Synthesis and Durability of Eco-friendly Zinc Oxide Nanoparticles for Multifunctional Compression Bandages

1.1.1 Comparison between calculated and measured compression using PicoPress

100% Cotton, CO-PA-PU, and VI-PU bandages were worn one by one on real leg to test the real compression pressure at ankle and mid-calf position in both static and walking conditions at different extension levels. Ankle and calf positions were adjusted at leg circumference of 25.6 and 38.9 cm respectively. Deviation percent was calculated as the difference between measured compression using Picopress and calculated pressure by Laplace's equation (5.10) [8, 9, 122, and 123], as illustrated in Tables 5.7 & 5.8.

$$Pressure\ (Pascal) = \frac{Tension\ (N)\ *\ No.\ of\ Layers}{Radius\ (m)\ *\ Bandage\ width\ (m)} \quad (5.9)$$

$$Pressure\ (mmHg) = \frac{T\ (N)\ *\ n}{R\ (m)\ *\ W\ (m)}\ *\ 0.0075 \quad (5.10)$$

The level of pressure exerted on a medical device matches with the Laplace's equation stating that the pressure (P expressed in Pa) of a compression applied to the skin surface is directly proportional to the tension (T in N) of the compression material and number of layers, and inversely proportional to the radius of curvature (R in m) of limb surface to which it is applied and the bandage width (W in m) [124].

$$\textbf{Deviation percent}\ (\%) = \frac{P_{Calculated} - P_{Picopress}}{P_{Calculated}}\ x\ 100 \quad (5.11)$$

Table 5.7. Calculated pressure by Laplace's equation vs. measured values at ankle position using Picopress (R= 4.07 cm)

Bandage type	No of layers	Extension (%)	Applied Tension (N)	Std. of tension	Measured compression Picopress (mmHg)	Calculated pressure values (mmHg)			
						Laplace's equation	Deviation percent (%)	Al Khaburi's equation	Deviation percent (%)
100% Cotton bandage	2	20	1.75	0.19	7.02	6.45	-8.84	6.29	-11.52
		30	2.81	0.07	10.84	10.36	-4.67	10.11	-7.24
		40	3.94	0.12	14.62	14.52	-0.68	14.17	-3.16
		50	6.06	0.31	21.71	22.33	2.79	21.80	0.41
		60	9.79	0.82	35.19	36.08	2.47	35.22	0.07
		70	13.37	1.41	45.71	49.28	7.24	48.09	4.96
		80	17.26	1.92	56.83	63.61	10.66	62.09	8.47

	3	20	1.8	0.22	10.58	9.95	-6.32	9.60	-10.22
		30	2.92	0.11	16.39	16.14	-1.53	15.57	-5.25
		40	4.05	0.17	21.83	22.39	2.50	21.60	-1.07
		50	6.24	0.39	32.67	34.50	5.29	33.28	1.83
		60	10.12	0.94	51.61	55.95	7.75	53.97	4.37
		70	13.85	1.55	68.38	76.57	10.69	73.86	7.42
		80	17.93	2.13	83.62	99.12	15.64	95.62	12.55
CO-PA-PU bandage	**2**	20	1.41	0.19	5.57	5.20	-7.19	5.07	-9.82
		40	3.58	0.13	13.81	13.19	-4.67	12.88	-7.24
		60	5.25	0.21	20.13	19.35	-4.04	18.88	-6.59
		80	8.64	0.49	32.15	31.84	-0.96	31.08	-3.45
		100	10.73	0.73	41.62	39.55	-5.25	38.60	-7.83
		120	13.97	1.65	47.93	51.49	6.91	50.25	4.62
	3	20	1.43	0.18	8.35	7.91	-5.62	7.63	-9.49
		40	3.64	0.15	21.06	20.12	-4.66	19.41	-8.49
		60	5.37	0.19	30.49	29.69	-2.71	28.64	-6.47
		80	8.91	0.53	46.43	49.26	5.74	47.52	2.29
		100	10.94	0.97	56.39	60.48	6.76	58.34	3.35
		120	14.23	2.19	71.69	78.67	8.87	75.89	5.53

The obtained results in Tables 5.7 & 5.8 and Figures 5.26 – 5.29 confirm that there are significant deviations when applying Laplace's equation for two and three layers bandaging ranging ±0.68 to ±15.64%. The highest deviation values were clearly significant at high extension levels 60-80%, this might be due to the compactness and high compression especially at ankle position. Moreover Jawad Al Khaburi developed this equation (5.12) to include the increase in limb circumference due to multilayer bandaging; this equation has decreased the deviation range to be ±0.07: ±12.55% as illustrated in the following equations [17, 125]:

$$P = \sum_{i=1}^{n} \frac{T_i\,(D_i+t_i)}{0.5*W_i*D_i^{2}+W_i*t_i\,(D_i+t_i)} * 0.0075 \qquad (5.12)$$

$$\text{Where} \quad D_i = D + \sum_{i=1}^{n} 2\,t_{i-1} \qquad (5.13)$$

Table 5.8. Multiple regression for the effect of bandage extension, number of layers, and bandage type on the measured pressure at ankle position

N=26	Regression Summary for Dependent Variable: **Measured pressure, Picopress** (Ankle position) R= .92307130 R^2 = .85206063 Adjusted R^2 = .83188708 F(3,22)=42.237 p-value = 0.000000002671713					
	b*	Std. Error of b*	b	Std. Error of b	t(22)	p-value
Intercept			-17.3050	10.53323	-1.64290	0.114621
Bandage Type	-0.342728	0.087243	-14.7613	3.75753	-3.92845	0.000718
No of layers	0.298003	0.082003	12.7969	3.52141	3.63404	0.001466
Extension	0.929065	0.087243	0.6829	0.06413	10.64922	0.000000

Results of Table 5.9 conclude that the deviation when applying Laplace's equation for mid-calf position is ranging ±0.27 to ±13.14%, while the deviation range of Al Khaburi's equation is ±0.14 to ±11.04%.

Table 5.9. Calculated vs. measured pressure values at mid-calf position (R= 6.19 cm)

Bandage type	No of layers	Extension (%)	Applied Tension (N)	Std. of tension	Measured compression Picopress (mmHg)	Calculated pressure values (mmHg)			
						Laplace's equation	Deviation percent (%)	Al Khaburi's equation	Deviation percent (%)
100% Cotton bandage	2	20	1.71	0.19	4.61	4.14	-11.25	4.08	-13.05
		30	2.74	0.07	7.13	6.64	-7.38	6.53	-9.12
		40	3.82	0.12	9.5	9.26	-2.63	9.11	-4.28
		50	5.89	0.31	14.21	14.27	0.44	14.05	-1.17
		60	9.55	0.82	23.08	23.14	0.27	22.77	-1.34
		70	13.15	1.41	30.85	31.87	3.19	31.36	1.62
		80	16.86	1.92	37.75	40.86	7.60	40.21	6.11
	3	20	1.76	0.22	7.08	6.40	-10.67	6.25	-13.34
		30	2.83	0.11	10.73	10.29	-4.31	10.04	-6.83
		40	3.97	0.17	14.11	14.43	2.22	14.09	-0.14
		50	6.11	0.39	20.92	22.21	5.80	21.69	3.53
		60	9.85	0.94	33.47	35.80	6.52	34.96	4.26
		70	13.46	1.55	44.21	48.93	9.64	47.77	7.46
		80	17.41	2.13	54.97	63.28	13.14	61.79	11.04
CO-PA-PU bandage	2	20	1.39	0.19	3.75	3.37	-11.33	3.31	-13.13
		40	3.54	0.13	9.33	8.58	-8.76	8.44	-10.52
		60	5.19	0.21	13.28	12.58	-5.59	12.38	-7.30
		80	8.54	0.49	21.65	20.69	-4.62	20.37	-6.31
		100	10.56	1.11	26.94	25.59	-5.28	25.18	-6.98
		120	13.61	1.90	33.15	32.98	-0.51	32.46	-2.14
	3	20	1.42	0.18	5.71	5.16	-10.63	5.04	-13.29
		40	3.61	0.15	14.41	13.12	-9.82	12.81	-12.47
		60	5.29	0.19	20.63	19.23	-7.29	18.78	-9.88
		80	8.71	0.53	32.89	31.66	-3.89	30.91	-6.39
		100	10.83	1.24	38.37	39.37	2.53	38.44	0.18
		120	14.11	2.38	45.94	51.29	10.43	50.08	8.27

Table 5.10. Statistical analysis of measured pressure at mid-calf position

N=26	Regression Summary for Dependent Variable: **Measured pressure, Picopress** (Mid-calf position) R= .92422059 R^2 = .85418370 Adjusted R^2 = .83429966 F(3,22)=42.958 p-value = 0.00000000228151764 Std. Error of estimate: 5.8675					
	b*	Std. Error of b*	b	Std. Error of b	t(22)	p-value
Intercept			-11.8498	6.884002	-1.72136	0.099220
Bandage Type	-0.323736	0.086614	-9.1788	2.455738	-3.73768	0.001141
No of layers	0.294456	0.081413	8.3238	2.301418	3.61683	0.001528
Extension	0.932014	0.086614	0.4510	0.041911	10.76051	0.000000

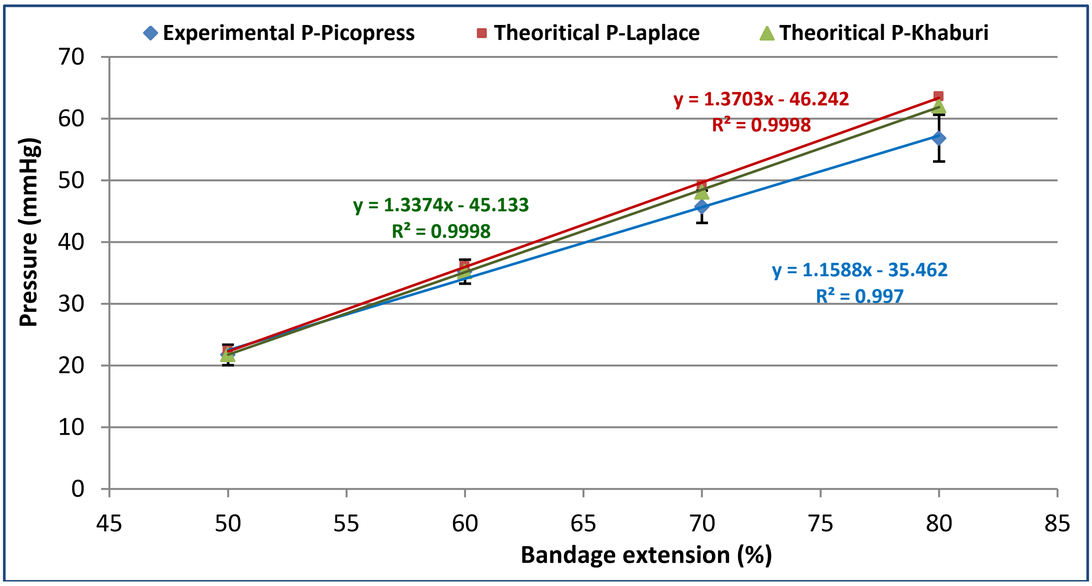


Figure 5.26. Measured bandage pressure by Picopress vs calculated by Laplace's and Al-khaburi's equations at ankle position using two layers of cotton bandage

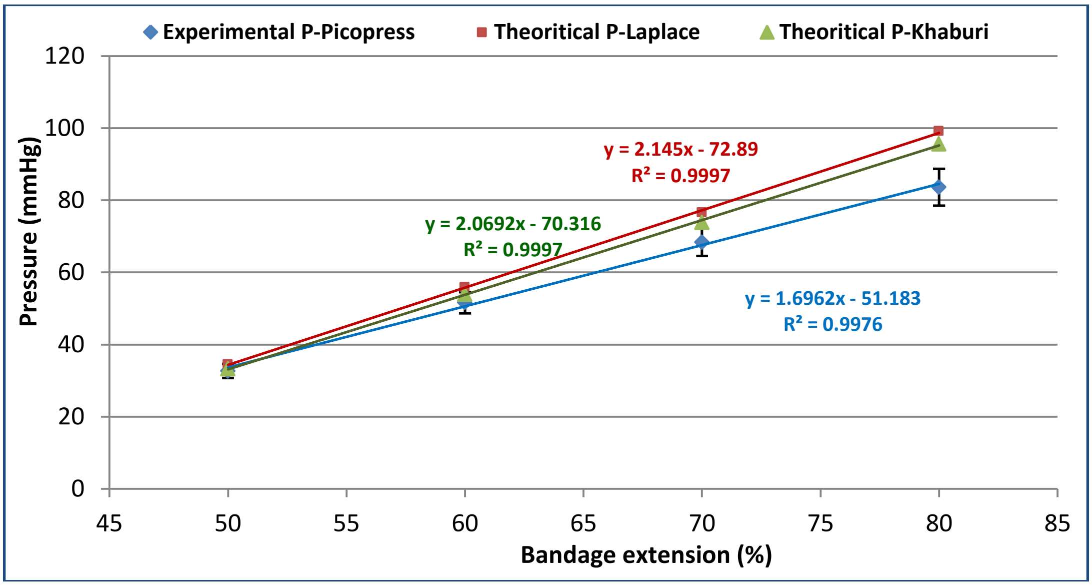


Figure 5.27. Measured bandage pressure by Picopress vs calculated values at ankle position using three layers bandaging

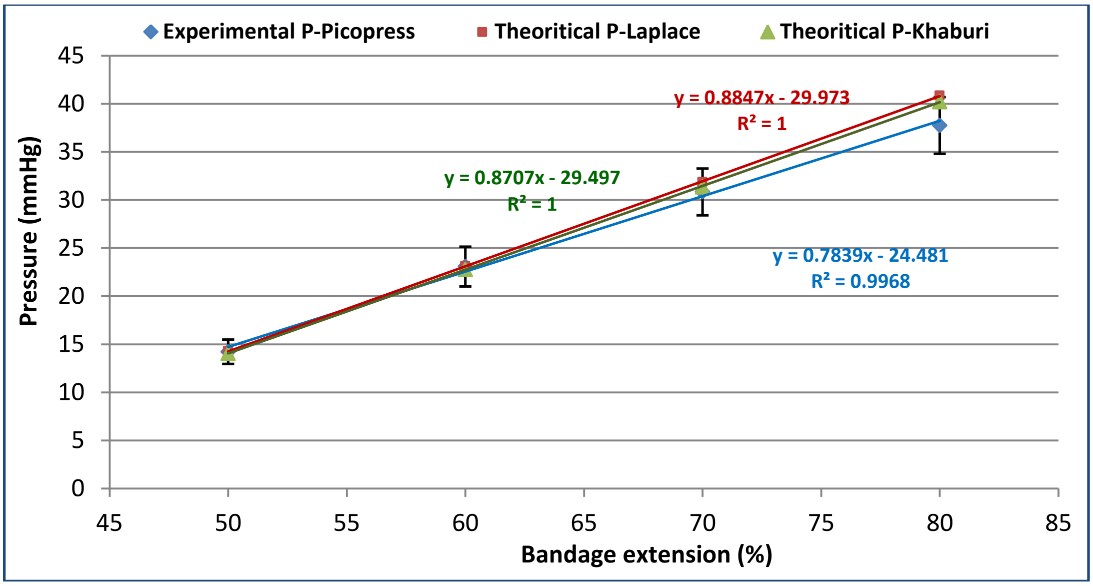


Figure 5.28. Measured bandage pressure by Picopress vs calculated values at mid-calf position using two layers bandaging

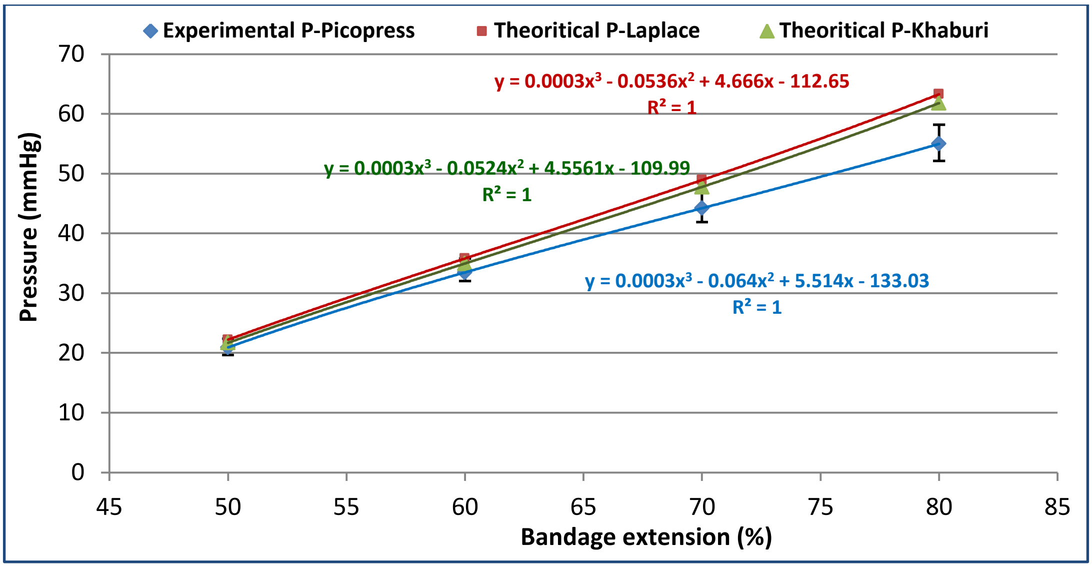


Figure 5.29. Measured bandage pressure by Picopress vs calculated values at mid-calf position using three layers bandaging

1.1.2 Effect of cyclic loading-unloading on bandage tension and durability

Two types of WCBs (100% Cotton short-stretch and CO-PA-PU long-stretch) were selected to investigate the relation between cyclic loading and the applied bandage tension at 60% and 120% extension. Elongation by 3 cm results in extension by 60% and dwell time for 2 seconds, then unloading 1 cm reduces extension to be 40% and dwell time for 2 seconds, then repeating whole cycle for 5 or 6 repeats then relaxation. Cyclic loading-unloading could simulate the walking action when wearing WCB, but the main obstacle is that the testing time is limited compared to the bandage application time. The uniaxial load of Cotton short-stretch WCB decreased by 11.82% after 6 cycles of loading-unloading, whereas CO-PA-PU long-stretch WCB lost only 4.81% of its applied load at

60% extension. Moreover CO-PA-PU lost 18.11% at 120% extension, see Figure 5.30. So that it is essential to include and compensate these reductions of bandage tension during its selection and application.

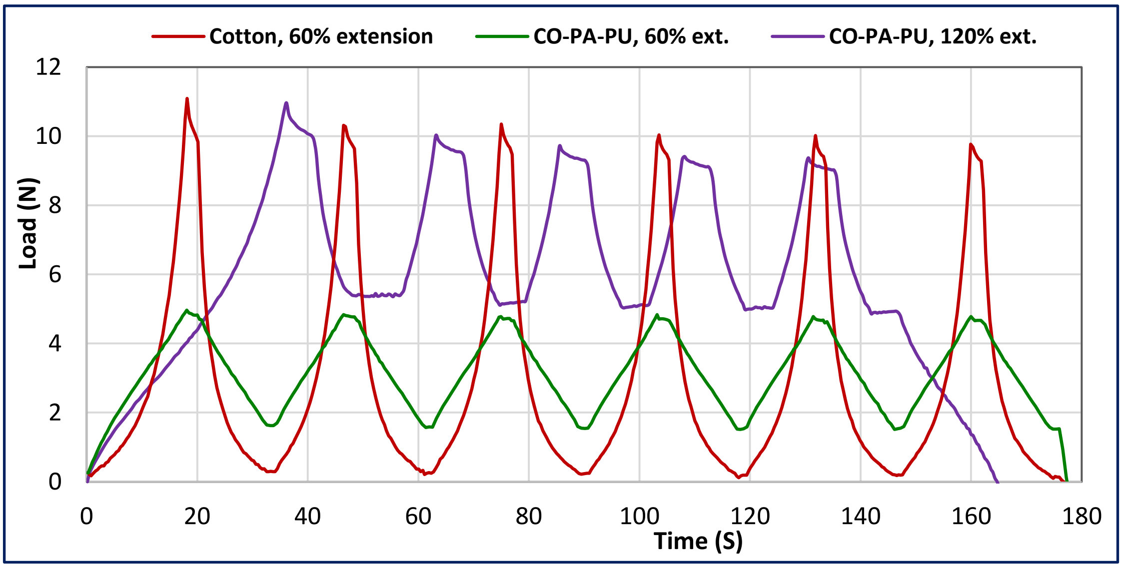


Figure 5.30. Effect of cyclic loading on bandage applied tension

1.1.2.1 *Stress-relaxation test for long and short-stretch WCBs*

Figures 5.31 & 5.32 illustrates that CO-PA-PU LSB recovered approximately 99% of its original length after stress-relaxation; this elastic recovery gives beneficial options through the optimum elasticity when applying the LSB. While Cotton SSB recovered only 93% of its gauge length after 5 days of cyclic load-relaxation. Even when this bandage was wrapped on human leg for five days (12 hr/day), there is a very little residual deformation after longer treatment time. On the contrary when Cotton WCBs used for the same time; there was a significant residual deformation, see Figure 5.31. Moreover it lost approximately 28.6% of its activity, as confirmed by the cyclic loading-unloading tests, see Figure 5.32.

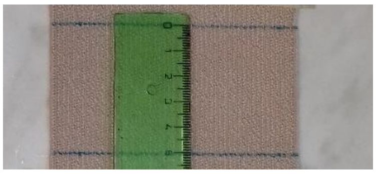
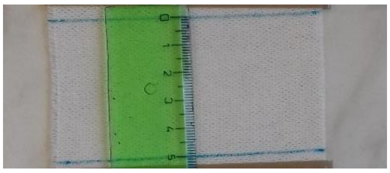
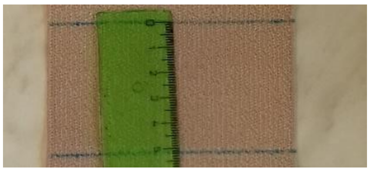
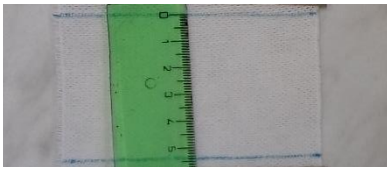
Bandage test results	CO-PA-PU LSB	Bleached Cotton SSB
Original gauge length 5 cm		
After 5 days of cyclic load-relaxation		

Figure 5.31. Effect of stress-relaxation on elastic recovery of long and short-stretch woven bandages

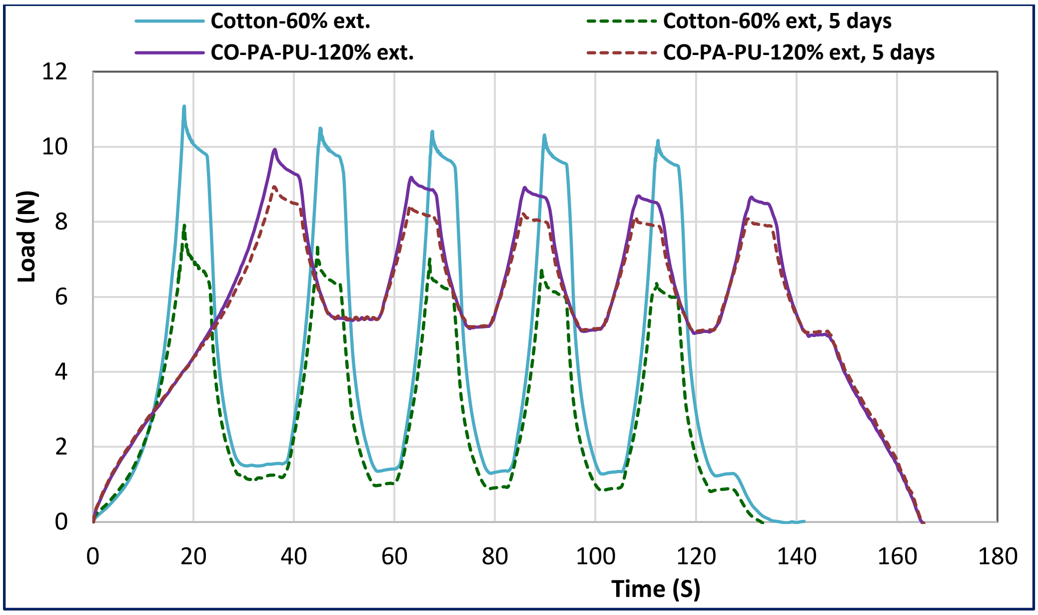


Figure 5.32. Effect of cyclic loading on applied load by long and short-stretch woven bandages

1.1.3 Verification of antibacterial activity of cotton WCB treated with Zinc Oxide NPs

The treated samples with three concentrations: 1%, 2%, and 3% ZnO Nanoparticles in powder form with 15 g/L binder showed a positive results of antibacterial activity for both gram-positive and gram-negative bacteria strains as listed in Table 5.11.

Halo zones did not appear in any of the tested samples as listed in Table 5.12. In samples 1-2, 1-3 and 2-3, 100% inhibition was found under the sample in both tested bacterial strains, i.e. the treatment did not allow the growth of bacteria under the WCB sample. This enhancement is very positive for the bandages' applications.

Table 5.11: The antibacterial activity of cotton WCB according to AATCC 147-2012

Sample number	***Escherichia coli*** inhibition zone size - mm / % inhibition below sample	***Staphylococcus aureus*** inhibition zone size - mm / % inhibition below sample
Standard 1	0 mm, 0%	0 mm, 0%
[1-1]	0 mm, 0%	0 mm, 0%
[1-2]	0 mm, 100%	0 mm, 100%
[1-3]	0 mm, 100%	0 mm, 100%
Standard 2	0 mm, 0%	0 mm, 0%
[2-1]	0 mm, 0%	0 mm, 0%
[2-2]	0 mm, 0%	0 mm, 0%
[2-3]	0 mm, 100%	0 mm, 100%

The quantitative method showed 95% inhibition in all tested WCB samples on both tested bacterial strains, which is 95% compared to the standard. Moreover the higher concentrations of ZnO Nanoparticles did not increase the antibacterial activity.

Table 5.12: The antibacterial activity of cotton WCB according to AATCC 100-2019

Sample number	***Escherichia coli*** % inhibition	***Staphylococcus aureus*** % inhibition
Standard 1	---	---
[1-1]	95%	95%
[1-2]	95%	95%
[1-3]	95%	95%
Standard 2	---	---
[2-1]	95%	95%
[2-2]	95%	95%
[2-3]	95%	95%

1.1.3.1 *Scanning electron microscopy and energy dispersive X-ray of the bandage samples*

The SEM of the un-treated and treated cotton WCB samples are displayed in Figures 5.33 and 5.34 to 5.36 respectively. The zinc oxide nanoparticles' size and its distribution are investigated for the treated bandage samples and the EDX mapping confirmed the percent of ZnO nanoparticles' in the total composition of bandage samples as illustrated in Figures 5.37 to 5.40.

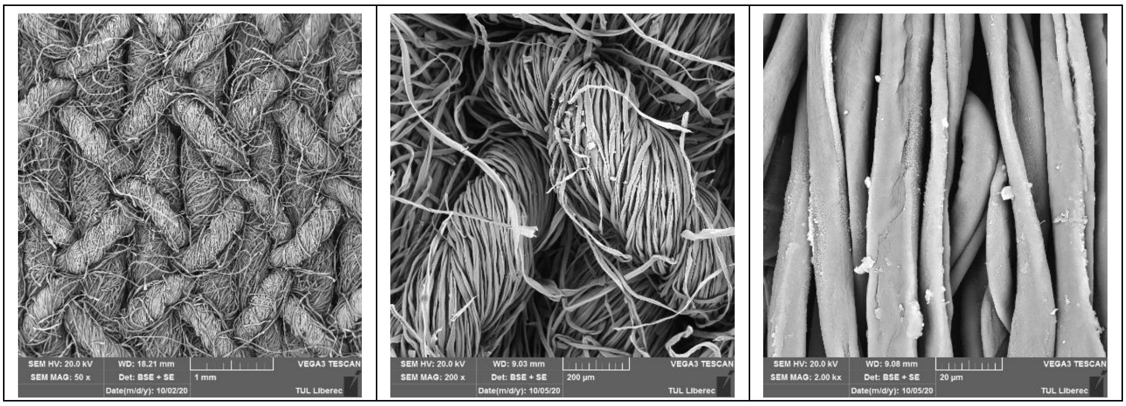


Figure 5.33. SEM of the un-treated cotton woven bandage

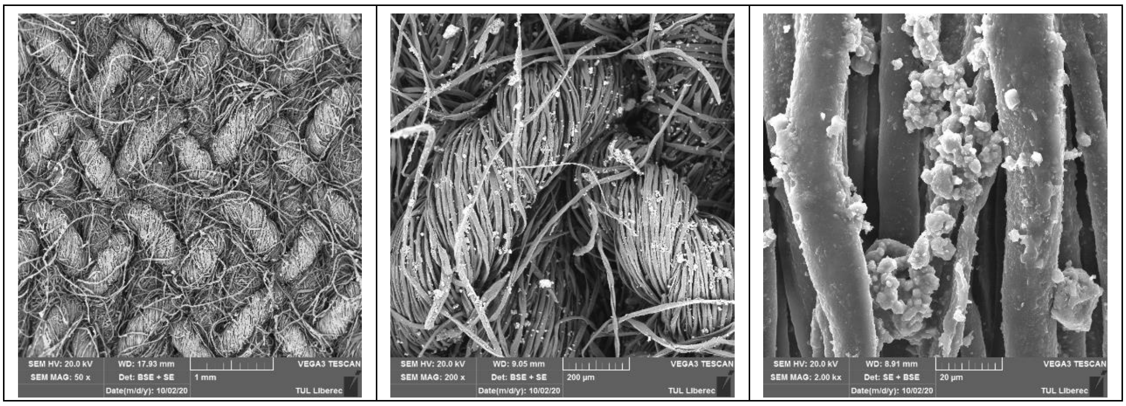


Figure 5.34. SEM of the treated cotton WCB with 1% zinc oxide nanoparticles

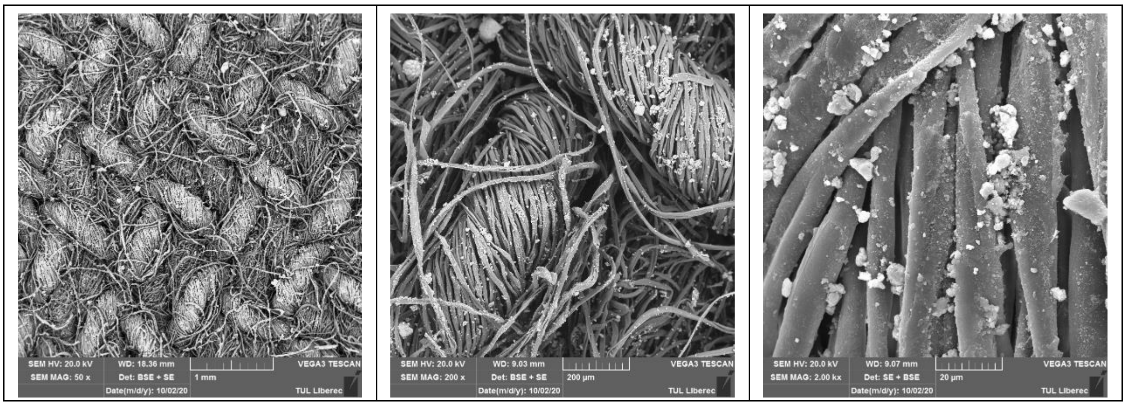


Figure 5.35. SEM of the treated cotton WCB with 2% zinc oxide nanoparticles

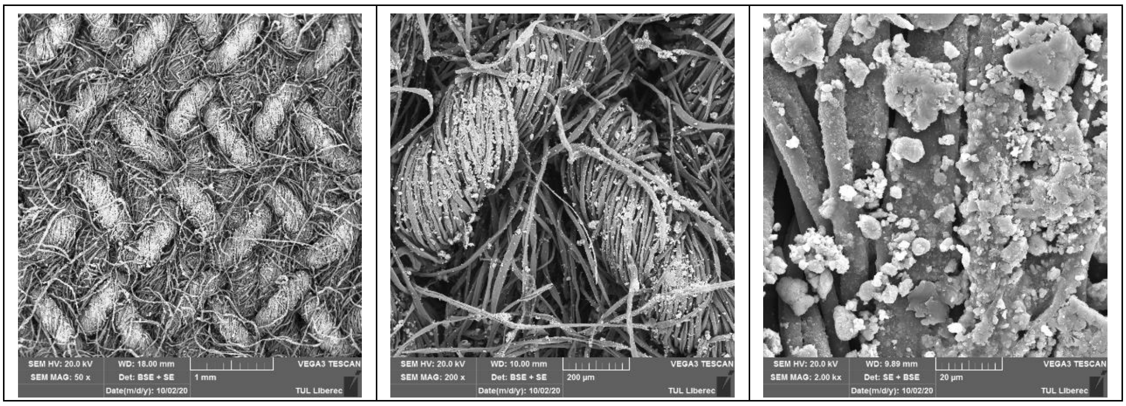


Figure 5.36. SEM of the treated cotton WCB with 3% zinc oxide nanoparticles

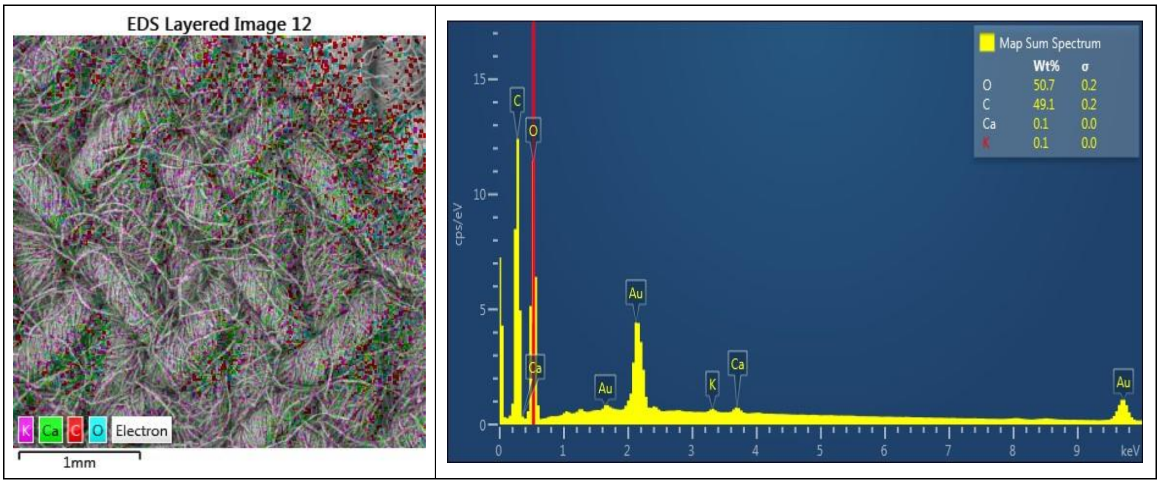


Figure 5.37. Energy dispersive X-ray map of the un-treated cotton WCB

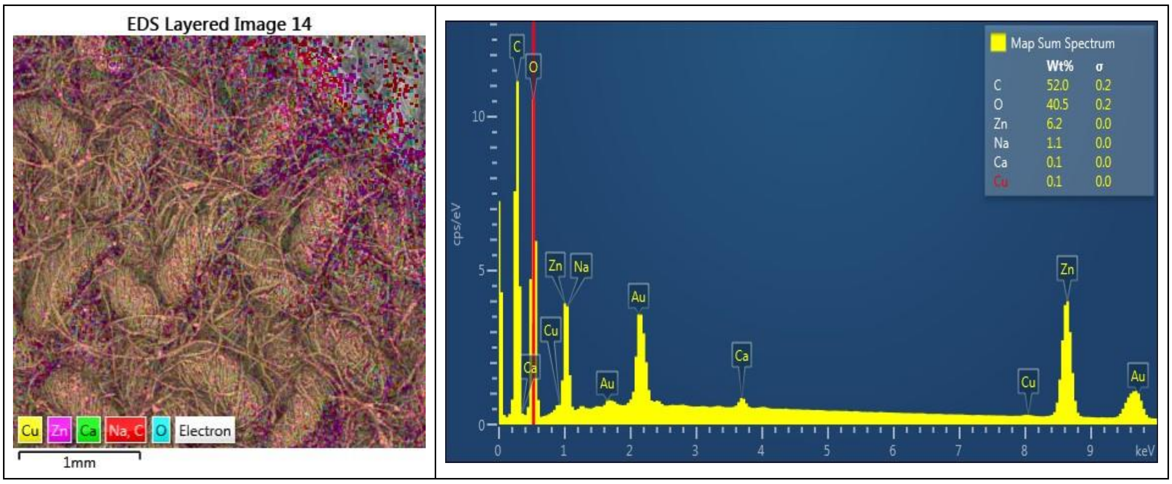


Figure 5.38. EDX map of the treated cotton WCB with 1% zinc oxide nanoparticles

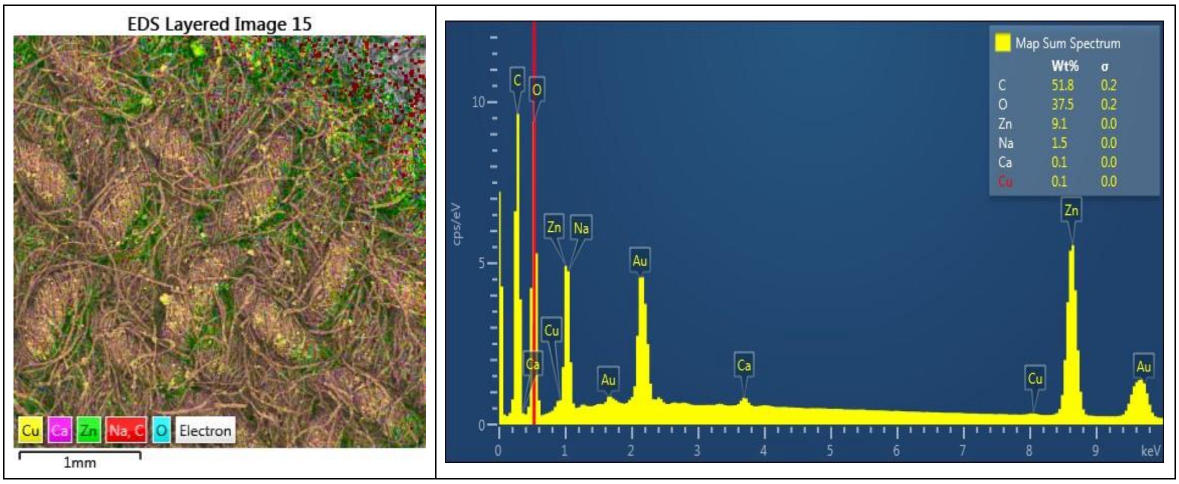


Figure 5.39. EDX map of the treated cotton WCB with 2% zinc oxide nanoparticles

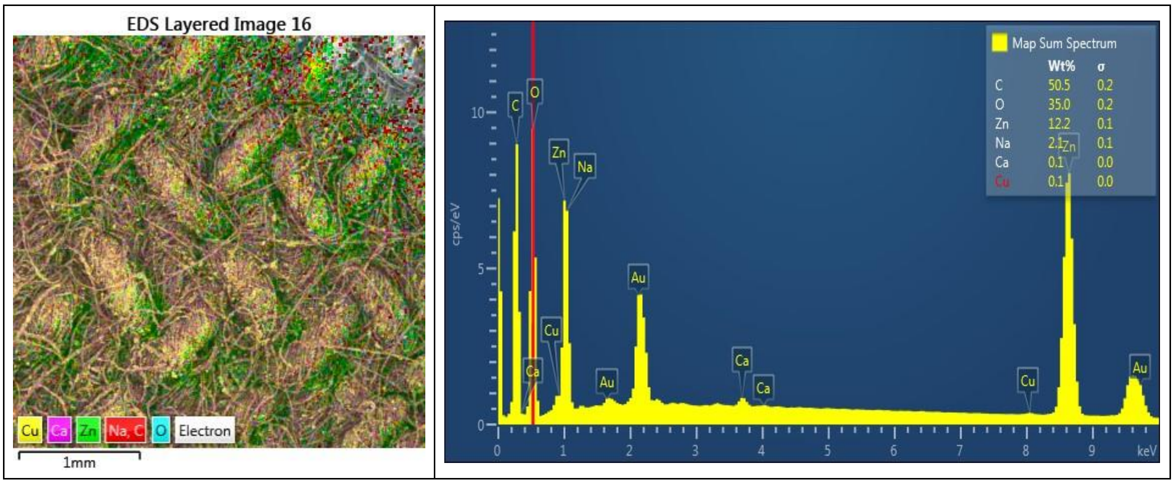


Figure 5.40. EDX map of the treated cotton WCB with 3% zinc oxide nanoparticles

Previous part for treated yarns only (different treatment method) not published in this article

1.1.4 Silver NPs activity of treated cotton yarns

Metal Nano particles (MNPs), such as Silver [79-84], Gold and Copper have achieved special attraction because of their catalytic [85], electronic [86] and unique optical properties [87] making them very attractive in the fields of particularly sensing, bio-conjugation, and surface enhancement Raman spectroscopy [88], [89]. One of the widespread approaches to the synthesis of MNPs involves the reduction reaction of metal ions in a polymeric solution [90-92].

- ***Method AATCC 147***

Treated test samples (D_1 and D_2) show comparable antibacterial activities on both tested strains (E.C. and S.A.). The antimicrobial activity of D_1 and D_2 is significantly appeared through clear inhibition zone compared to the standard sample (D_0) that does not show any inhibition of bacteria strains (as illustrated in Table 4.11 and Figure 4.6.

- ***Method AATCC 100***

The number of surviving bacterial colonies are considered and counted in this test method, see Table 4.12. Compact incidence means that the number of surviving bacterial colonies is not countable, as shown in Figure 4.7.

Table Error! No text of specified style in document.**1:** Inhibition zone of treated yarns according to AATCC 147

Method ATCC147	**Sample D_0 standard**	**Sample D_1**	**Sample D_2**
Escherichia Coli	No effect	Inhibition zone ∅ 1,44 mm	Inhibition zone ∅ 1,58 mm
Staphylococcus Aureus	No effect	Inhibition zone ∅ 2,06 mm	Inhibition zone ∅ 2,01mm

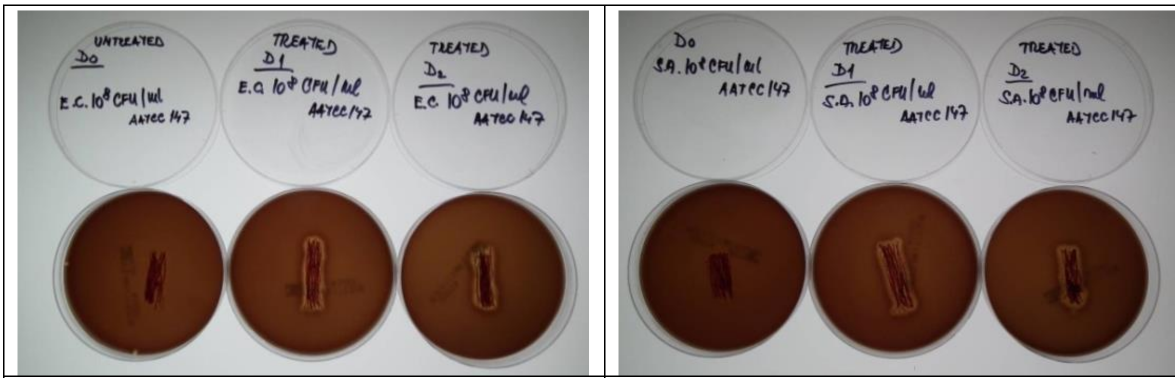


Figure 4.6. Inhibition zone of treated yarns against: **a)** Escherichia Coli **b)** Staphylococcus Aureus

Table 4.12: Antibacterial assessment by quantitative test according to AATCC 100

Method ATCC100	**D_0 standard**	**Sample D_1**	**Sample D_2**
Escherichia Coli	Compact incidence	0	0
Staphylococcus Aureus	Compact incidence	1	0

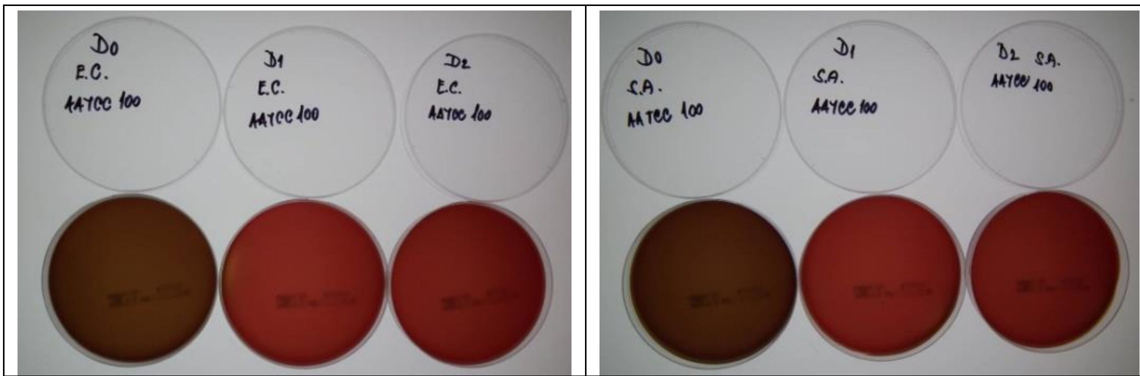
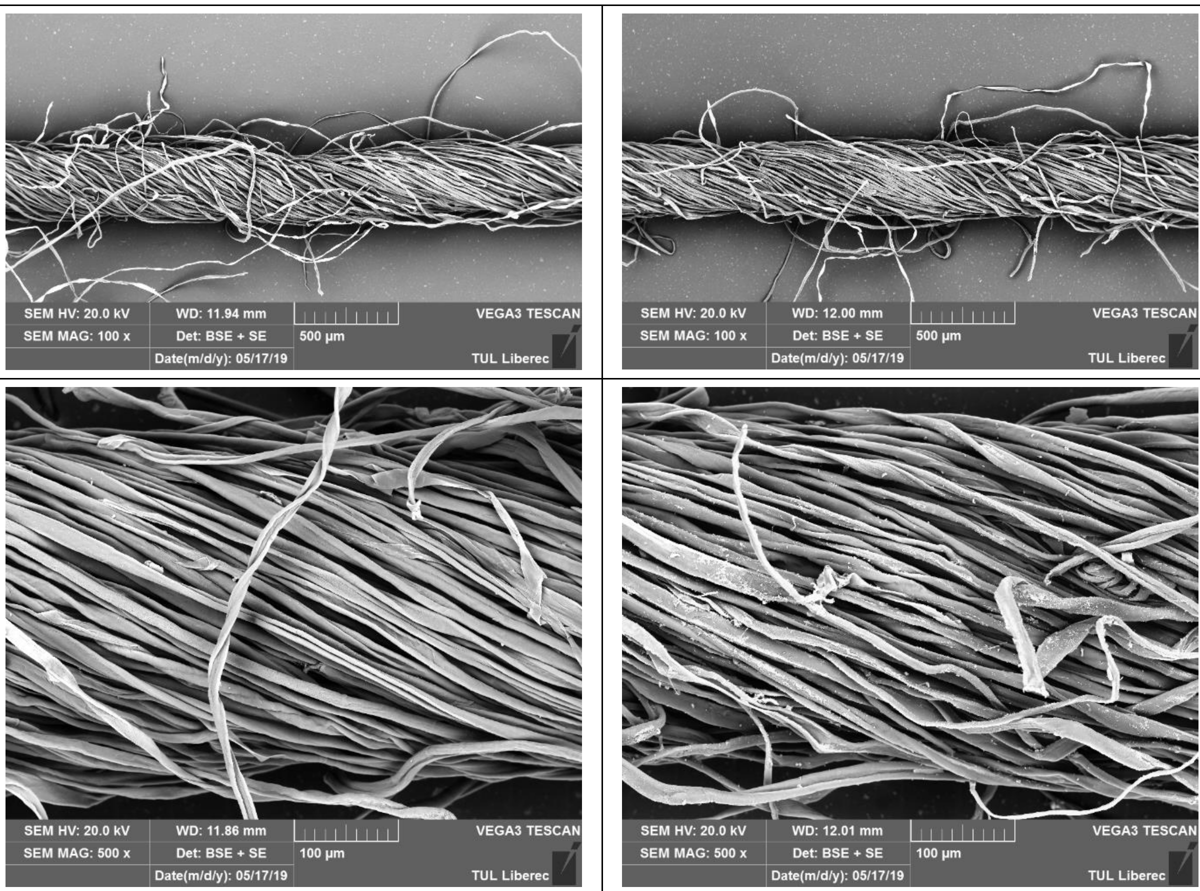


Figure 4.7. Surviving bacterial colonies of: **a)** Escherichia Coli **b)** Staphylococcus Aureus

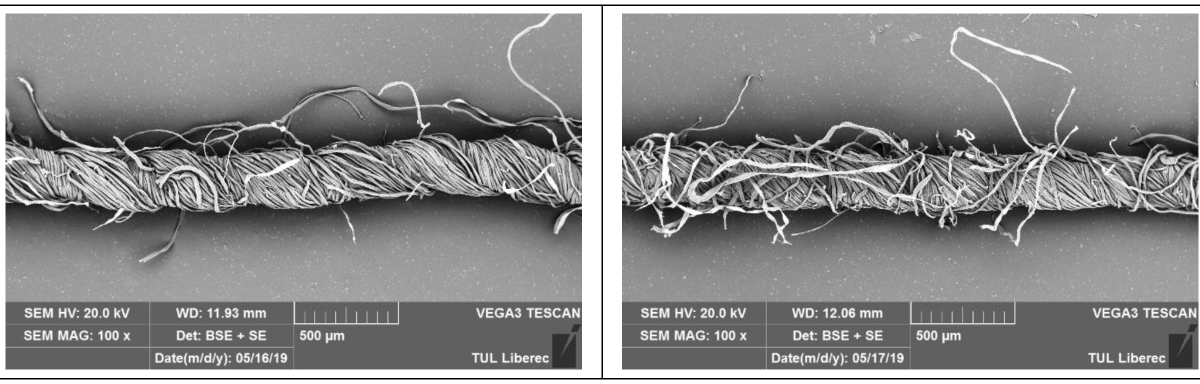
1.1.4.1 *Scanning electron microscopy and energy dispersive X-ray of the yarns*

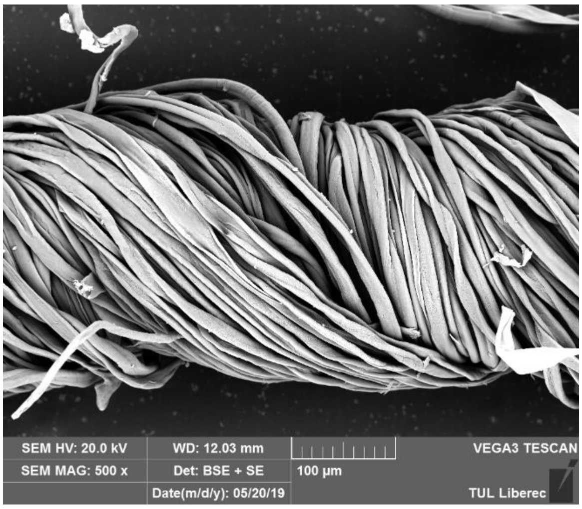
The scanning electron microscopy of the treated and un-treated single and plied cotton yarn samples are illustrated in Figures 4.8 and 4.9 respectively. The silver NPs size and distribution are totally clear for the treated yarn samples. Moreover the energy dispersive X-ray mapping for the yarn samples confirmed the NPs percent in the total composition of yarn EDX mapping, see Figures 4.10 & 4.11.



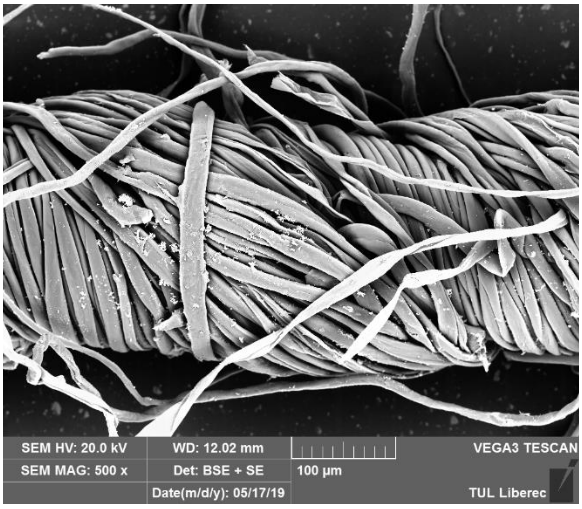
Un-treated single yarn	Treated single yarn

Figure 4.8. Scanning electron microscopy of the un-treated and treated single yarns



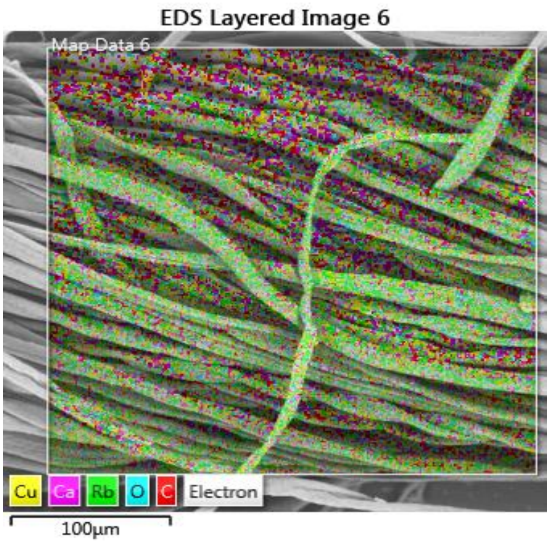


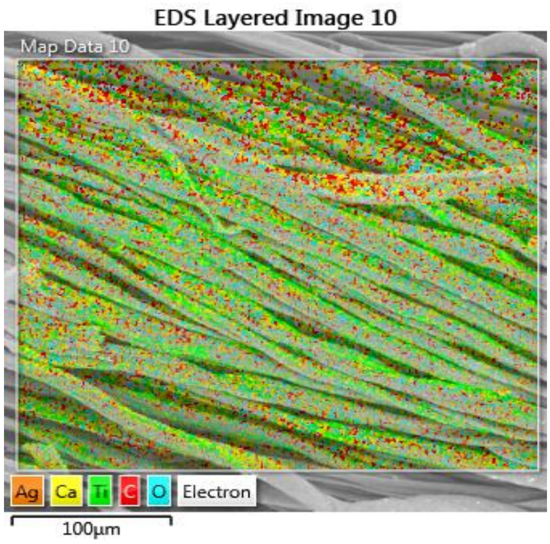
Un-treated plied yarn

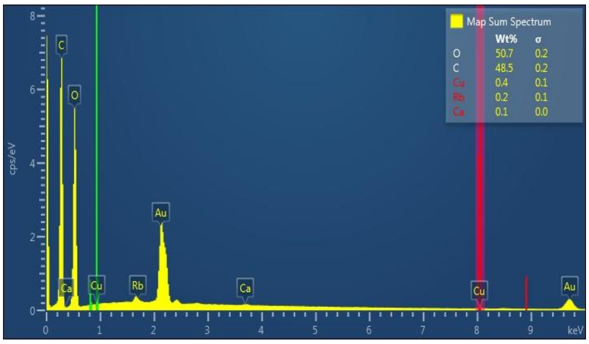


Treated plied yarn

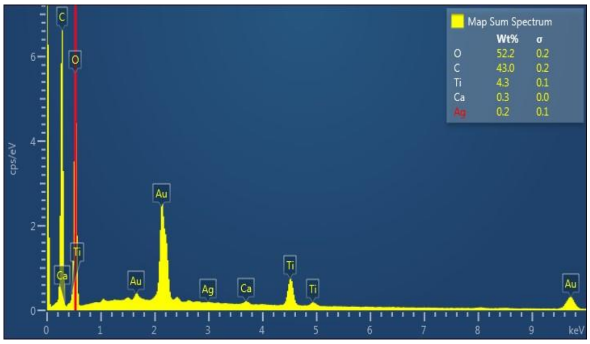
Figure 4.9. Scanning electron microscopy of the un-treated and treated plied yarns





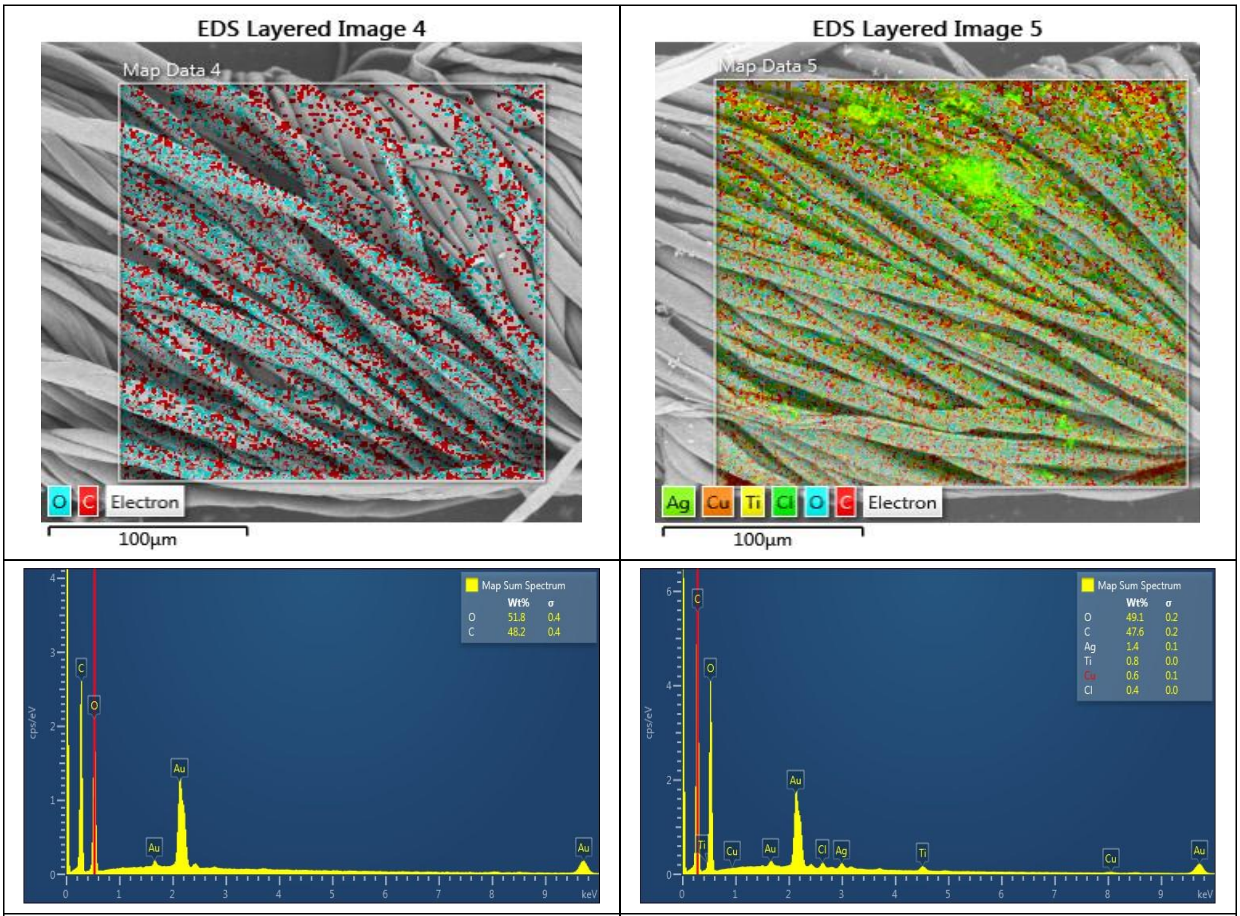


Un-treated single yarn



Treated single yarn

Figure 4.10. Energy dispersive X-ray mapping of the un-treated and treated single yarns



Un-treated plied yarn	Treated plied yarn

Figure 4.11. Energy dispersive X-ray mapping of the un-treated and treated plied yarns