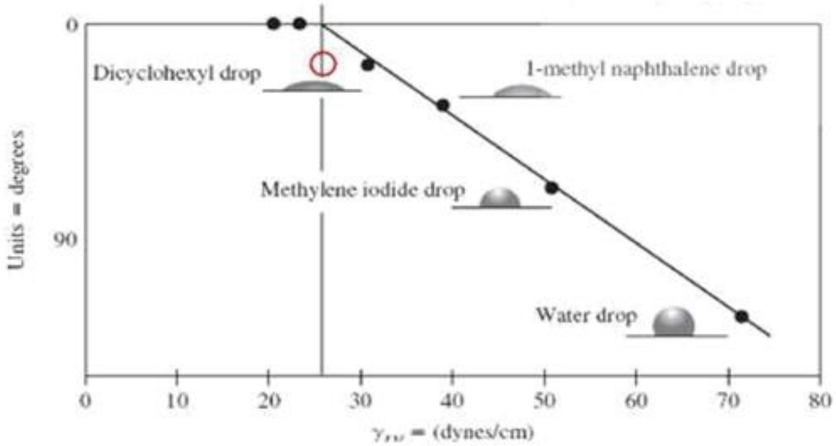
Features	Description
Fiber type	Bleached Cotton
Fabric type	Knit
Fabric Structure	Plain Single Jersey
GSM	150
Sample Size	35cm x 35cm

Table 2. Specification of Cotton fabric (Woven)

Features	Description
Fiber type	Bleached Cotton
Fabric type	Woven
Fabric Structure	1x1 Plain Weave
GSM	110
Sample Size	35cm x 35cm

When a drop of liquid on a solid surface does not spread, the drop will assume a shape that appears constant and exhibits an angle, called the contact angle. The angle is characteristic of the particular liquid/solid interaction; therefore, the equilibrium contact angle serves as an indication of wet ability of the solid by the liquid. As seen in figure 1 the interfacial forces between the liquid and vapor, liquid and solid and solid and vapor all come into play when determining whether a liquid will spread or not on a smooth solid surface. The equilibrium established between these forces determines the contact angle. (Davis R et al, 2011)

Figure 1. Spreading of liquids on smooth surfaces.



γL/V is the interfacial energy between liquid/vapor, γS/L is the interfacial energy between solid/liquid, γS/V is the interfacial energy between solid/vapor and ϕ is equilibrium contact angle. The work of adhesion between the liquid and solid is given by the Dupre equation:

$$WA = \gamma S/V + \gamma L/V - \gamma S/L$$

On the other hand, a liquid drop on a smooth solid surface is subjected to the equilibrium forces described by the Young equation:

$$\gamma S/V = \gamma S/L + \gamma L/V \, COS\phi$$

The relationship between the work of adhesion and contact angle is derived by the combination Young-Dupre equation:

$$WA = \gamma L/V \, (1+COS\phi)$$

While the interfacial energy between a liquid and its vapor can be measured directly (this quantity is the liquid's surface tension), that between a solid air cannot. The expression above is useful in characterizing the surface energy of solids, From this equation, it can be reasoned that as the contact angle ϕ approaches 180°, the work of adhesion approaches 0, and the liquid drop will not stick. As ϕ approaches 0, the work of adhesion increases and reaches maximum value, 2 γL/V. The surface tension of a liquid that just spreads on a solid (=0) would be representative of the surface energy of a solid and could be used to describe the surface. **(**Dr. Charles Tomasino, 1992)

Water repellency is obtained by reducing the free energy of a fiber surface by using various chemicals which have lower surface energies. These lower surface energy bodies have lower adhesive interactions between the fiber and the liquid than the internal cohesive interactions within the liquid. This prevents spreading of liquid droplets on the surface of the textile fabric. For any liquid, the critical surface energy or tension (γc) of the solid surface must be lower than the surface tension of the liquid for the liquid to be repelled. Surface tension is defined as the force per unit length (dynes/cm) acting on the surface of a liquid which resists wetting on a surface. It is also important to understand critical surface tension. For a given homologous series of organic liquids, the contact angle (ϕ) is measured on a low surface energy solid. The plot of cosine of the contact angle measured versus the surface tension of the liquid gives a straight line. The intercept of this line at $\cos \phi = 1$ (contact angle = 0) is defined as the critical surface tension (γ_c). (Ceria A & Hauser PJ., 2010)

Fluorochemical water repellents

Fluorochemical repellents have much lower surface energies than hydrophobic and silicone repellents imparting both water repellency and oil repellency together. Hydrocarbon and silicone repellents offer only water repellency. Uniform distribution, packing, proper orientation, structure and length of the fluorocarbon segment, amount of fluorocarbon chemical applied on the fiber, composition and geometry of fabric determines repellency of fluorocarbon finishes. The $–CF_3$ end group should be present in any fluorochemical to form a low energy surface. Generally, seven fluorinated carbon atoms along with trifluoromethyl as terminal group is sufficient enough to form a dense layer on the outer side of the fabric to cover inner non-fluorinated segments achieving good repellency. If the inner non-fluorinated atoms are not covered with fluorinated atoms, wet ability of the material increases significantly. (Grajeck, E. J. & W. H. Petersen, 1962)

Bio-nic Finish

A novel fluorocarbon(FC) development is inspired by nature where FC polymers are applied together with dendrimers causing self-orientation and the chains are enriched on the surface and crystallize with the dendrimers. It obtains same result as conventional FC without decompose persistent & bio accumulative compounds. Dendrimers are highly branched oligomers with non-polar chains forming a star brush structure. (Rastogi, D. et al, 2013)

C6 Technology

Many fluorocarbon originated water repellent products are based on 8-carbon chain structure (C8) but in manufacturing a trace amount of Perfluorooctanoic acid (PFOA) & Perfluorooctane Sulfonate (PFOS) generated as a byproduct. There are potential health & safety concerns with both PFOS and PFOA. Both are toxic, persistent & bio accumulating. To overcome this problem 6-carbon chain structure (C6) based water repellent chemicals are introduced which is free from PFOA & PFOS. (Malshe, P. et al, 2013)

Duel Action fluorocarbon

Naturally, water repellency impedes the access of the washing liquor during laundering. Therefore, so-called dual-action fluorocarbon block copolymers were developed which combine repellency in the dry state and soil-release effects in an aqueous environment. Dual active fluorocarbons enable a better removal of oily stains and dirt in domestic washing or laundering. With conventional FC products, the wash water is hindered from wetting and penetrating the fabric. Dual action fluorocarbons are called Hybrid fluoro-chemicals because they are block copolymers containing hydrophobic (like the usual FCs) and highly hydrophilic segments. (Easter, E. P. & Ankenman, B. E., 2010)

Fluorocarbon with boosters

Some new FC products, drying in air is sufficient laundry–air–dry or LAD products. Tailored FCs and blocked isocyanates, the so-called boosters, are used for this effect. Depending on the kind of blocking group, the isocyanate is activated at different temperatures and then reacts with the functional groups of the FC, the fiber or with itself (crosslinking). This fixation on the fiber surface provides durability to washing, dry cleaning and rubbing as a second important effect. Boosters also cause better film formation and thereby higher repellency effects. (Wang, Z. et al, 2013)

Chemical's name	Composition	Properties	Manufacturer
Nuva TTC	Dispersion of a fluorine compound	Liquid milky white dispersion weakly Cationic durability high.	Clariant
RUCOSTAR EEE 6	Fluorocarbon resin with hyper branched dendrimers	Nonflammable, solvent free, confers a soft handle. Free of PFOA, PFOS	RUDOLF
Lurotex protector RP ECO	C6 fluorocarbon finish with an unblocked isocyacyanate booster	Soft handle high durable no yellowing at high temperature curing free of hazard substance	BASF

Table 3. Specification of water repellents chemicals

Most of the fluorocarbon chemicals are applied by the pad-dry-cure method. The fluoro polymers can also be applied by exhaust and spray methods. The fabric is impregnated with fluoro polymer followed by drying at around 110^0C or higher to remove water and moisture depending on the nature of the chemical and cured at 150-182^0C for 1-3 minutes. Heat treatment orients the perfluoro groups on the fabric surface forming a dense fluorocarbon layer providing optimal repellency. `

Testing Parameters

AATCC test method 22-2001 water repellency spray test was used to evaluate the repellency of the fabric. The samples were conditioned for 24 hours at 20°±1°C at a relative humidity of 65±2% prior to testing. The specimens were stretched on a hoop, which was held at angle of 45° &250 ml of water was poured through a spray nozzle. Any wetting or spotted pattern observed was compared with the photographic rating chart. A fabric with complete non-wetting was given a100 rating; while a fabric with complete wetting was assigned a 0 rating.

AATCC 124-2001 washing condition was set for the cotton specimens. ISO test method 9237 was used to determine the breathability of untreated and treated samples using air permeability tester. ASTM test method D5045-06 was used to determine the tensile strength of the treated and untreated woven fabrics using a Goodbrand Fabric strength tester. ASTM test method D3786 standard test method was used to determine the treated and untreated knit fabric strength using Trust Burst. ASTM test method D 4966 standard test method was used to determine the abrasion resistance both woven & knit fabric using Martindale Abrasion tester.

Results and Discussions

Water repellency Ratings-Spray test

The water repellency spray ratings were carried out before washing of woven & knit fabric samples which are treated with 10g/l Nuva TTC,10g/l Rucostar EEE6 & 10g/l Lurotex Protector RP ECO followed by drying at 110°C & curing at 140°C,160°C & 180°C.

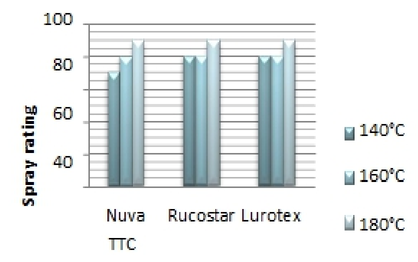


Fig 2. Spray rating test result at chem. conc. 10g/l before wash for woven fabric

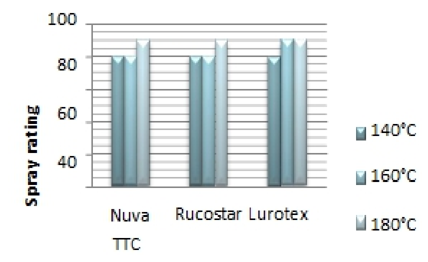


Fig 3. Spray rating test result at chem. conc. 10g/l before wash for knit fabric

Figure 2. showed that three samples were treated with 10g/l chemicals but their repellency ratings varied with curing temperatures. All chemicals showed better repellency which were cured at 180°C rather than samples which were cured at 140°C & 160°C because high temperature is suitable for curing & curing is the main condition for showing good repellency because during curing water repellent chemicals crosslinking with the fiber molecules

Figure 3. also showed the same character from the curing temperature point of view but showing better result than woven samples. Fabric compactness play a role in that case.

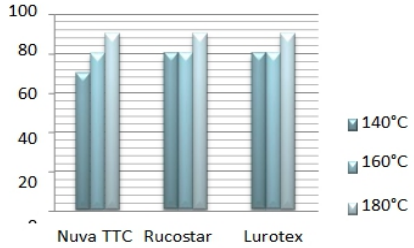


Fig 4. Spray rating test result at chem. conc. 10 g/l after 5 wash for woven fabric

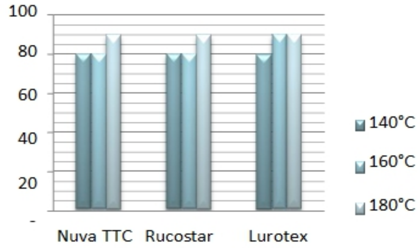


Fig 5. Spray rating test result at Chem. conc. 10 g/l after 5 wash for knit fabric

Figure 4 and **Figure 5** showed the repellency rating after 5 cycle wash & it indicated there are no change in repellency rating compared to before wash even those samples which are cured at 140°C.

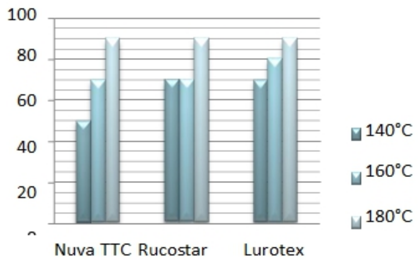


Fig 6. Spray rating test result at chem. conc.10g/l after 15 wash for woven fabric

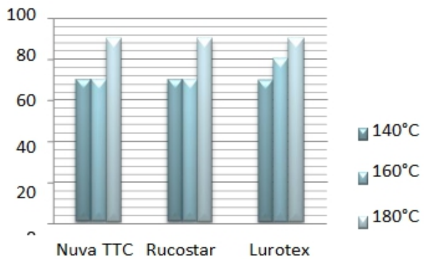


Fig 7. Spray rating test result at Chem. conc. 10 g/l after 15 wash for knit fabric

Figure 6 and **Figure 7** showed the repellency ratings both woven & knit sample after 15 cycle wash. These figures indicated that samples cured at 180°C both woven & knit fabric showing same repellency character with before wash samples which means curing temperature is also important for the durability of the water repellency.

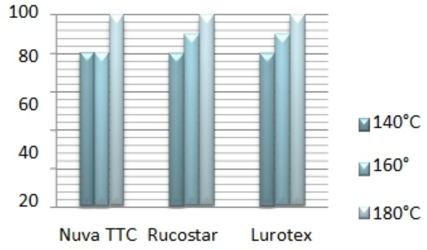


Fig 8. Spray rating test result at chem. conc. 30g/l before wash for woven fabric

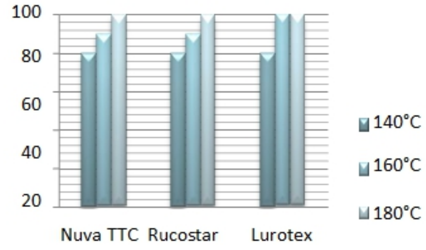


Fig 9. Spray rating test result at Chem. conc. 30 g/l before wash for knit fabric

Figure 8 and **Figure 9** showed the water repellency ratings both for woven & and knit fabric which were treated with 30g/l Nuva TTC,30g/l Rucostar EEE6 & 30g/l Lurotex Protector RP ECO followed by curing at 140°C,160°C ,180°C. It showed that with the increasing of chemical concentration, the repellency character both woven & knit samples increased. Even at curing temperature 140°C samples showed better repellency then the samples treated with 10g/l. So chemical conc. has also an impact at repellency ratings. Knit samples which were treated with Lurotex protector RP ECO showed 100 repellency rating even at 160°C curing temp.

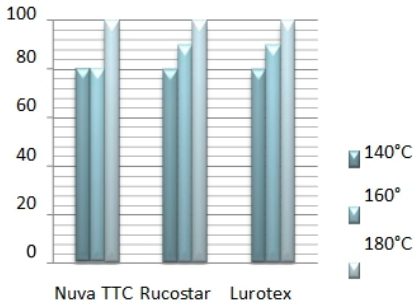


Fig 10. Spray rating test result at chem. conc. 30g/l after 5 wash for woven fabric

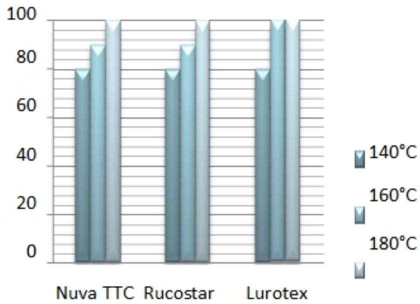


Fig 11. Spray rating test result at chem. conc. 30 g/l after 5 wash for knit fabric

Figure 10 and **Figure 11** showed the water repellency ratings for woven and knit samples after 5cycle wash & there was no change in repellency ratings as there was no change in case of 10g/l treated samples.

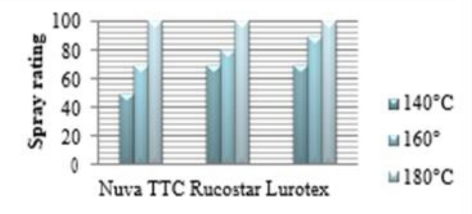


Fig 12. Spray rating test result at chem. conc. 30g/l after 15 wash for woven fabric

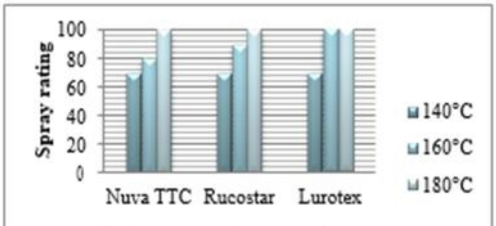


Fig 13. Spray rating test result at Chem. conc. 30 g/l after 15 wash for knit fabric

Figure 12 and **Figure 13** showed repellency ratings after 15 cycle wash. The samples repellency ratings did not change even after 15 wash except only those samples which were cured at 140°C temperature.

Air permeability test

Air permeability was normally used as an indicator to study the breathability of water repellent fabrics. Breathability is one of the most important factors of the clothing which decides comfort of the fabric. Air permeability was measured for the untreated & samples which were treated by 10g/l,30g/l, 50g/l chemical conc. for all 3 water repellent chemicals both knit and woven samples.

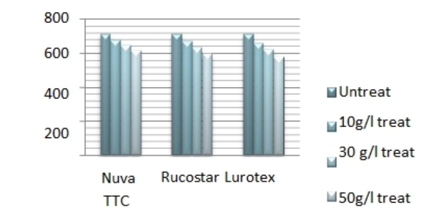


Fig 14. Air permeability test result for woven fabric

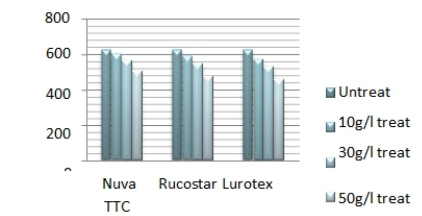


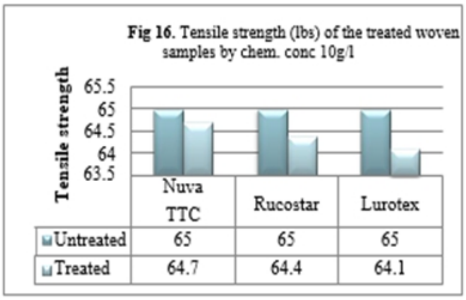
Fig 15. Air permeability test result for knit fabric

Figure 14 and **Figure 15** showed the air permeability result both for woven & knit samples. Both figures indicated that air permeability value decreased with the increasing of chemical conc. Because with the increasing of chemical conc. chemical coating layer increased. As a result, spacing of fabrics decreased and thus air permeability decreased.

Tensile strength test of woven fabric

ASTM test method D5045-06 was used to evaluate the strength of untreated & treated woven fabric.

Figure 16 showed that tensile strength of the treated fabric slight lower than the untreated samples which was negligible.



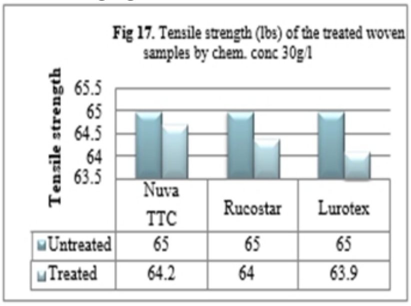
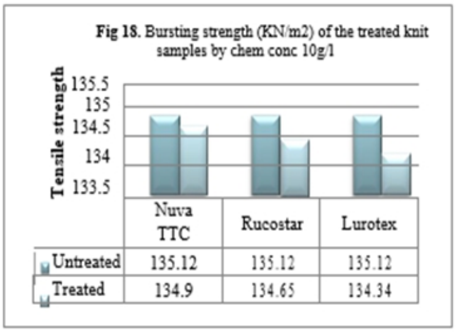
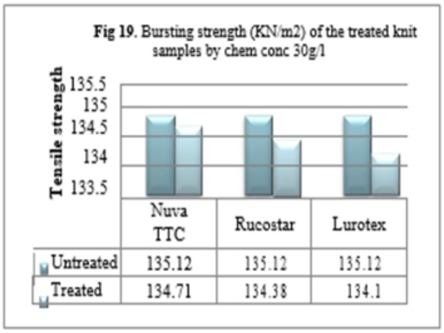


Figure 17 showed the tensile strength test result when the samples were treated with 30g/l chemical conc. In this time tensile strength also decreased which was slight more than previous case but it was in acceptable range.

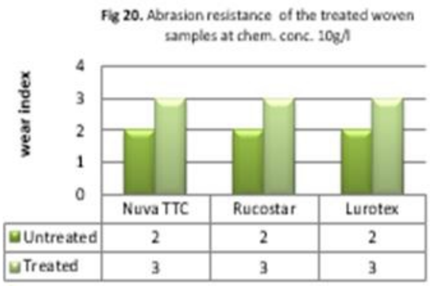
Bursting strength test of knit fabric

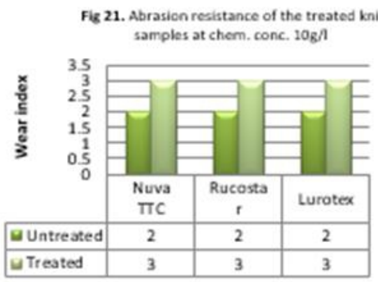




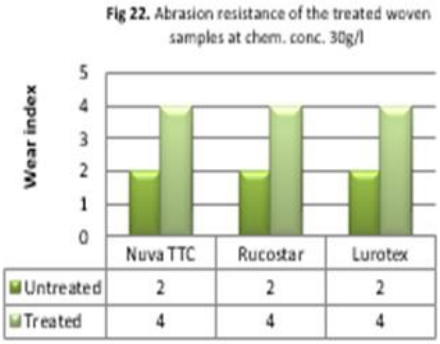
ASTM test method D3786 was used to evaluate the treated knit fabric strength. **Figure 18** showed bursting strength of the cotton knit fabric & this time also slight deterioration occurred but it was in acceptable range. **Figure 19** showed the bursting strength of the cotton knit fabric treated with chemical conc. 30g/l & this time as well slightly decreased bursting strength of the cotton knit fabric but it was in minimum range.

Abrasion resistance test





ASTM test method D 4966 was used to evaluate the abrasion resistance of the untreated & treated samples. **Figure 20** and **Figure 21** showed that abrasion resistance of the untreated and treated samples with chem. conc. 10g/l in which the treated samples were slight better than the untreated woven & knit fabrics.



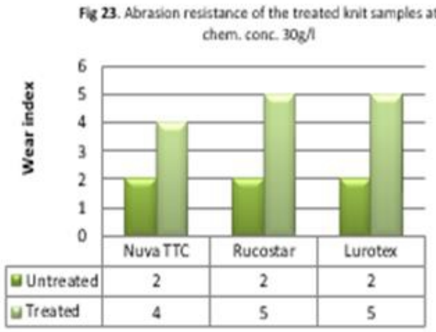


Figure 22 and **Figure 23** showed with the increasing of chemical concentration abrasion resistance increased. As fluorocarbon produces a soft smooth surface so it played an important role to improve the abrasion resistance of the fabric.

Conclusion

The health and environmental attributes of water repellent chemistries, including raw materials and byproducts are critical factors to consider. The water repellent chemicals used in this work showed to be less toxic and bio accumulative, as these are free from PFOA & PFOS. The quality of treated samples was also satisfactory and if the process parameters are maintained accurately, then desired results can be found. By-products of short-chain fluorinated chemistries are persistent in the environment. The move from fluorinated to non-fluorinated repellent chemistries is much more challenging one and also require an in-depth research to realize the practical application of non-fluorinated repellent finishes on textile products. Research and development efforts are also needed to make certain that non-fluorinated chemistries can provide the desired fabric attributes as well as meet their defined performance requirements. Lack of hazard data should not correspond to the assumption that these chemistries are safer or have favorable human health and environmental properties.

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