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A Comparative Study of the Impact of Beva 371 and Nano Vinyl Acetate Derivatives on Textiles Properties for Historical Textiles Conservation, Practical Application

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HISTORICAL textiles in museums are exposed to various processes of deterioration. Therefore, adhesives and polymers are used to fix and strengthen weak textiles. One the long term these adhesives are prone to stiffness, weakness, discoloration, and rigidity among other factors. Historical textiles exposed in museum to processes of deterioration factors. Therefore, adhesives and polymers used to fix and strengthen weak textiles. These adhesives are prone to stiffness, weakness, and color change and rigid after long term and other damage. Therefore, this research attempts to use nanomaterials to improve the properties of polymers used in historical textiles conservation. Results of the physical, chemical and optical properties of the Beva 371 and Nano-Vinyl acetate derivatives and were applied to fix and strengthen historical textiles. The dyed wool fabrics by natural dyes treated with Beva 371 and Nano Vinyl acetate derivatives adhesive. Accelerated thermal ageing was done of treated wool fabrics. A close examination and tests were done by using SEM-EDX, FTIR, Tensile strength , Elongation, change of colors (CIE L*a*b*) coordinates. The final step is to apply the Nano-Vinyl acetate derivatives on Historical Coptic Textiles. Scientific examinations, the stability of dyes and fibers, mechanical and chemical cleaning processes, fixing and strengthening of historical textiles on new support by using Nano-Vinyl acetate derivatives was done. The article presents, for the first time, interesting and important results of Beva 371 and Nano- Vinyl acetate derivatives and their application on historical textiles.

Keywords: Vinyl Acetate, Adhesive, Textiles, Ageing, Restoration.

Introduction

Since its advent in the 1970s, the use of the Beva 371 adhesive has expanded from the field of preservation of historical textiles. However, no extensive study and testing has been accomplished for these specific uses. In other words, the use of adhesive in preserving the historical fabric, can give many benefits for conservators. First, strengthen and fixing the weak and fragile historical textiles. Secondly, adhesives must not penetrate the historical textiles. Accordingly, applying adhesives to restore historical textiles could cause more damage on the long-term. Therefore, Nano adhesive could play a positive role in a successful conservation treatment of historical textiles. [1-6]

Many studies in the Historical Textile Conservation field addressed accelerated ageing (thermal – Light- acidity) and its effect on the mechanical, optical and chemical properties of textile fibers. This technique is used to study the efficiency of polymers and adhesives used in the maintenance of historical textiles over the long term. [7-12].

The Historical Textile restoration is a specialized process. The first of these steps is documentation by using different scientific investigations. Then, various cleaning processes (mechanical-chemical) must be done to remove the distillation of historical textiles. After that, the process of strengthening weak textiles on a new holder by using different adhesives. This research

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focuses on the practical steps to strengthen a historical object dating back to the Coptic era in the Atfih Museum, Egypt [13-15].

Materials and Methods

Materials

Beva 371 (Vinyl acetate derivatives) is adhesive that to meet the requirements of art conservation professionals and since 1970 is the most widely used over the world. Vinyl acetate derivatives has been found to have numerous other applications, such as mounting of paper to canvas, textile to textile, canvas to wood. Vinyl acetate derivatives can applied by brush, roller, or thinned and sprayed into place. It was supplied by TALAS Co., http://www.talasonline.com/Beva-371-Solution-Gallon.

Reagent grade vinyl acetate VAc and butyl acrylate BuA were supplied by Aldrich.

Vinyl Versatate (VEOVA10-10 > 99%) was supplied by shell chemicals Company. The inhibitors in both monomers were removed using inhibitor remover which are (disposable column for removing hydroquinone and mono methyl ether), and the treated monomers were stored at (-2°C) until used.

Potassium persulfate (KPS, 99%), Sodium lauryl sulfate (SLS.98%), sodium metabisulfite 95% were supplied by Aldrich, and 2,2-Azobis (2-methyl propionitrile) 98% was obtained from sigma-Aldrich. The water used was deionized water.

Methods

Dyeing

Extraction of dye

The process of dyeing with natural dyes 10% (w / v) performed as follows: First, turn the dyes into powder. Then soak the dyes in water for 12 hours, and then boiling for 2 hour. After that, liquidate the solution to separate the solid parts from the dye solution [16].

Dyeing procedure

Dyeing processes done by the exhaustion method according to Bechtold, Turcanu et al. (2003). The dyeing bath liquor ratio (LR) is 1:20 (1g dye: 20 ml bath volume). The dyeing processes time for 1.5h at 80 ^{o}C. After dyeing some mordents, such as alum, Copper sulfate and Iron III chloride were added in concentration (50 g L–1) to give a final dye bath concentration of 2.5 g L–1 or 5 g L-1 mordant. The final step is washing bath to remove the unfixed dyestuff (5 min at room temperature, LR 1:20) [16-18].

Samples preparation

In-situ emulsion polymerization of nano VAc and VEOVA10 copolymer :

Emulsion copolymerization of VAc and VEOVA10 with feed monomer composition ratio 4:1 having solid content about 10 %. It was prepared via emulsion polymerization technique by semi-continuous technique under nitrogen and mechanical stirring 300rpm. Small amount of BuA was added to the feed co-monomers because it helps the initiation of vinyl esters polymerization much more readily. The reaction was carried out in 250ml three necked flask equipped with: reflux condenser, stainless steel stirrer and two separate feed streams. The first stream was for the addition of pre-emulsion (VAc and VEOVA10 monomers with emulsifier SLS), the other feed is for the initiator solution. The following ingredients were added onto the round flask successively; part of the emulsifier dissolved in water, 10% of the amount prepared initiator (KPS) solution, 2.5% of the amount of the prepared pre-emulsion and inorganic additive (1% of monomer content). The reaction content was kept in thermostatic water bath at 85^{o}C. After 10 min, the rest of pre-emulsion and dissolved initiator is added drop-wisely during period of 3hrs.

After the reaction was continued, a calculated concentration of 2.2-Azobisisobutyronitrile was separately added to the reactor along 30min, then the reaction was continued for another 1 hr. At the end, the latex was cooled down to room temperature [19-20].

Tensile Strength samples

Dyed wool samples for tensile strength test must be 25 x 5 cm (length x width) in warp direction. The samples were prepared by reveling method on each side forming 1.5 cm wide strips with a 2.5 mm fringe down each side. Tensile strength test technique needs five samples for each test.

Treatments

The fabric samples coated with the Vinyl acetate adhesives and Nano- Vinyl acetate adhesives in 5% concentration according to the standard method of conservation.

Accelerated ageing

Different studied presented interesting information about accelerated ageing for organic materials. Artificial ageing by heat for a rise up to 100 °C of textiles or paper for 72 h (3 days) is equivalent to around 25 years of natural ageing under normal condition of ageing in museums. Heat ageing of our samples were done in a temperature-controlled oven "Herous-Germany" on special frames. The coated fabric samples by Vinyl acetate derivatives and Nano- Vinyl acetate derivatives were thermally aged at 100 °C for different times such 72h and 144h according to Feller [21-22].

Examinations and analysis

Morphological study of wool samples

The coated fabrics by Vinyl acetate derivatives and Nano-Vinyl acetate derivatives adhesive before and after ageing ware investigated by using Scanning Electron Microscope module (Quanta 200 ESEM FEG from FEI) (SEM). This type of investigation is used to show the change of fibers resulting from the treatment by adhesives and the damage by heat ageing according to Batcheller [23] and Mohamed [24] .

Morphological study of the prepared VAc and VEOVA10 copolymer adhesive

The prepared VAc and VEOVA10 copolymer adhesive investigated by using transmission electron microscope (TEM) in order to measure the particle size. This measurement was done by using JEM-1230-electron microscopy operated at 60 kV.

Before taking a TEM image, the sample was diluted at least 10 times by water. A drop of well-dispersed diluted sample was placed onto a copper grid (200 mesh and covered with a carbon membrane) and dried at ambient temperature. A drop of phosphotungstic acid (0.4%) as a stain was deposited over the dried sample Xiao and Wang [25].

Change color measurement

The color change of untreated and treated dyed wool fabrics by Vinyl acetate derivatives adhesive or Nano-Vinyl acetate derivatives adhesive) were measured by using a double beam Optimatch spectrophotometer (Datacolor international Spectraflash SF450-UK) according to the CIE-Lab values. The colors change are given in CIE Lab coordinates are, L value (100 = white, and 0 = black), while a* value (positive sign = red, and negative sign = green), and b* value (positive sign = yellow, and negative sign = blue) according to Booth [26] and Wyszecki and Stiles [27], Berns, Billmeyer [28].

Tensile strength and elongation

Mechanical properties such as Elongation and tensile strength of treated and untreated fabrics were measured by using a Lloyd Tensile Testing Machine Type T5K. The measurement was done in metrology lab according to ASTM (2000), D 5035-95. The spacing of initial jaw was 50 mm and the speed of the test was 25 mm/ min, at temperature 23 C, and R.H. 65% [29]

Fourier transform infrared spectral analysis (FTIR)

The chemical structural changes of treated and untreated dyed wool fabrics carried out by using BRUKER – FTIR- TENSOR 27. Information of chemical functional groups of a wool sample will be by vibrational bands appear in the infrared spectra. This data will give a general characterization and identification of specific compounds of treated and untreated fabrics

Derrick [30-31].

Results and Discussions

Morphological study of the prepared Nano- VAc and VEOVA10 copolymer

The prepared Vac/VEOVA 10 copolymer examined using TEM under two different magnifications and are represented in fig 2. From the figure, it is clear that, the prepared copolymer was in homogenous form with particle size in range of 55-75 nm.

The effect of ageing on mechanical parameters of treated samples

Table 1 and 2 show the results of strength and elongation of wool fabrics dyed with safflower dye mordanted with alum that treated by Vinyl acetate derivatives and Nano Vinyl acetate derivatives before and after thermal ageing. It is

TABLE 1. The elongation and force of dyed wool coated Vinyl acetate derivatives after ageing

Wool Samples	Samples after dyeing		Samples after applying Vinyl acetate derivatives		Samples + Vinyl acetate derivatives + ageing 100C for 72 h		Samples + Vinyl acetate derivatives + ageing 100C for 144 h	
	Elongation %	Max Force N	Elongation %	Max Force N	Elongation %	Max Force N	Elongation %	Max Force N
Saff+ Alum	27.57	25.13	27.49	27.91	27.32	27.40	27.19	27.32
Saff+ Iron	36.27	24.21	36.25	26.81	33.11	26.25	32.48	26.08
Saffl + Cu	28.78	24.36	31.15	26.87	30.09	26.69	28.60	26.59
Saff without	31.88	23.42	38.52	25.14	37.37	25.06	37.18	24.62
Mad+ Alum	36.45	24.53	36.21	25.29	35.93	24.97	34.72	24.62
Mad+ Iron	35.25	24.35	35.09	25.36	34.26	24.99	34.19	24.55
Mad+Cu	32.23	24.46	32.19	25.75	31.79	25.22	31.64	25.17
Mad without	23.59	23.59	23.47	25.44	23.32	24.99	23.19	24.31

TABLE 2. The elongation and force of dyed wool coated Nano Vinyl acetate derivatives after ageing

Wool Samples	Samples after dyeing		Samples after applying Nano Vinyl acetate derivatives		Samples + Nano Vinyl acetate derivatives + ageing 100C for 72 h		Samples + Nano Vinyl acetate derivatives + ageing 100C for 144 h	
	Elongation %	Max Force N	Elongation %	Max Force N	Elongation %	Max Force N	Elongation %	Max Force N
Saff+ Alum	27.57	25.13	31.32	28.79	31.39	28.96	31.45	29.10
Saff+ Iron	36.27	24.21	36.78	28.11	36.84	28.36	36.91	28.45
Saffl + Cu	28.78	24.36	29.83	27.54	29.91	27.65	29.95	28.64
Saff without	31.88	23.42	34.29	27.19	35.18	27.28	36.00	27.51
Mad+ Alum	36.45	24.53	36.57	27.11	36.69	27.28	36.76	27.45
Mad+ Iron	35.25	24.35	40.32	28.20	40.46	28.41	40.50	28.56
Mad+Cu	32.23	24.46	34.12	27.26	34.22	27.47	34.28	27.67
Mad without	23.59	23.59	33.27	27.32	33.32	28.47	35.38	28.62

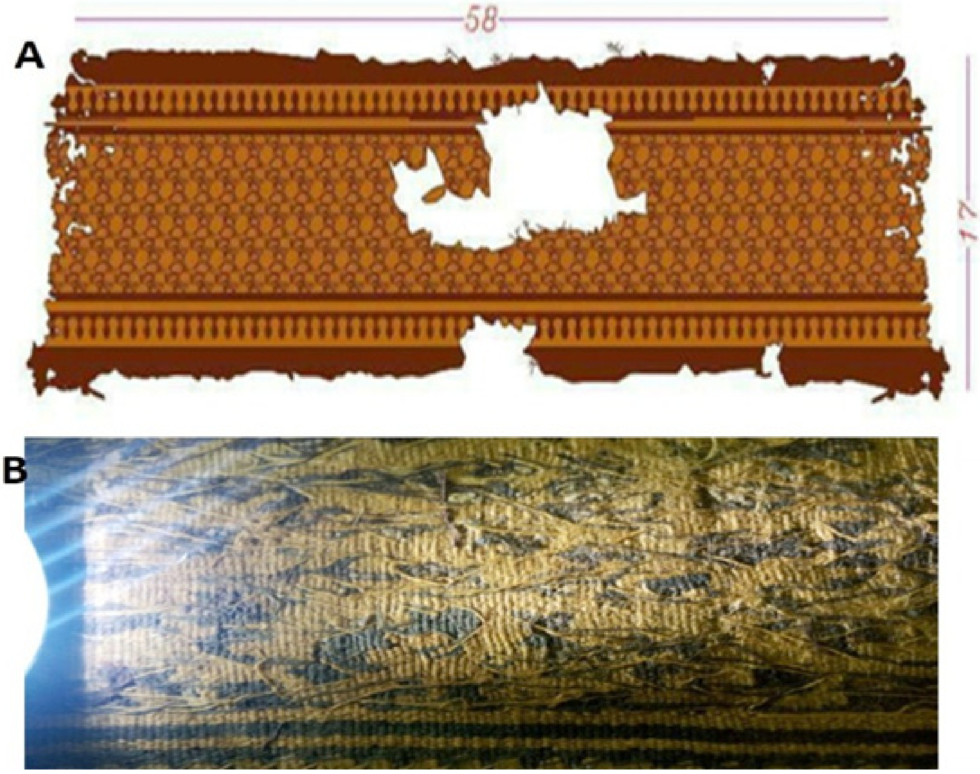


Fig 1. The Coptic object in Atfih museum. The front face of the object that shows a very weak state (A). The back face of the object with focus details that shows a very weak state (B). It noticed the object is a bad condition and need to consolidate by adhesive on new support fabric.

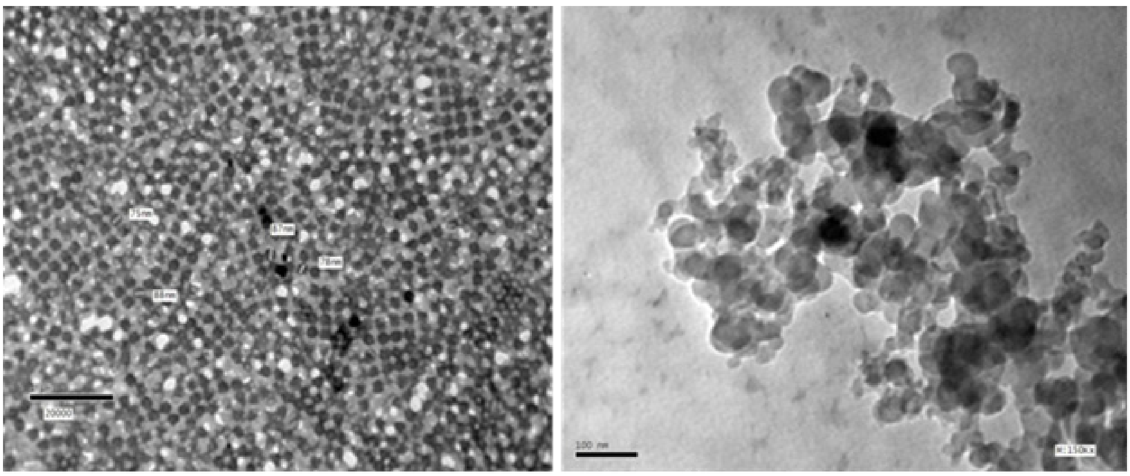


Fig 2. TEM of the prepared nano- VAc and VEOVA10 copolymer under two different magnification

observed that the tensile strength of wool fabric is 25.13 MPa while after treated by Vinyl acetate derivatives is 27.91 MPa but after treated by nano- Vinyl acetate derivatives is 28.79 Mpa. The results show that the tensile strength of treated fabric by Nano Vinyl acetate derivatives increased more than that treated fabric by Vinyl acetate derivatives. All treated samples by Nano Vinyl acetate derivatives showed improvement in tensile strength than those treated by Vinyl acetate derivatives. Additionally, treated samples by Nano Vinyl acetate derivatives showed improvement in elongation than the ones treated by Vinyl acetate derivatives. It is clear that the treated wool fabrics with Vinyl acetate derivatives adhesive became more rigid as the elongation of the sample decreased. The effect of ageing on treated fabrics by Nano Vinyl acetate derivatives adhesive is less than treated fabrics by Vinyl acetate derivatives adhesive. The results indicate that the percent of the increase in the tensile strength depends on type of the adhesives. This data indicates that using Nano- Vinyl acetate derivatives adhesive in textiles conservation is better than using Vinyl acetate derivatives adhesive. Therefore, Nano-Vinyl acetate derivatives adhesive is suitable for conservation of wool fabrics more than Vinyl acetate derivatives adhesive.

The effect of ageing on optical parameters of treated samples

Table 1, 2 and Fig.2 show the color change such as K/S and Lab value of treated samples by Vinyl acetate derivatives adhesive and Nano Vinyl acetate derivatives adhesive before and after thermal ageing. It is clear for the reader that the brightness index (L) of treated samples became slightly darker. The treated samples by Vinyl acetate derivatives became darker than those treated by Nano- Vinyl acetate derivatives. The red-green coordinate (a) show that the treated fabrics by Vinyl acetate derivatives become slightly green. The wool dyed fabric by safflower that treated by Vinyl acetate derivatives was 18.71 after ageing was 18.15. On the other side, the traded fabric by Nano-Vinyl acetate derivatives was 18.71 and after ageing was 17.91. While the value yellow–blue coordinate (b) of treated fabric show the samples become

The effect of ageing on fiber morphology of treated samples

Fig.3 shows the coating of Vinyl acetate derivatives and Nano-Vinyl acetate derivatives over the fibers before and after ageing by using SEM images. It was observed that the Nano-Vinyl acetate derivatives make homogeneous coverage on the fiber surface more than Vinyl acetate derivatives. One the other hand, it was noticed that the characteristics of fiber morphology surface became clearer after being treated by Nano- Vinyl acetate derivatives. The layer of Nano-Vinyl acetate derivatives is very thin over the fibers more than the layer of Vinyl acetate derivatives. In other words, the fiber surface does not disappear and the layer is very thin.

The effect of ageing on fiber chemical structure

Fig 5 shows changes in chemical structure of the treated wool fabrics by using Vinyl acetate derivatives and Nano- Vinyl acetate derivatives that were assessed by ATR-FTIR spectroscopy. The infrared region shows that amid I bands centered at 1700-1600cm-1 region are attributed to most C=O stretching oscillation in protein structure. In addition, amid Ⅱ bands in 1590-1460 cm-1 region is assigned to N-H deflection and C-N bending vibration, and amide Ⅲ in 1190-1280 cm-1 is attributed to N-H bending and C-N stretching vibrations. On the other hand, the application of both Vinyl acetate derivatives and Nano- Vinyl derivatives led to the presence of new characteristic bands.

Applied the Nano Vinyl acetate derivatives on the Historical Coptic Textiles

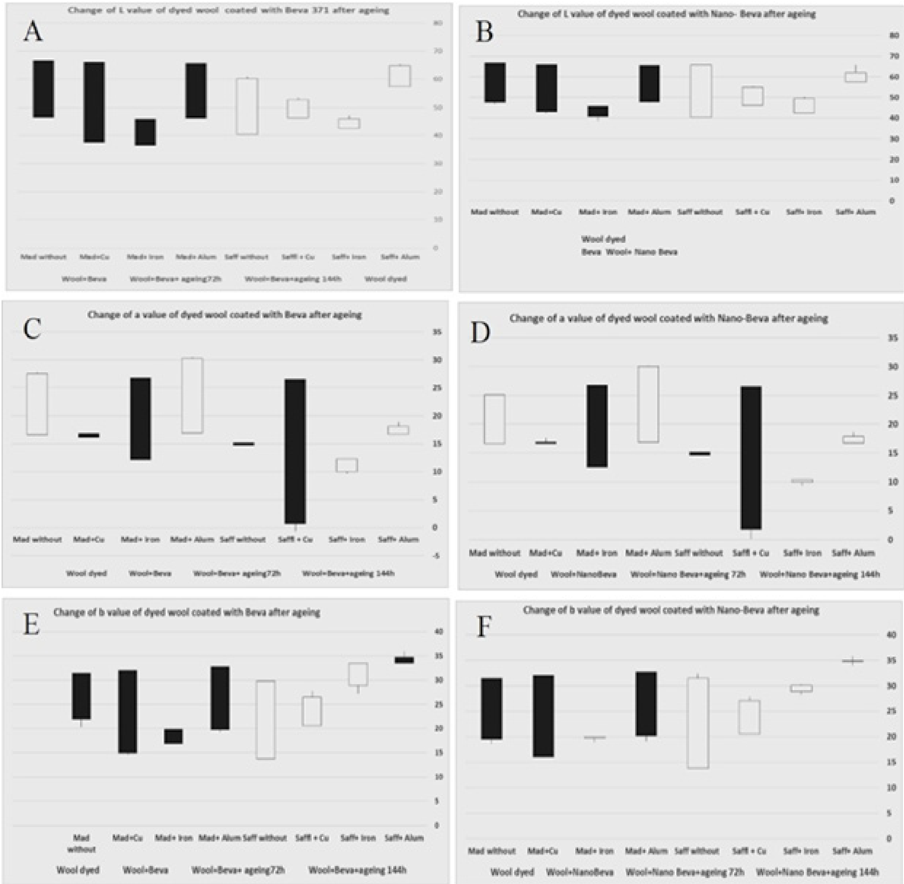
Following the experimental part of this research which presented interesting results about using Vinyl acetate derivatives and Nano-Vinyl acetate derivatives on Textiles conservation. This part will focus on the practical. This part will focus on the practical application of using Nano-Vinyl acetate derivatives on the rare historical Coptic textile.

The Historical Textile Object

The object dates back to the Coptic period in Egypt. It is Tapestry weave and found in Atfih Museum. It contains different types of decorations made by different types of colors. Fig. 1 shows the details of the historical object. The object contains different types of damage such as weakness part, lost parts, stain and dirt.

Investigation of the Object

A close examination was done on the object in order to identify the type of fibers, natural



(A and B) respectively show the L value corresponding to the brightness (100 = white, and 0 = black),

(C and D) show a* value to the red–green coordinate (positive sign = red, and negative sign = green),

(E and F) show b* value to the yellow–blue coordinate (positive sign = yellow, and negative sign = blue).

Fig. 3. Color change of dyed wool coated with Vinyl acetate derivatives and Nano- Vinyl acetate derivatives after ageing.

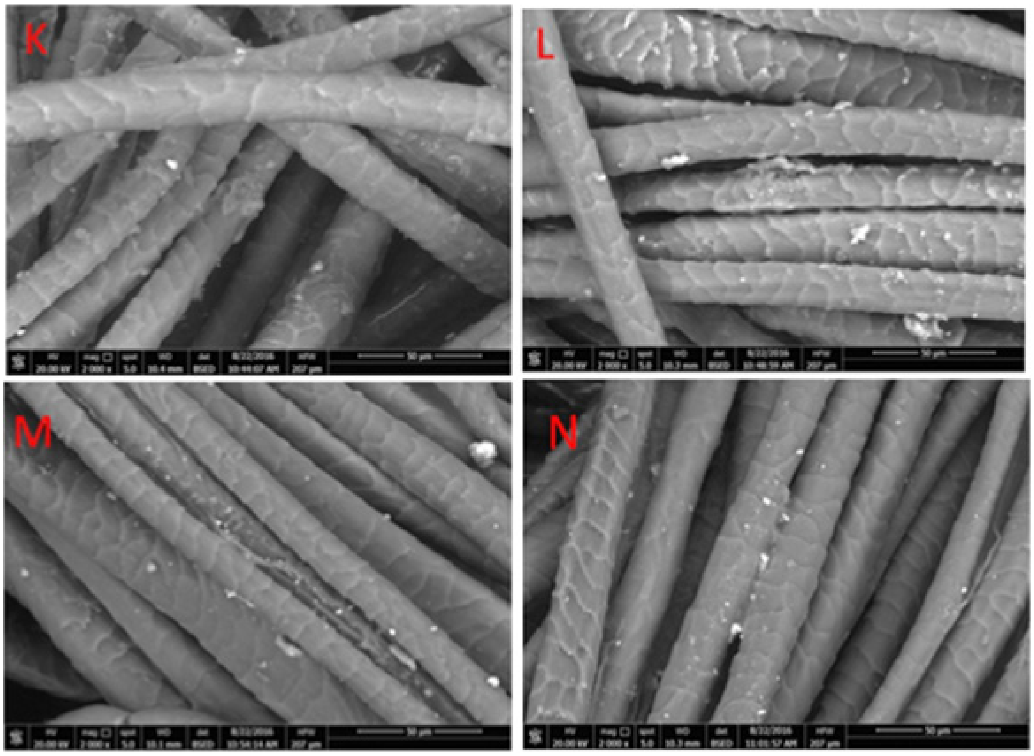


Fig. 4. Dyed wool fabric coated with Vinyl acetate derivatives without ageing (K), coated with Vinyl acetate derivatives with ageing 144h (L) dyed wool fabric coated with Nano - Vinyl acetate derivatives without ageing (M) dyed wool fabric coated with Nano - Vinyl acetate derivatives without ageing (N)

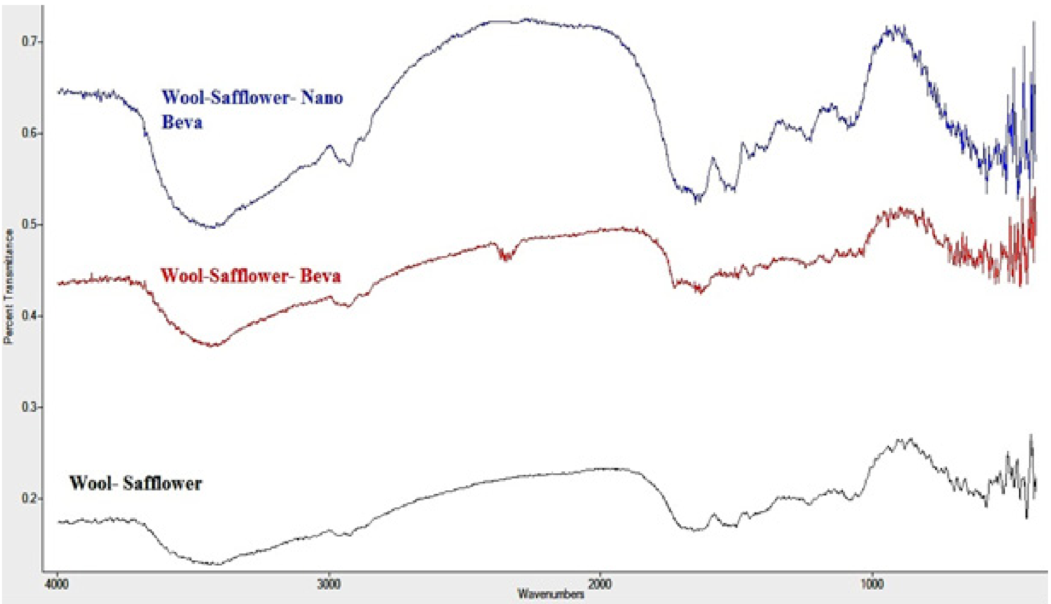


Fig. 5. FTIR of dyed wool with safflower mordanted by Cupper treated by Vinyl acetate derivatives and Nano-Vinyl acetate derivatives

dyes, mordents, dirt and stain. As shown in Fig.6 examination of object by using SEM-EDX shows the type of elements of object such as mordents and type of dirt. Furthermore, the image by using SEM show the wool fibers as the main fibers of the object. USB Microscopy shows the weave type of the object and the main color. In addition, full documentation of the object before restoration was done to record all the details such as lost parts, weak parts, and dirt as shown in Fig.5 [13, 14, 32]

Cleaning of the object

After documentation and examination of the object, stability of dyes on the object was tested. The selection of the appropriate cleaning method depends on the nature of the soil present and on the materials, structure and condition of the textile. Mechanical cleaning by using fine brushes to remove dust that is not chemically linked to the object as shown in Fig.7 A, B and C. Aerobic aspiration of dust was done by using a vacuum cleaner. The next step is temporary support of object by net fabrics before wet cleaning. Then, wet cleaning procedure used water with other detergent agents, to assist the cleaning process. The ratio was one part detergent Synperonic N to 100 parts of distilled water as shown in Fig.6 D and E. Then a second and third cleaning bath with distilled water only was applied for 10 mins. The roll of wet cleaning is reduced the soiling, relaxed the fibers. Drying processes of object after wet cleaning was done by using free acid paper as shown in Fig. 6 F. The drying process of wet textiles can provide an opportunity to realign distorted fibers [33-38].

Supporting the Historical Object by Nano-Vinyl acetate derivatives

The important step after cleaning and removing all stains and dirt from the historical textile, is to provide the fabric with a new support to increase its strength. Firstly, Nano-Vinyl acetate derivatives adhesive applied on the new silk criplin support by using a fine brush as shown in Fig.8A. While Fig.8B shows the coated silk support by adhesive on the back of historical textiles to adhere together. Then, adhere the historical textiles to the coated silk support by using hot iron as shown in Fig.8C. Fig.8D shows the historical textile adhered to the new silk support and is ready for the last step by fixing it to the new linen support. For this, a wooden frame was prepared and a new undyed linen support was prepared and washed to remove any chemical residues from the sizing and finishes. The undyed linen was then attached to the wooden frame with tacks. Then, the historical textile object was placed carefully over the linen fabric support. In order to mount the historical textiles to new linen fabrics. An overcast stitch was used to support the edges of the adhered historical object to linen support as shown in Fig. 8E and F. The historical object is ready now for display in the museum [6, 13, 34]

Conclusion

This work of research tried to improve the mechanical, optical and chemical characterization of Vinyl acetate derivatives used as adhesive in repairing damaged historical textiles. Therefore, Nano-Bev 371 was prepared and deep studies were carefully done in order to understand the behavior of Vinyl acetate derivatives and Nano-Vinyl acetate derivatives adhesive after ageing. Interesting results were provided about the Vinyl acetate derivatives and Nano-Vinyl acetate derivatives adhesive. The results confirmed that Nano-Vinyl acetate derivatives adhesive enhance the durability of surface morphology of fibers after ageing more than Vinyl acetate derivatives. Furthermore, there are no noticeable changes in the color of treated wool textile by Nano-Vinyl acetate derivatives adhesive samples before and after the thermal ageing. It was observed that the mechanical properties such as tensile strength and elongation of wool fabrics treated by Nano-Vinyl acetate derivatives adhesive better than wool fabrics treated by Vinyl acetate derivatives adhesive before and after ageing. It is clear that Nano Vinyl acetate derivatives adhesive is suitable for conservation of wool fabrics more than Vinyl acetate derivatives adhesive. The study presents a practical application of using Nan-Vinyl acetate derivatives adhesive on the Historical Coptic Textile. First, the historical textile was closely examined. Then, different types of cleaning were done to remove the soil and dirt from the historical object. The Nano- Vinyl acetate derivatives adhesive was applied on the new silk support and the historical object was then adhered to this silk support.

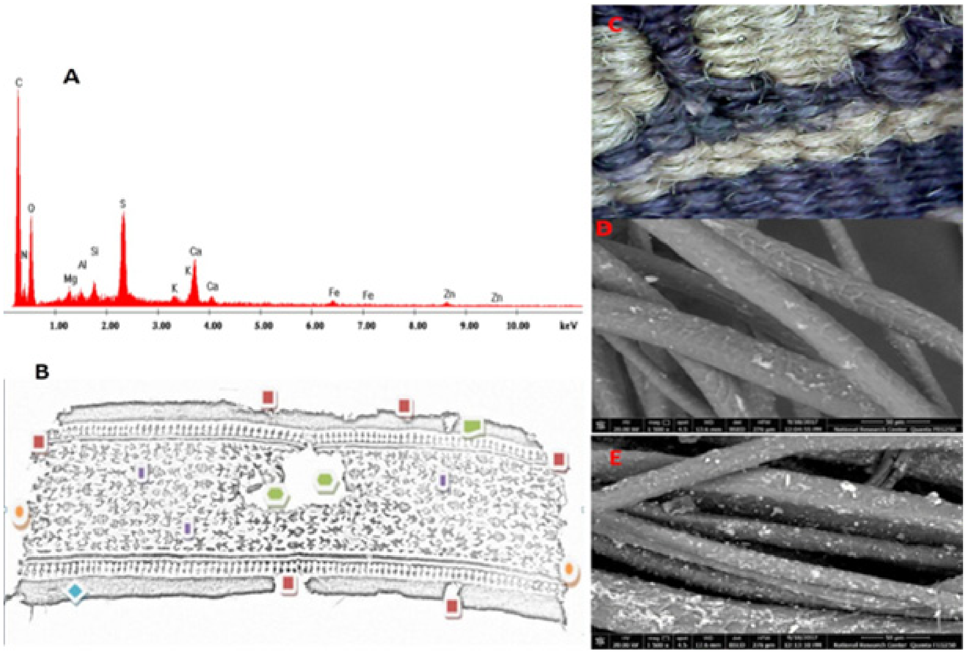


Fig. 6. The elements such as mordents, and dirt on the object by using SEM-EDX (A). Documentation of object by drawing that shown the lost parts, weak parts, and dirt, and stain (B). Image by USB Microscopy of object that shown the weave type and color of object (C). SEM images of object that show the type of fibers and dirt (D and E).

Fig. 7. The mechanical cleaning of the object by using fine brushes (A-C). Supporting of the object before wet cleaning (D). Wet cleaning of object by using water and detergent (E). Drying process of object by using free acid paper (F). Removing the temporary support after drying.

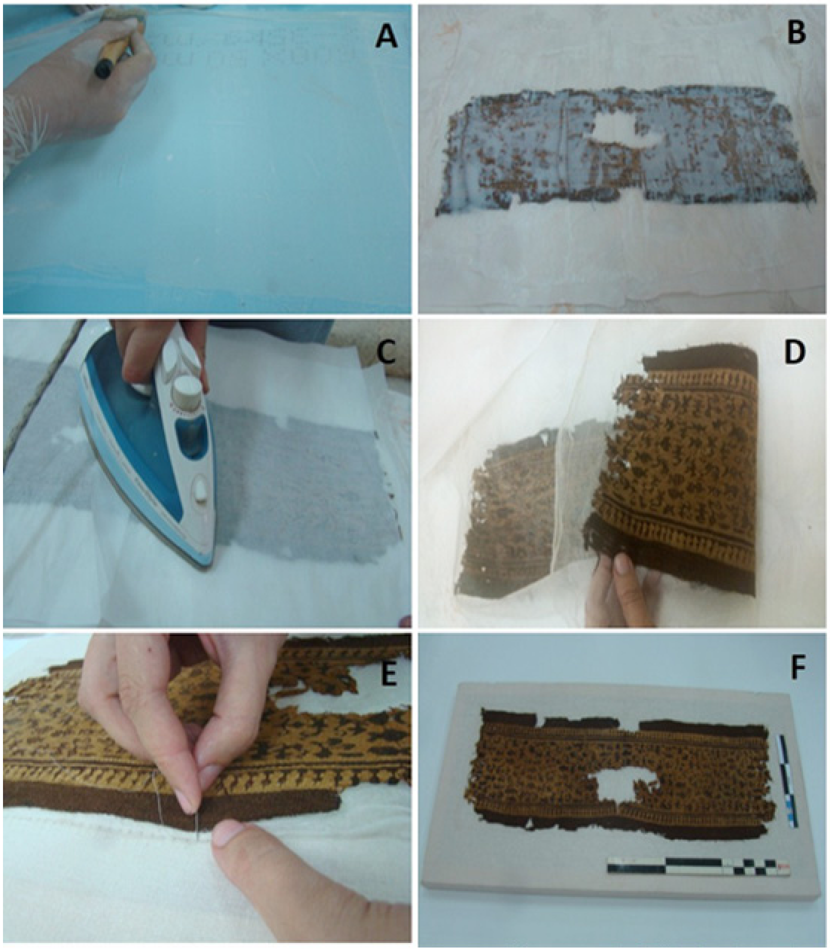


Fig. 8. Applying the Nano-Vinyl acetate derivatives on new silk criplin support (A). Silk support coated with Nano-Vinyl acetate derivatives on the backside of the historical textiles (B). Adhering the historical textile on the new silk support by using hot iron (C). The historical textile fixed on new silk support (D). The historical textiles on new support fabrics to display on museum (F)

TABLE 3. The Lab value of samples after applying Vinyl acetate derivatives and ageing

Wool Samples	Dyed Samples	Samples after applying Vinyl acetate derivatives			Samples + Vinyl acetate derivatives + ageing 100C for 72 h			Samples + Vinyl acetate derivatives + ageing 100C for 144 h		
	K/S	L	a	b	L	A	B	L	a	B
Saff+ Alum	5.0825	65.34	18.89	35.95	64.91	18.41	35.04	64.81	18.15	33.49
Saff+ Iron	11.5408	47.01	9.74	27.34	46.56	10.08	27.19	46.01	12.38	31.15
Saffl + Cu	8.3263	53.22	0.60-	27.76	52.84	0.20	26.93	52.75	0.68	26.46
Saff without	5.3056	61.04	14.87	29.81	60.83	14.76	28.94	60.25	14.73	29.78
Mad+ Alum	5.1361	47.35	30.14	19.28	46.37	30.48	19.78	46.03	30.26	19.74
Mad+ Iron	10.5160	36.86	12.96	17.17	36.72	12.87	17.59	36.48	12.13	16.96
Mad+Cu	6.6974	38.86	16.93	14.69	37.81	16.93	15.52	37.61	16.11	14.91
Mad without	5.5348	47.38	27.56	21.29	46.96	27.81	20.33	46.38	27.57	21.91

TABLE 4. The Lab value of samples after applying Nano Vinyl acetate derivatives and ageing

Wool Samples	Dyed Samples	Samples after applying Nano Vinyl acetate derivatives			Samples + Nano Vinyl acetate derivatives + ageing 100C for 72 h			Samples + Nano Vinyl acetate derivatives + ageing 100C for 144 h		
	K/S	L	a	b	L	A	B	L	a	B
Saff+ Alum	5.0825	65.80	18.71	34.01	65.72	18.46	35.84	65.25	17.91	34.85
Saff+ Iron	11.5408	50.12	9.36	28.27	49.58	10.33	30.26	49.45	10.37	30.06
Saffl + Cu	8.3263	55.64	1.27	27.77	55.50	0.12	27.15	55.09	1.75	27.06
Saff without	5.3056	64.27	14.92	32.37	65.61	14.87	30.05	65.70	14.62	31.44
Mad+ Alum	5.1361	47.78	30.15	19.17	47.72	29.42	19.61	47.87	30.10	20.13
Mad+ Iron	10.5160	38.78	13.28	18.96	39.78	13.24	19.13	40.69	12.57	19.96
Mad+Cu	6.6974	42.86	17.56	15.93	42.35	17.24	16.08	43.05	16.67	16.05
Mad without	5.5348	47.43	23.67	18.72	47.08	24.83	18.99	47.78	25.08	19.53

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