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MASKING AND MISINTERPRETING COTTON FIBERS: DANGERS ASSOCIATED WITH THE FIBER ANALYSIS OF ARCHAEOLOGICAL TEXTILES

Mary Ballard and Irene Skals

ABSTRACT
Several years ago an investigation of fiber analysis was undertaken on archaeological fabrics from a site at Bab edh Dhra along the south-eastern shore of the Dead Sea. The Early Bronze Age fragments (*c.* 3000 BC) were consolidated with poly(vinyl acetate) resin (PVA) in the field. The disengagement of fiber from resin proved to be extremely difficult. Subsequent experimental work on the removal of fresh PVA resins from modern cotton cloth has produced results which suggest that even reversible solvent/consolidant systems can permanently affect – and compromise – fiber-related investigations.

INTRODUCTION

During the late 1970s and early 1980s the Smithsonian Institution conducted a major research program on human biological history in Jordan, Bahrein and the Kingdom of Saudi Arabia. At Bab edh Dhra in Jordan, an Early Bronze Age cemetery was explored to study skeletal remains [1]. Textile fragments were recovered from shaft tombs A-110-NE and A-114-N. These were consolidated in the field with an adhesive resin, under harsh conditions (temperatures on site reached 40-45°C) [2]. The fragments were then brought to the Smithsonian Institution in Washington for analysis. No specific documentation was available on the treatment given to these textiles. Conservators associated with this and other Smithsonian research sites in the Middle East at the time reported that only ethanol and acetone were available as solvents and that either poly(ethyl methacrylate)/poly(methyl acrylate) copolymer (Acryloid B-72) or poly(vinyl acetate) resins (PVA) were usually employed [3, 4].

CONDITION

The textile fragments arrived at the Conservation Analytical Laboratory in an extremely friable state. The fragments were brown and charred: some were simply mineralized deposits, without form. The textiles were stiff with resin and the gloss of the resin was visible to the unaided eye. In one package, 10 fragments were glued directly to the poly(ethylene) film. Fragments from A-110-NE had a warp- or weft-faced plain weave; there was also a 2:1 twill. The majority were balanced plain weaves, with low- or no-twist, S-plied yarns. The tabby weave textiles had thread counts of 11 × 16, 11 × 18 and 12 × 18 threads per cm; the faced fabric, 9 × 22 threads per cm. A-114-N fragments were S-spun plain weave with a thread count of 16 × 39 threads per cm. Soil, described by the site archaeologists as silty, was present on all fragments [2].

While it was obvious that these fragments were impregnated with resin, the type of resin was not known. A small sample of the adhesive was analysed by infrared spectroscopy and identified as poly(vinyl acetate). As there are many types of PVA, and many formulations, different solvents were tested in order to determine the most effective solvent to redissolve the PVA used on these archaeological textiles. The first trials were made using drops, which only spread the adhesive more and, in some cases, softened it; in other cases, the drops of solvent caused the resin to crystallize on the surface of the fibers. Soaking the fibers in solvent for extended periods was also tried. The solvents that were tested were ethanol, acetone, toluene, xylene, trichloroethane and perchloroethylene. The fibers and the adhesive reacted in slightly different ways to each of these solvents; the method that was eventually chosen involved soaking the fibers in toluene for up to 24 hours. This did not dissolve the PVA completely, but subsequent examination of each sample under the light microscope showed cotton fibers and, in addition, a lot of unidentifiable material: partly adhesive, partly dirt and charred fiber dust.

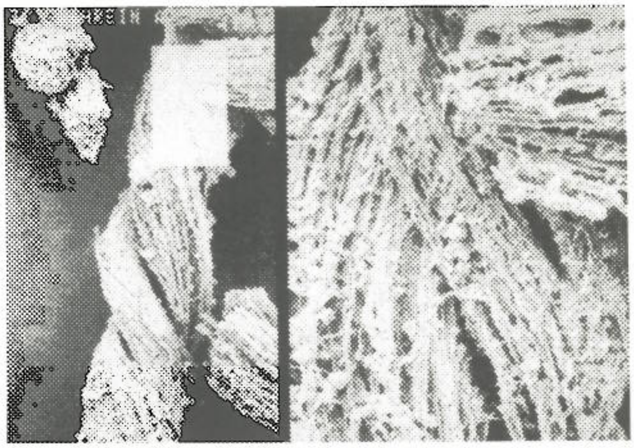

Fig. 1 Fragment from A-110-NE, at 36× magnification on the left and at 144× magnification on the right.

Untreated small samples were also examined by scanning electron microscopy but the fibers could not be discerned (Fig. 1), due to the quantity of resin and soil. Elemental analysis carried out with energy dispersive X-ray spectroscopy indicated the presence of aluminum, silicon, chlorine and calcium. Rock salt crystals (sodium chloride) were found embedded in one sample from A-110-NE.

OBSERVATIONS

The difficulty associated with fiber identification in these Jordanian samples was unusual. Charred fibers, even in an archaeological context, have been identified by the authors and by other textile fiber microscopists [5-7]. Did the problem lie in our particular methodology, was it inherent to the fiber, or did it result from the treatment in the field? Although conservators in other disciplines have successfully treated specimens containing consolidants and adhesives, the use of these polymers in textile conservation has raised various issues over several decades. Yet starch sizes and, more recently, poly(vinyl alcohol) and poly(methyl methacrylate) sizes are routinely employed in the finishing of cotton fabrics [8].

Poly(vinyl acetates) are brittle polymers which are widely used and have been extensively studied by conservation scientists [9, 10]. The AYAA, AYAC, AYAF and AYAT resins commonly available in North American conservation laboratories have molecular weights ranging from 83,000 to 167,000 [11]. Despite developing a slight acidity on aging, they are considered chemically stable [10]. Mechanically, the PVA resins have a glass transition temperature (T_g) of about 28°C, above which they become less brittle and more rubber-like [9]. This increased plasticity and workability makes them particularly suitable for use in archaeology in warm climates.

A study on preservatives for archaeological bone cites two potential drawbacks of PVA resins: the difficulty of cleaning bone previously joined with these consolidants, and the possibility of chemical contamination of the organic fraction recovered from the treated bone [12]. Certainly the dirt on the textiles obscured analytical features and was made more difficult

Table 1 Specific areas of some fibers (from Wypych [16]).

Fiber	*Specific surface area (m^2g^{-1})*
Polyester yarn	0.13
Texturized polyester	0.15
Nylon 6	0.08
Rayon	0.26
Aramid	0.23
Cotton	1.30

to remove by the PVA consolidation. A study on wood consolidants (Acryloid B-72 in toluene and paraffin wax) found that preferential, uneven coating obscured 'substantial details' of distinguishing microscopic characteristics of specific types of wood. Further, solvent action alone physically distorted fragile voids and cracked cell walls [13].

Are the substituted groups in the fibrous cellulose substrate more reactive than other materials to the resin polymer? Cotton cellulose is negatively charged and attracts metal oxides. Chemical moieties such as cationic surfactants are actually bonded to the fiber [14, 15]. Yet the poly(vinyl acetate) polymer has no groups especially attractive to cotton. Perhaps the intense adhesion of the resin to the fiber is simply a function of the high surface area of the cotton fiber which, in turn, provides a higher density of chemical adhesion (Table 1) [16].

If this was the case, lack of agitation or circulation of the solvent would impede dissolution even when the solubility parameters of solvent and solute were well matched. It was also quite possible that the aged cotton fiber was more degraded than other fibers in comparable circumstances. Cotton ranks much lower than wool (or nylon and polyester) in its ability to resist damage by abrasion [17]. Thus the cotton fiber, even when new, is more susceptible to structural damage as a result of mechanical wear. The harsh, silty conditions of the archaeological site would have caused damage during, or even before, excavation and retrieval. Degradation of the human remains by microbial action certainly took place; it is not known whether cellulolytic fungi and bacteria were also active.

EXPERIMENTAL

It was decided to determine to what extent the poly(vinyl acetate) resin system is bound to cotton cloth when the resin/solvent system is known and new, when the fiber is modern, when the fabric is clean, and when the climatic conditions that can be maintained in a conservation laboratory are available. Thirteen squares of de-sized, bleached, combed, plain-weave cotton fabric, each measuring 5.2 × 5.2cm (2 × 2 inches), were notched for identification and weighed to tolerances of a thousandth of a gram on an AE-163 Mettler balance. Ten clean glass jars were

Table 2 Add-on (percentage weight gain) of poly(vinyl acetate) resin on modern cotton fabric squares.

PVA type	*Sample*	*First bath*	*Second bath*
5% AYAA	(b)	9.0%	51.1%
	(a)	11.5%	–
10% AYAA	(b)	18.2%	133.1%
	(a)	19.3%	–
5% AYAC	(b)	9.2%	22.4%
	(a)	9.4%	–
10% AYAC	(b)	16.8%	49.6%
	(a)	23.9%	–
5% AYAF	(b)	12.6%	29.9%
	(a)	8.7%	–
5% AYAF	(b)	7.9%	32.8%
	(a)	8.0%	–
Control		±0.04%	–

each filled with 60g of acetone. To each jar were added 6g of AYAA, AYAC, AYAF or AYAT pellets. Because 10% w/w solutions of AYAF and AYAT failed to dissolve entirely, 5% w/w solutions of all four resins were also prepared.

Each square was immersed in one resin solution (approximately 15ml per cotton square) contained in a clean aluminum cup at room temperature. This was done twice, for a total of 12 squares; one square was left untreated as a control. The fabrics were individually hung to dry under a fume hood for one week, after which the weight gain of each sample was measured. One of each sample pair was subsequently bathed again in a fresh quantity of the same resin solution. These samples were hung to dry and, again, the weight gain was measured. This 'add-on' is the percentage of resin by weight compared to the original weight of each individual square. Table 2 lists the results after the first and second baths.

After these measurements were completed, small samples were set aside for examination under scanning electron microscopy. While the weave structure was discernible with a 50% add-on, and even vaguely recognizable with 133% added to the weight of the fabric, the clarity of the yarn and fiber diminished gradually; plastic interstitial transverse networks developed between the fibers with as little as 8% add-on (Fig. 2). Aspects of cotton fiber morphology could still be differentiated at 19% add-on (Fig. 3) and even up to 50% add-on (Fig. 4), though with decreasing confidence.

Each square was then cut into four sections; each section was notched for identification and weighed so that the effect of various rinsing procedures could be assessed. The control was also divided, marked by notching, and weighed. Four levels of rinsing were used in order to determine the reversibility of the PVA resin add-on:

Fig. 2 Cotton coated with 8% AYAT resin add-on after one bath in a 5% solution, 300× magnification.

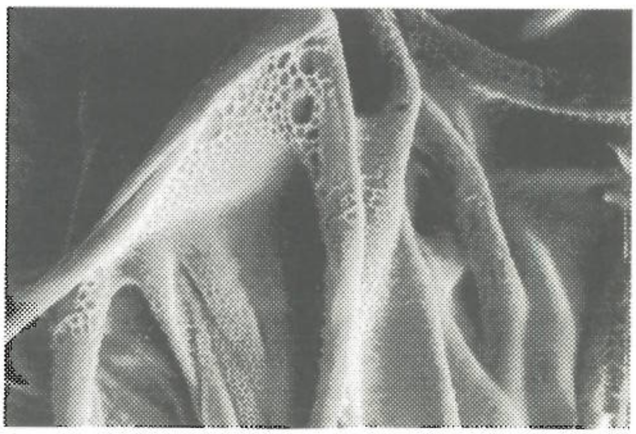

Fig. 3 Cotton coated with 19.3% AYAA resin add-on after one bath in a 10% solution, 450× magnification.

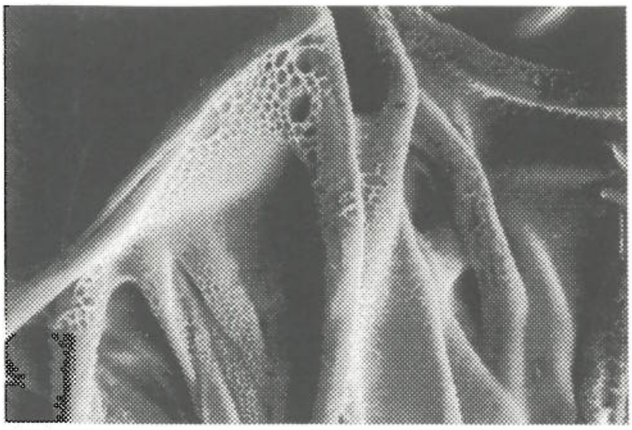

Fig. 4 Cotton coated with 51% AYAA resin add-on after two baths in a 5% solution, 500× magnification.

1 a bath containing 30ml of acetone, with no agitation
2 a two-rinse system with no agitation, using first the previous bath, then a clean bath of acetone
3 a three-rinse system using the two previous baths in sequence and a final fresh bath
4 agitation of the sample by hand-shaking in 30ml of acetone in a clean, closed, glass jar.

The rinses each lasted one minute and agitation was carried out for two minutes. All samples were hung to dry under a fume hood. The decrease in weight was determined by comparing the final weight to the added weight, and the results are tabulated in Table 3.

There are two notable instances where *less* than the add-on was removed and where *more* than the add-on came off. It must be assumed that the resin on the samples, when hung to dry, continued to flow before evaporation was complete. It appears, therefore, that the quartered samples were not entirely uniform. If this explanation is correct, then the quantitative value of the decrease in weight is not precise. The amount of resin actually remaining – if any – was not known.

In order to determine whether any PVA resin remained on the rinsed samples, colorimetric tests were undertaken using a dilute potassium iodide solution, in the way that starch size residues are tested [18]. Unsized, bleached cotton shows a pale yellow; poly(vinyl acetate) residues appear pink to maroon red [19]. A tristimulus colorimeter (Minolta CR100 Chroma Meter) was calibrated. An untreated clean cotton square was treated with 0.1ml of solution so that the unreacted color could be utilized as the baseline target. The color difference between the target and each rinsed sample was measured. Table 4 tabulates the results as ΔE in the CIE (Commission International de l'Eclairage) L*a*b* system; Table 5 shows the Δa* values, specifically the difference in redness between target and sample.

Had there been no residual PVA resin on the rinsed samples, no color difference greater than that found in the control would have appeared: the target, the control and any other clean samples would have the same appearance. To what extent is a positive stain important? It shows that, with just one complete wetting (immersion), a subsequent single rinse will not remove all residues, and neither will two rinses. While three rinses will reduce single add-ons of AYAC lower than 8% to a level below the threshold of the control, this rinsing will not achieve the same result for 8% by weight of AYAT on the fabric. It is worth noting that the data for Δa in Table 5 indicate a significant level of contamination on all the treated samples compared to the control. In the experiment no amount of rinsing or agitation reduced the colorimetric values of the samples to those of the control, although the values did gradually decrease with factors such as an increase in the amount of solvent, the time the textile was held in the solvent, and the degree of agitation. Under ideal conditions, continued extraction or agitation would, presumably, reduce the residual PVA to a negligible amount.

DISCUSSION

It is reasonable to ask whether archaeological textiles would maintain their integrity if they were subjected to such 'ideal' conditions. Other factors which should be considered are: how much resin was on the archaeological textiles in the first place? Also, does the soil provide an additional obstacle to the cleaning operation? Archaeological fibers are often already degraded, perhaps charred. Soil is frequently deeply embedded. Should experiments be conducted on actual specimens?

Cotton fibers cannot be distinguished by their length, diameter or diffraction patterns; and not by their convoluted form, in spite of a number of studies to assess this possibility [20]. Since cotton is a hair seed, the fibers are not uniform in size and the range of lengths is altered further by processing. Unlike hair, no particular type of cotton can be identified from the finished fabric, and there is no DNA to assist in identification: cotton fibers come from extracellular seed hairs and have no genetic material [21].

Given the fragile condition of archaeological textiles, they probably cannot survive prolonged agitation or a long series of immersions in solvent; further treatment may therefore be impossible to carry out successfully. Does this matter? To put it more formally: what does the museum world want from these specimens? And on a more practical level, could the objects have been saved without consolidation? Was there anything else the archae-

Table 3 Add-on (percentage weight gain) of poly(vinyl acetate) and decrease (percentage weight loss) during cleaning of modern cotton fabric squares.

		Add-on		*Total weight loss*			
PVA type	*Sample*	*First bath*	*Second bath*	*One rinse*	*Two rinses*	*Three rinses*	*Agitation 2 min*
5% AYAA	(b)	9.0%	51.1%	28.9%	43.6%	65.7%	47.5%
	(a)	11.5%		8.0%	9.1%	12.6%	10.2%
10% AYAA	(b)	18.2%	133.1%	42.8%	81.0%	111%	135%
	(a)	19.3%		15.1%	20.8%	17.0%	16.8%
5% AYAC	(b)	9.2%	22.4%	21.5%	22.2%	20.6%	21.6%
	(a)	9.4%		7.8%	9.1%	10.1%	8.8%
10% AYAC	(b)	16.8%	49.6%	47.0%	43.4%	41.0%	67.2%
	(a)	23.9%		24.6%	26.9%	20.6%	20.2%
5% AYAF	(b)	12.6%	29.9%	23.4%	35.5%	30.1%	25.6%
	(a)	8.7%		10.6%	7.5%	7.7%	7.1%
5% AYAT	(b)	7.9%	32.8%	19.4%	43.4%	36.7%	30.1%
	(a)	8.0%		6.9%	6.8%	6.6%	7.6%
Control		±0.04%	–	no change	0.2%	0.2%	no change

Table 4 Add-on (percentage weight gain) of poly(vinyl acetate) and colorimetric change (ΔE) when cleaned sample is treated with potassium iodide solution.

		5% AYAA	*10% AYAA*	*5% AYAC*	*10% AYAC*	*5% AYAF*	*5% AYAT*	
	a:	*11.5%,*	*19.3%,*	*9.4%,*	*23.9%,*	*8.7%,*	*8.0%,*	
	b:	*51.1%*	*133.1%*	*22.4%*	*49.6%*	*29.9%*	*32.8%*	*Control*
Rinse		27.9	22.7	14.0	16.8	24.4	31.1	6.5
1×		58.4	48.1	40.8	45.2	50.3	48.6	
Rinse		14.7	16.0	8.9	15.6	15.6	29.4	6.5
2×		44.5	43.6	32.3	41.6	41.6	37.1	
Rinse		16.9	13.3	4.8	6.2	12.8	22.2	7.2
3×		48.0	49.1	21.1	22.9	30.1	39.9	
2 mins		9.8	11.5	6.1	7.6	10.6	13.9	7.5
agitation		49.3	44.6	24.4	35.9	31.0	30.6	

ological conservator on site could have done to preserve the specimens under such extreme and difficult circumstances? What is it that we want to save?

We have the textiles and we can determine weave and thread counts on most fragments. The archaeologist is satisfied that an incidental discovery has been preserved; the curator of ancient Near Eastern artifacts may also be satisfied with the outcome. However, there is another completely different field of research for which the present state of these textile fragments is unsatisfactory: that of the textile historian. These researchers use textiles to explore trade patterns, economic activity, and the extent of technological and aesthetic communication in earlier periods of human existence. For historians in this area, the emergence of cotton fabric as traded goods and as woven cloth remains a difficult field of study. Rare examples of cotton fabric from the Graeco-Roman era have been found, but it remains unclear whether these (luxury?) items spread from a single vortex in the Indus Valley (as with the Mohenjo-Daro discovery [22]) or from Nubia [23] or from Jordan [24]. If the present fragments are indeed cotton burial clothing they would be some of the earliest examples of cotton clothing that survive. Sadly for textile historians, investigation of the substantive details of processing operations and age – yarn character, combed and carded quality, C-14 dating, mordant analysis – has now apparently been precluded by on-site treatment. Indeed, there is an inevitable reluctance to announce that these fabrics are truly cotton on the basis of a few identifiable fibers, given the possibility of inadvertent contamination from modern clothing, papers, tissues and packing materials. The reluctance to publish these results is matched only by a reluctance to perpetuate present attitudes to treatment.

CONCLUSION

Ostensibly, cotton is an easy fiber to recognize and to differentiate from other natural fibers. However, such a discovery may produce difficult questions for the archaeologist, the textile historian and the conservator. Botanical and technical, economic and technological issues begin with the identification of cotton rather than end with it. A knowledge of all these factors, together with the natural physical and chemical properties of cotton fibers, may rightly induce caution on the part of the conservator planning an on-site treatment or a preservation procedure.

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SUPPLIERS

AYAA, AYAC, AYAF and AYAT are poly(vinyl acetate) resins manufactured by Union Carbide, USA and available from Conservation Materials Ltd, 1395 Greg Street, Suite 110, Sparks, NV 89431, USA.

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Table 5 Add-on (percentage weight gain) of poly(vinyl acetate) and colorimetric change (Δa) when cleaned sample is treated with potassium iodide solution.

		5% AYAA	*10% AYAA*	*5% AYAC*	*10% AYAC*	*5% AYAF*	*5% AYAT*	
	a:	*11.5%,*	*19.3%,*	*9.4%,*	*23.9%,*	*8.7%,*	*8.0%,*	
	b:	*51.1%*	*133.1%*	*22.4%*	*49.6%*	*29.9%*	*32.8%*	*Control*
Rinse		17.9	16.2	10.5	13.1	16.6	16.8	0
1×		26.3	22.7	21.6	23.4	24.9	24.9	
Rinse		11.7	12.6	5.6	7.4	12.5	15.1	0.1
2×		19.8	21.9	15.5	19.8	21.8	20.0	
Rinse		11.2	11.2	2.2	5.5	10.7	11.5	0.1
3×		21.6	23.1	11.4	22.8	15.8	21.1	
2 mins		8.4	10.4	2.8	6.6	9.0	8.7	0.1
agitation		21.6	24.5	15.4	22.5	16.3	18.9	

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