ENHANCED WASHING DURABILITY OF ELECTROCONDUCTIVE $Ti_3C_2T_X$ MXENES ON COTTON FABRIC USING VARIOUS PROTECTIVE COATINGS

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Abstract

The incorporation of electroconductive compounds onto the textiles' surfaces leads to the fabrication of flexible electronic textiles (e-textiles) for numerous application fields, i.e., sport, medical, protective, fashion, military, etc. Their long-term functionality during daily usage depends on the sufficient durability of applied electroconductive compounds against washing, which can be significantly improved by the employment of protective layers. Thus, this study investigated the efficacy of different coatings for the protection of $Ti_3C_2T_x$ MXenes dip-coated onto cotton fabric against laundering without essentially influencing fabrics' electroconductive properties. Two Mxene-functionalised samples were protected with three different compounds, i.e., modified acrylate resin (MAR), waterborne polyurethane resin (WPR) and biantennary oligoglycine peptide (tectomer - 2 tailed) utilising spray-coating, dip-coating and impregnation procedures, respectively. MXene-functionalised/protected samples were washed up to 20 washing cycles and characterised by the determination of their electrical resistance, mass loss, changes in surface morphologies, water contact angle and optical properties. Based on these results, WPR provided the most suitable protection of MXenes on cotton fabric, followed by MAR, balancing high conductivity with long-term stability. Tectomer is not recommended for MXene protection due to its low durable performance against harsh washing conditions.

Keywords: $Ti_3C_2T_x$ MXenes, protective coatings, cellulose fabric, washing durability

1. INTRODUCTION

The application of MXenes often does not lead to permanent effects on the textile surface during daily use (limited wash durability) due to the inhomogeneity and roughness of textiles as well as the small sheet size and weak interlayer interaction between MXene sheets [1]. Consequently, textiles lose their electroconductive functionalities after laundering. Moreover, it is necessary for MXene to avoid its restack and oxidisation, which will hinder its relative capacitance and stability.

Several researchers enhanced the durability of MXenes on textiles and simultaneously added some advanced functionalities by employing different adhesives or polymers. Luo et al. [2] coated, firstly, an interface polydopamine layer on the elastic textile substrate to smooth the surface and enhance adhesion and, secondly, a protective polydimethylsiloxane (PDMS) layer over the Mxene network to obtain the superhydrophobic, breathable and elastic smart textile device. Ma et al. [3] also applied a thin layer of PDMS as an adhesive for MXene to prepare a hydrophobic and multifunctional textile composite. Wang et al. [4] prepared highly conductive and hydrophobic textiles with exceptional electromagnetic interference (EMI) shielding efficiency and excellent Joule heating performance by depositing in-situ polymerised polypyrrole (PPy) modified MXene sheets onto polyethylene terephthalate textiles followed by a silicone coating. Yan et al. [5] electrochemically deposited PPy on the surface of MXen-decorated plain cotton textiles to further improve the capacitive performance of the MXene-based electrode and avoid the oxygen oxidation of MXene.

In this research, $Ti_3C_2T_x$ MXene nanosheets applied on cotton fabric according to an optimised dip-coating procedure were further protected against peeling-off due to harsh washing conditions, i.e., water, temperature and physical-mechanical forces, by employing three different compounds, modified acrylate resin (MAR), waterborne polyurethane resin (WPR) and tectomer (TEC). MXene-functionalised/protected fabrics were characterised before and after washing (up to 20 washing cycles) by measuring the electrical resistivity and determining the mass loss and water contact angle. Moreover, the changes in optical properties and surface morphologies were inspected.

2. EXPERIMENTAL PART

2.1 Materials

Trials were performed using an industrially bleached plain-waived cotton fabric with a mass/unit area of 92.7 ± 0.6 g/m^2, warp density of 51 threads/cm, weft density of 44 threads/cm, and thickness of 0.18 mm. Two titanium aluminium carbide Ti_3AlC_2 MAX precursor powders, in sizes of 40 μm and 100 μm, for the synthesis of MXene nanosheets were supplied by Sigma-Aldrich. Lithium fluoride (LiF; 99.99 wt%) and hydrochloric acid (HCl; 37 wt%) as etchants were purchased from Apollo Scientific Ltd. and Honeywell, respectively.

Two types of $Ti_3C_2T_x$ Mxene flakes, small- (S) and large-sized (L), were synthesised from 1 g of MAX precursor powders (two sizes) by a top-down minimally intensive layer delamination (MILD) approach [6]. Briefly, LiF was initially dissolved in a 250 mL polytetrafluoroethylene beaker containing an HCl solution. The solution was continuously stirred at 35 °C for 30 minutes and 400 rpm, resulting in total dissolution of the LiF. Then, 1 g of Ti_3AlC_2 (MAX powder) was gradually added to the above mixture and left to etch the Al layer under continuous stirring. After completion of the reaction, the obtained mixture was washed with deionised (DI) water and centrifuged numerous times at 3,500 rpm for 5 minutes per cycle until a stable dark green supernatant solution with pH 6 and a swelling clay precipitate was produced.

2.2 Dip-coating of MXenes and application of protective coatings

Cotton fabric (Co) was sectioned into samples of sizes 2×2 cm^2 and modified by two synthesised $Ti_3C_2T_x$ MXene nanosheets (S and L) employing a dip-padding procedure. The individual fabric sample was dipped three times into 10 mL MXene aqueous dispersion (10 mg/mL) for 5 min, followed by an intermediate/final vacuum-assisted drying at 60 °C, preparing two samples (CoS and CoL).

Three different protective compounds were applied onto MXene-decorated samples, i.e., modified acrylate resin using a pre-optimised spray-coating (CoS-MAR and CoL-MAR), waterborne polyurethane resin by pad-drying (CoS-WPR and CoL-WPR) and tectomer by impregnation (CoS-TEC and CoL-TEC).

2.3 Washing

To evaluate the washing durability of the prepared MXene-modified and MXene-modified/protected cotton fabrics, samples were washed up to 20 times (washing cycles) at a temperature of 40 °C for 30 min. The washing solution consisted of a standard reference detergent without optical brighteners, with a concentration of 1 g/L and a liquor-to-fabric weight ratio of 50:1. After each washing cycle, the samples were rinsed in tap water for 1 min and then dried at 60 °C for 20 minutes. After each washing cycle, the mass loss of the samples was calculated.

2.4 Analytical procedures

Fourier Transform Infra-Red (FTIR) spectroscopic measurements of samples were performed using a Spectrum GX spectrophotometer (Perkin Elmer) with a Golden Gate ATR attachment and a diamond crystal. The absorbance spectra were obtained within the range of 4.000-400 cm^{-1}, with 32 scans and a resolution of 4 cm^{-1}. By using a two-point probe multimeter 34410A 6 1/2 Digit (Agilent technologies), the electrical

resistance of selected samples was measured across the entire surface area between two consistently sealed connections before and after 5,10,15 and 20 washing cycles. In addition, the specific electrical resistivity (in Ω·cm) was calculated as a product of the measured electrical resistivity (in Ω) and the cross-sectional area of the fabric (in cm^2) divided by the length between two consistently sealed probe connectors (in cm). The Water Contact Angle (WCA) of MXene-coated/protected samples before and after washings was performed by means of the goniometer OCA 35 (DataPhysics Instruments) using the sessile drop technique. Optical properties were evaluated by measuring the reflectance of samples before and after each set of wash cycles (5, 10 and 20) using a two-ray spectrophotometer Spectraflash SF600 Plus (Datacolor, Trenton, NJ, USA), from which the CIE L*a*b* colour differences in all three directions of colour space were calculated.

3. RESULTS AND DISCUSSIONS

3.1 FTIR analysis of MXene-coated/protected fabrics

Figure 1 depicts FTIR results, confirming the successful application of protective compounds onto MXene-coated samples.

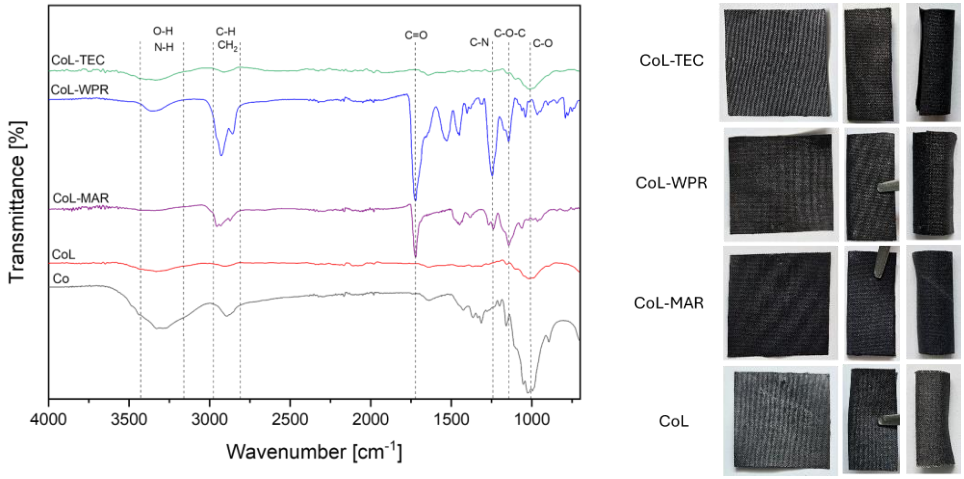


Figure 1 FTIR spectra of pristine (Co), MXene-coated (CoL) and MXene-coated/protected (CoL-TEC, CoL-WPR and CoL-MAR) cotton fabrics (left); and digital photographs of their foldability and rollability (right)

As noticed from **Figure 1**, the pristine cotton fabric shows a broad peak around 3200-3400 cm^{-1}, which was attributed to the stretching of the O–H groups; the peak near 2890 cm^{-1} was assigned to the band of C–H stretching vibrations, and the peak at 1210 cm^{-1} was the stretching of the C–O bond [7]. After the application of MXenes, the characteristic cotton peaks are diminished. A similar was noticed for the TEC-protected sample, implying that the MXene peak dominates over characteristic peptide peaks of TEC. Additionally, the MXene-modified/WPR-protected cotton spectrum has completely attenuated cotton peaks and shown absorption bands corresponding to N–H (3340 cm^{-1}), C–H (2920 cm^{-1}), C=O (1720 cm^{-1}), C–N (1240 cm^{-1}), and C–O–C (1100–1250 cm^{-1}) bonds, significant for WPR. For the sample protected with MAR, the most prominent peak appears at about 1720 cm^{-1} (C=O), at ~1140 cm^{-1} (C–O in the ester groups), and at 2950–2860 cm^{-1} (C–H) [8].

Moreover, the MXene-modified/protected fabrics maintained flexibility regardless of the protective coating used, demonstrating their potential in wearable electronic devices.

3.2 Washing durability of Mxene-functionalised/protected cotton fabric

With the aim to evaluate the efficiency of the selected compounds to protect MXenes onto cotton fabric against peeling off and oxidation, MXene-functionalised/protected samples were washed up to 20 cycles and

comprehensively characterised in terms of measuring the electrical resistance (**Figure 2**), determination of mass loss after 20 washings, WCA analysis (**Figure 3**) and investigation of changes of hue in a CIE L*a*b* colour space after 5, 10, and 20 washing cycles (**Table 1** and **Figure 4**).

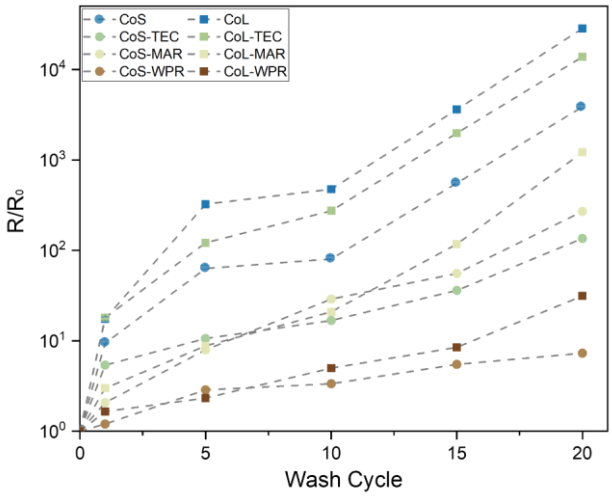
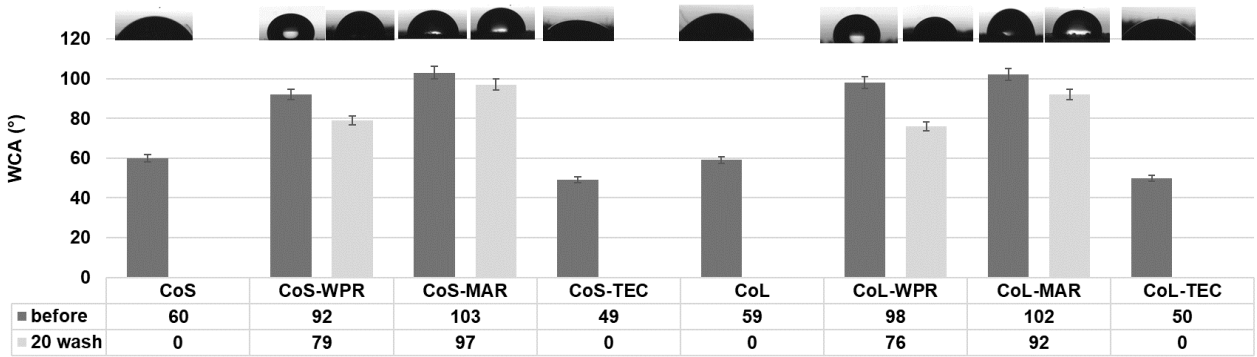


Figure 2 The electrical resistance relative to the initial value of the MXene-coated and MXene-coated/protected samples, up to 20 wash cycles

After five washes, both samples, CoS-PUR and CoL-PUR, exhibited a minimal raising of resistance, i.e., for 4.99% and 3.34 %, respectively, compared to their starting values, as seen in **Figure 2**. A similar trend was observed in MAR-treated samples with adequate protection during the early washing cycles, with a resistivity of 12.81 Ω·cm (CoS-MAR) and 6.34 Ω·cm (CoL-MAR) after five washes. Moreover, the CoS-MAR had a mass loss of only 0.92 % after the 20 washing cycles, while the CoL-MAR had a slightly higher mass loss of 1.30 %. Nevertheless, if the number of washing cycles exceeds 10, the resistivity rapidly escalates and can eventually reach the resistance level of untreated raw samples, losing electrical conductivity. The effectiveness of TEC protection varied significantly depending on the size of the applied MXenes.



	CoS	CoS-WPR	CoS-MAR	CoS-TEC	CoL	CoL-WPR	CoL-MAR	CoL-TEC
before	60	92	103	49	59	98	102	50
20 wash	0	79	97	0	0	76	92	0

Figure 3 WCA of MXene-coated and MXene-coated/protected samples before and after 20x washings

The WCA analysis (**Figure 3**) revealed excellent hydrophobic properties of the MXene-functionalised/MAR- or WPR-protected samples with high contact angles of around 100 °, regardless of MXene nanosheets lateral size. Unprotected samples had contact angles of ~60 °, presumably due to the inherent hydrophilic nature of both MXenes and the cotton. The protected samples remained hydrophobic even after 20 washing cycles. For MAR-protected samples, the WCA decreased for 6 ° (CoS-MAR) and 10 ° (CoL-MAR), and for WPR-protected samples for 13 ° (CoS-WPR) and 22 ° (CoL-WPR), demonstrating the robustness and efficacy of the coating in preserving the surface's hydrophobic properties. Meanwhile, TEC was the least effective compound for the

protection of MXenes against washings since the water drop spread immediately after surface contact after 20 washes. Consequently, water quickly penetrates through the pores during repeated washings, causing a loss of conductivity, as previously confirmed by an enlargement in electrical resistance.

Table 1 CIE colour differences of samples after 5, 10 and 20 washing cycles

Sample	CIE L*a*b* values			CIE colour differences											
				after five washing cycles				after ten washing cycles				after 20 washing cycles			
	L*	a*	b*	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
CoS	36.53	3.17	-4.05	-2.07	-1.98	1.29	3.14	-1.60	-2.80	2.00	3.79	0.33	-3.55	3.05	4.69
CoS-WPR	29.01	2.42	-1.54	-0.60	-0.46	-0.27	0.80	-1.53	-0.88	-0.41	1.81	-2.16	-1.58	-0.69	2.76
CoS-MAR	28.86	5.04	-9.47	0.55	-1.05	0.43	1.26	1.08	-1.09	-0.40	1.59	0.17	-1.91	0.84	2.09
CoS-TEC	33.17	2.44	-4.40	1.55	-1.28	1.49	2.50	1.06	-1.89	2.00	2.95	2.96	-2.70	3.14	5.09
CoL	38.77	3.06	-3.96	-1.63	-2.19	1.89	3.32	-1.13	-2.89	2.63	4.07	1.33	-3.49	3.57	5.17
CoL-TEC	36.24	2.22	-3.91	-0.81	-1.33	1.38	2.08	1.84	-1.81	2.01	3.27	6.60	-2.56	3.31	7.81
CoL-MAR	28.74	3.79	-6.62	0.38	-1.09	0.33	1.20	1.06	-0.74	-0.58	1.42	1.06	-1.52	0.13	1.86
CoL-WPR	28.95	2.11	-1.43	0.19	-0.16	-0.16	0.30	0.32	-0.36	-0.25	0.54	-0.14	-1.06	-0.36	1.13

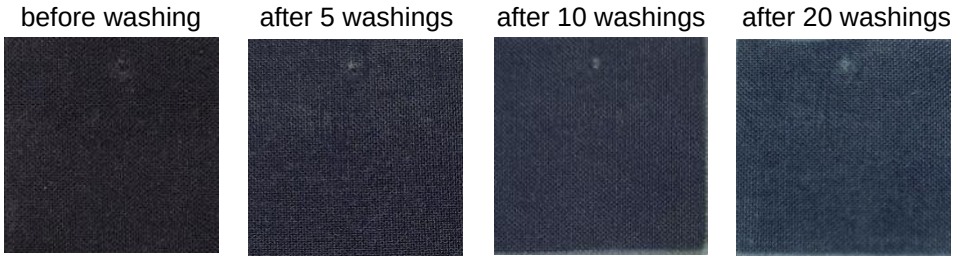


Figure 4 Photos of the CoL sample before and after washings

It is visually perceivable from **Figure 4** that with an increasing number of washing cycles, the sample CoL without protection becomes lighter and progressively exhibits a more greenish hue, i.e., the total colour change (ΔE) is 5.17. Values on the b-axis shift towards positive, and values on the a-axis towards negative (**Table 1**). Similar can be noted for all other samples. However, the changes are not linear and depend on the uniformity of the MXene deposition, the type of protective coatings, and the measurement location on each sample. The total colour change (ΔE) was significantly higher in samples without protective coatings. On the other hand, the ΔE values of WPR- and MAR-protected samples increased from 0.30 after 5 cycles up to 1.13 after 20 cycles (CoS-WPR) and from 1.20 after 5 cycles up to 1.86 after 20 cycles for the CoS-AR sample. The highest colour difference was observed in the CoS-TEC sample, with an ΔE of 7.81. The TEC was thus found unsuitable for the protection of MXenes, as also confirmed by low WCA and the high electrical resistance measured after washings.

CONCLUSION

In the presented study, the $Ti_3C_2T_x$ MXene nanosheets synthesised from small or large MAX precursors were successfully applied onto cotton fabric by the dip-padding procedure. The larger MXene flakes (in lateral size) imply higher electrical conductivity but lower adhesion and a greater tendency to oxidation. Therefore, three different protective compounds were applied to MXene-functionalised fabric, and two of them (WPR and MAR) significantly increased its hydrophobicity and, thus, protection against water accessibility. Moreover, the

adhesion of MXenes was enlarged even after 20 washing cycles. This approach significantly expands the potential applications of MXene-decorated fabrics in smart textile applications by providing good durability of electroconductive functionalisation. TEC is not recommended for MXene protection due to its low adhesion and hydrophobic performance.

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