

Investigation onto the Effect of Surface Etching using Chemical Etchants on the Dye-Ability of UHMWPE Fibre

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RECEIVED ON 11.04.2020, ACCEPTED ON 20.12.2020

ABSTRACT

Ultra high molecular weight fibre cannot be dyed using conventional dyeing techniques as they are extremely hydrophobic and do not possess any polar groups. Wet etching of the surface was used as the pre-treatment process to improve the dyeability of the Ultrahigh Molecular Weight Polyethylene (UHMWPE) knitted fabric using potassium dichromate and sulphuric acid as etchants. The surface modified fabric was dyed at 130°C using High Temperature (HT) dyeing technique with disperse dye and evaluated in terms of Colour Strength (K/S), washing fastness, rubbing fastness, and tenacity. It has been observed that wet etching improved the colour strength substantially with an overall good fastness to washing and rubbing but the tenacity decreased with an increase in etching time.

Keywords: Chemical etching, Dyeing, Fastness Properties, Surface modification, Ultrahigh Molecular Weight Polyethylene.

1. INTRODUCTION

The UHMWPE has high chemical resistance, good flexibility and remarkable strength along with low density that makes it suitable for many technical applications. However, low melting point, and no chemical interaction of the interface limits the possible applications at high temperatures and coloration of this fibre [1- 4]. It has been found that UHMWPE fibre cannot be dyed without prior surface modification using conventional dyes and dyeing methods. Most of the previous work was done to develop special hydrophobic dyes having long alkyl substituents to dye this fibre using conventional methods of dyeing. It was reported that for dyes to have affinity to the highly hydrophobic fibres like UHMWPE, they essentially have strong hydrophobicity [5 - 9]. Disperse azo dyes were also used by the researchers to dye UHMWPE fibre using the supercritical CO₂ dyeing technique. Acceptable fastness to sublimation, storage and washing were obtained using this technique [11].

It has also been reported that if certain functional groups are incorporated into the fibre then the overall wettability and dyeability of the fibre improves. Atmospheric plasma surface etching and wet etching using various chemical etchants were also explored by the researchers to graft oxygen containing functional group into the outer layer of a fabric thus enhancing the wettability and dyeability of a fabric significantly [2, 4]. However, longer plasma treatment time has an adverse effect on the tear strength of a fibre [4]. The integration of roughness, outer layer removal, and changes in oxygen bonding using chemical etchant aids in explaining the better adhesion on chromic acid etching despite the fall in surface oxygen. The escalation in roughness similarly provides sites for mechanical interlocking among a dye and the fiber [2].

It has also been reported that the UV/ozone irradiation on the UHMWPE film roughens the surface and improves surface energy of the UHMWPE film which

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in turns decreases the contact angle with the water. The dyeing ability of UHMWPE films towards cationic dyes improves because of higher hydrophilic surface and tough electrostatic attraction among the anionic dyeing sites and cationic dyes are introduced during UV irradiation of the UHMWPE film [10].

It can be clearly seen from the previous work that wet etching was scarcely investigated as an effective method to improve the dyeability of that fibre. More emphasis was on the development of superhydrophobic dyes to dye these UHMWPE fibres. The present study aims to improve the dyeability of UHMWPE fabric through fibre surface modification by chemical etchant without compromising the washing fastness, rubbing fastness and strength of the material using conventional dyes and dyeing methods.

2. EXPERIMENTAL SETUP

2.1 Materials and Methods

The UHMWPE, filament of 400 denier was kindly supplied by Midas Safety Clothing. Potassium dichromate and sulphuric acid (99% of purity) of analytical grade was purchased from Merck. Disperse dye Foron BLACK-603 and dispersing agent Unividine PB were kindly supplied by Archroma.

2.2 Surface Modification

Potassium dichromate and sulphuric acid were used to modify the surface of UHMWPE knitted fabric. The etching solution was prepared by mixing potassium dichromate (IV) ($K_2Cr_2O_{17}$), sulphuric acid (H_2SO_4), and distilled water in a 7:150:12 mass ratio as suggested by Silverstein [2]. The etching time given was varied from 5 min, 30 min, 3.5 hour, and 24 hour. Once the etching process completed, the material was rinsed initially with distilled water for 2 min and then washed in an ethanol solution for 2 min. This washed sample was lastly dried at room temperature.

2.3 Dyeing

Modified Ultra-high molecular weight polyethylene knitted fabric was dyed at 130 °C for 30 min as per

recipe given in **Table 1** using the dyeing profile given in Fig. 1.

S. No.	Ingredients	Quantity
1.	Foron Black-603	4% owf
2.	Dispersing agent	3%
3.	Liquor ratio	40:1
4.	Temperature	130°C
5.	Time	30 min

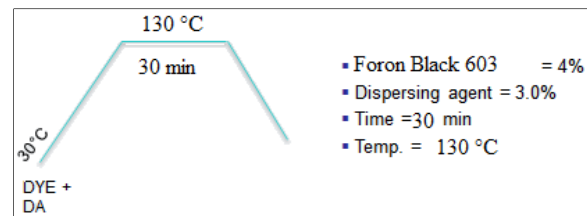


Fig. 1: Dyeing Profile of UHMWPE Fibres using Disperse Dye

3. TESTING

3.1 Colour Strength

Colour strength of the dyed fabric was determined by calculating the K/S value using equation (1). The %R of the dyed fabric was assessed using datacolor 650 spectrophotometer with large aperture, UV filter off and specular included mode.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where, K is the absorption coefficient, S is the scattering coefficient and R is the minimum reflectance of the coloured specimens. To analyze the effect of etching time on dyeability of UHMWPE, equation (1) is used to calculate the K/S values of treated and untreated samples of UHMWPE.

3.2 Fastness Properties

Colour fastness to rubbing was performed using AATCC-08 test procedure, while colour fastness to washing was done using ISO-CO4. An Average value of the five test samples, both for washing (staining and change of shade) and rubbing (wet and dry) was used in analysing the effect of surface modification to the dyeing of UHMWPE knitted fabric.

3.3 Tenacity

In order to investigate the effect of etching on the strength of the UHMWPE knitted fabric, tenacity was evaluated using the standard test procedure ASTM D 2256.

3.4 FTIR and SEM Analysis

FT-IR spectra of treated and untreated dyed fabric were analyzed to identify the presence of any new chemical group onto the treated fabric using Attenuated Total Reflection (ATR) mode. Scanning Electron Microscopy (SEM) analysis was conducted to evaluate the structural changes of the treated and the untreated dyed fabric.

4. RESULTS AND DISCUSSION

4.1 Effect of Etching Time on Dyeability

In order to analyze the effect of etching time on the colour strength of the UHMWPE knitted fabric, etching time was varied from 5min, 30 min, 2.5 hour and 24 hour. The wet etched fabric was later dyed using exhaust dyeing technique at 130°C for 30 min as per recipe given in Table 1.

It has been observed that the dyeability of UHMWPE knitted fabric improved significantly with an increase in the dipping time in the etchant solution as shown in Fig. 2. This may be attributed due to a roughening of the fibre surface as well as introduction of the carbonyl groups to the fibre due to etching treatment given to

the fabric prior to dyeing. SEM images of the untreated and treated fabrics are shown in Fig. 3, where it can be seen clearly that that the treated fabric surface is considerably rough (see Fig. 3(b)) than the untreated fabric (see Fig. 3(a)), which is one of the reason of improved dyeability of UHMWPE fibre.

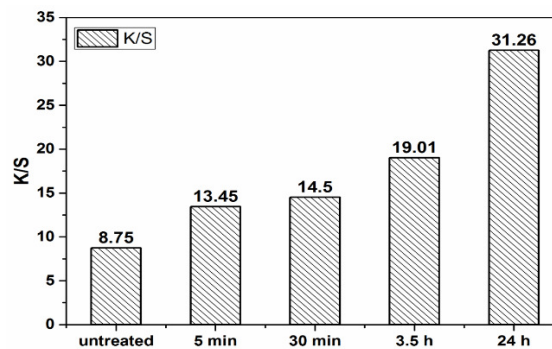


Fig. 2: Comparison of Color Strength of Untreated and Treated UHMWPE

FT-IR testing of the untreated and the treated samples have been conducted to ensure if any new chemical group has been imparted in the fibre as a result of this etching treatment or not. It is evident from Fig. 4(a) that the original UHMWPE fibers have no absorption around 1640 cm^{-1} in the spectra curves and after chromic acid treatment there was an absorption in the spectra at about 1640 cm^{-1} (see Fig. 4(b)), clearly showing that carbonyl groups have been introduced as a result of this etching treatment using sulphuric acid and potassium dichromate. The introduction of these groups along with roughness of the surface were responsible for better colour strength and improved wash and rubbing fastness sites onto the fabric.

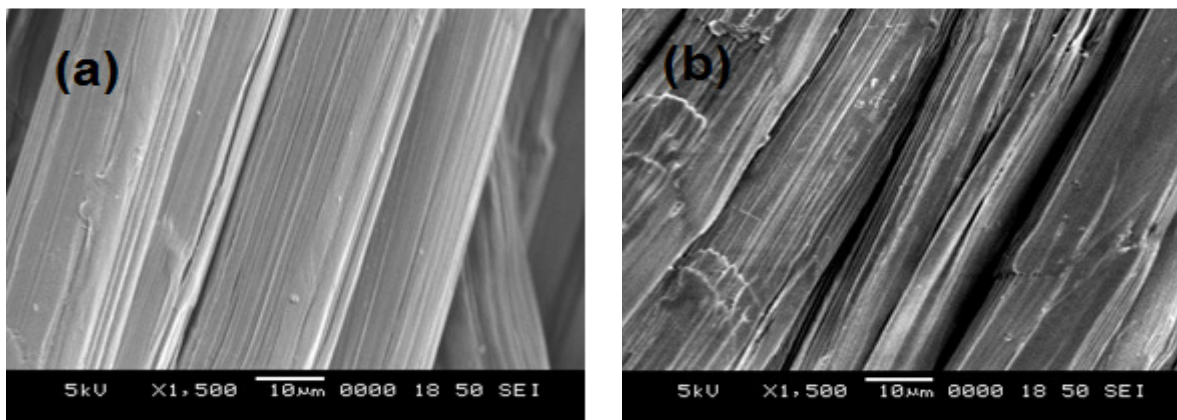


Fig. 3: SEM images (a) untreated and (b) treated UHMWPE

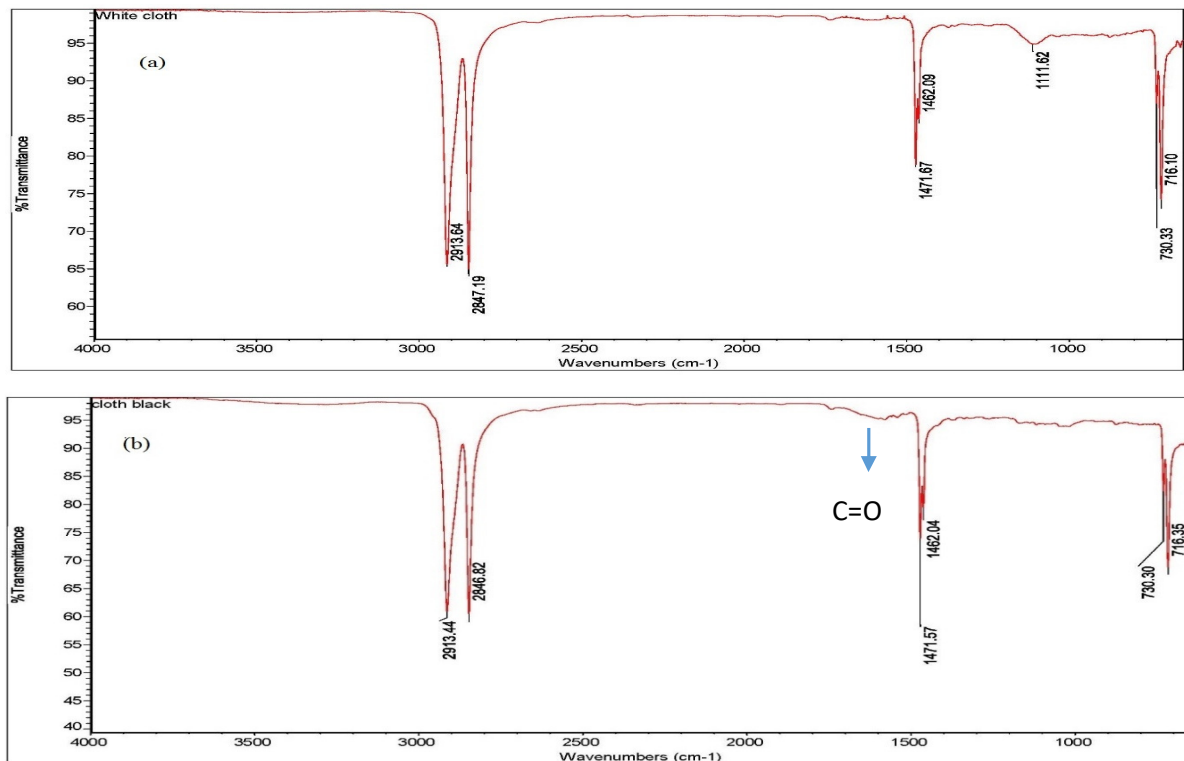


Fig. 4: FT-IR spectra of the (a) untreated and (b) treated UHMWPE

Though this etching treatment considerably enhanced the colour strength of the fabric but it can be observed that the tenacity of a material has been dropped significantly with an increase in etching time as shown in Fig. 5. This reduction in tenacity is due to the excessive roughing of the fibre.

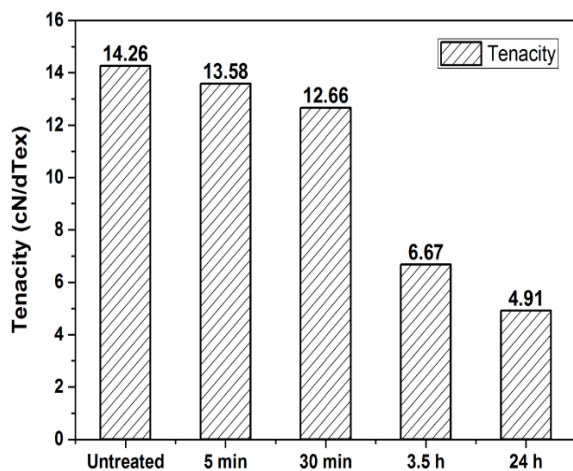


Fig. 5: Comparison of Tenacity of Untreated and Treated UHMWPE

5. EFFECT OF ETCHING TIME ON FASTNESS PROPERTIES

Fastness to washing and rubbing of the UHMWPE filament dyed with and without etching treatment are summarized in Table 2. It is evident from Table 2 that an increase in the dipping time improved the fastness properties to washing and rubbing. However, dipping greater than 30 min has an adverse effect on the fastness properties as well as on the strength of the material. Washing fastness and dry rubbing were found to be good showing color change rating of 4 for both the trials. However, wet rubbing fastness was rated 3 when etching time increased up to 3.5 hrs or more nevertheless this rating is practically adequate enough in terms of dark shades.

6. CONCLUSION

It can be concluded that the dyeing of UHMWPE fibre cannot be dyed using conventional dyes without modifying the surface of the fibre. In this study wet etching technique is used to enhance the roughness of

Table 2: Fastness properties of Surface Modified Dyed UHMWPE

S. No.	Properties	Untreated	Etching 05 min	Etching 30 min	Etching 3.5 h	Etching 24 h
1	Dry Rubbing	3-4	4	4	4	4
2	Wet Rubbing	4	4	4	3	3
3	Wash Fastness	4-5	4	4	4	4

the surface and to incorporate the carbonyl groups into the fibre as this technique does not require any special equipment or conditions making it conventionally suitable for production scale. It has been observed that treatment with chromic acid prior to dyeing of ultra-high molecular weight polyethylene substantially improved the color strength as well as fastness to rubbing and washing but the strength of the treated material decreases with an increase in treatment time. It can further be concluded that a treatment time of 30 min is sufficient to get adequate results in terms of colour strength and fastness without compromising the strength of the material to higher extent.

ACKNOWLEDGEMENT

The authors express their earnest thanks to Midas Safety & Clothing for providing material and Archroma Pakistan for providing chemicals and auxiliaries. This research work was carried out at Textile Engineering Department, NED University of Engineering and Technology.

REFERENCES

1. Yu J., Hu Z., Liu Z., "Study on The Modification of Ultrahigh Molecular Weight Polyethylene Fiber with Polar Polymers", *Research Journal of Textile and Apparel*, Vol. 10 No. 1, pp. 1-7, 2006.
2. Silverstei M. S., Breuer O., Dodiuk H., "Surface modification of UHMWPE fibers", *Journal of Applied Polymer Science*, Vol. 52, No. 12, pp. 1785-1795, 1994.
3. Chiu H.T., Wang J.H., "The relationship between zeta-potential and pull-out shear strength on modified UHMWPE fiber reinforced epoxy composites", *Polymer Composites*, Vol. 19, No. 4, pp. 347-351, 1998.
4. Bartusch M., Hund R.D., Hund H., Cherif C.,

"Surface functionalisation of UHMW polyethylene textile with atmospheric pressure plasma", *Fibers and Polymers*, Vol. 15, No. 4, pp. 736-743, 2014.

5. Yun D. W., Jang J., "Surface Modification of Ultra High Molecular Weight Polyethylene Films by UV/ozone Ir Radiation", *Textile Coloration and Finishing*, Vol. 23, No. 2, pp.76-82, 2011.
6. Kim T. K., Yoon S. H., Hong J. P., Kim H. J. Bae J. S., "Coloration of Pure Polypropylene Fiber with Super Hydrophobic Dyes; Application of Anthraquinone Derivatives with linear Alkyl Substituents", *Textile Coloration and Finishing*, Vol. 18, No..5, pp.30-34, 2006.
7. Kim T. K., Jung J. S., Yoon S. H., Kim M. K. Son Y. A., "The Coloration Properties of Alkyl-substituted Anthraquinoid Dyes for Pure Polypropylene Fiber", *Textile Coloration and Finishing*, Vol. 19, Issue 6, pp. 28-34, 2007.
8. Kim T. K., Jung J. S., Son S. I., Yoon S. H., Kim M. K. Bae J. S., "Synthesis and application of alkyl-substituted disazo yellow dyes for unmodified polypropylene fiber", *Fibers and Polymers*, Vol. 9, No. 5. pp. 538-542, 2008.
9. Kim T. K., Jung J. S., Jang K. J., Yoon S. H., Kim M. K., "Synthesis and application of alkyl-substituted high chroma yellow dyes for unmodified polypropylene fiber", *Fibers and Polymers*, Vol. 10, No. 2, pp. 148-153, 2009.
10. Kim T. K., Jang K. J., Jeon S. H., "Synthesis of Red Disperse Dyes with Various Diazo Components and Coloration of Unmodified Pure Polypropylene Fibers", *Textile Coloration and Finishing*, Vol. 22, No. 1, pp. 1-7, 2010.
11. Bach E., Cleve E., Schollmeyer E., "The dyeing of polyolefin fibers in supercritical carbon dioxide Part II: The influence of dye structure on the dyeing of fabrics and on fastness properties", *The Journal of The Textile Institute*, Vol. 89, No. 4, pp.657-668, 1998.