Degradation Behavior of Nano-Glue Adhesive due to Historical Textiles Conservation Process

H. E. Ahmed¹, W.S. Mohamed²*, H. Saad³, H.E. Nasr², M.Morsy⁴
N. Mahmoud¹
¹Conservation Dept., Faculty of Archaeology, Cairo University, ²Polymer and Pigment Dept, Chemical Industry Division, National Research Centre, ³Conservation Dept., Faculty of Archaeology, Fayoume University, ⁴Textiles Metrology, National Institute of Standards, Egypt.

Flexible textiles in museums need to consolidate by natural adhesives such as animal glue due to conservation process. Sometime the animal glue becomes shrunken, cracked, and rigid after long term. The article is aimed to study using Nano animal glue adhesive in historic textiles conservation field in order to consolidate the fragile textiles. For this, an extensive experimental work was done to study the ageing behavior of Nano animal glue after artificial ageing process. Firstly, Wool fabric dyed with natural dyes such as madder and safflower dye mordanted with different mordents to similarity for the historical textiles. The wool dyed fabrics were coated with animal glue adhesive and nano animal glue adhesive. The treated wool fabrics were aged by accelerated thermal ageing for different time.

A comparative study was done in order to characterize changes in properties as well as the physical and chemical degradation of treated wool fabrics before and after thermal ageing. Different type of analysis methods such SEM, FTIR, the colors are given in Commission internationale de l’éclairage (CIE L*a*b*) coordinates and mechanical properties. This article presents interesting results concerning the effect of ageing on characterization of nano glue adhesive furthermore for treated wool fabrics.

Keywords: Nano glue, Adhesive, Textiles, ageing, CIE L*a*b*, SEM, XRD, FTIR.

Introduction

Over the past forty years, conservators are using adhesive techniques for consolidation of the fragile historic textiles as showing in Fig. 1. These experiences have provided a good knowledge of the failures and successes of these adhesives treatments. By other hand, the frame of using adhesive in textile conservation treatments, it covers the following; firstly, treatments by using adhesive are only suitable for deteriorated textiles and degraded silks; secondly, adhesives should not penetrate into historic textiles. So, adhesives must be applied as sparingly as possible [1-7].Due to conservation procedure, animal glue adhesive can be found on historic textiles as consolidation step, or when the historic textiles to a solid surface adhered. It is noticed by the aged condition animal glue paste may be present in shrunken, brittle form, cracked, rigid. Also, it is not provide enough and good adhesion for supporting the historic textiles [8-9]. Natural the animal glues polymers are derived from collagen. Collagen is major structural protein of skins, tissue, bones and cartilage. The animal glue is characterized by the properties of different chemical and physical according to the source and methods of preparation. In the manufacture of artifacts and objects, some knowledge exists that the animal glues are more suitable for specific purposes [10-12].

Some researchers such as Osman, et al.; Garside, et al.; Kim, et al.; Kim and Wyeth; and Leene, et al., studied the effect of artificial aging such as the thermal and light on treated textiles by adhesives. They evaluated the changes in the optical, chemical and mechanical characterization. The result of this research has found that the accelerated aging make a deterioration of aged fabrics [13-15].
Fig. 1. Show the fragile historic textile in faculty of Archeology museum – the Islamic art section-, Cairo University. One can see the object condition and why it is need to conserve and consolidate by adhesive.

Materials and Methods

Materials

Gelatin type A from porcine skin (175 Bloom), glutaraldehyde grade I 25% aqueous solution was obtained from Merck Darmstadt, Germany. Acetone, ethyl alcohol and acetonitrile were purchased from Alnasr Co. (Egypt).

Methods

Dyeing

Extraction of dye

The dyeing with madder or safflower dye 10% (w/v) were carried out according for to the following steps:

- The first step is grinding the natural dye to be a fine powder.
- Soaking the natural dyes powder in the distilled water for 12hr in order to extract the color from the dyes powder.
- Then with the stirring heating the extract to the boiling temperature degree for 2hr. It is noticed must be adding water to compensate the evaporated water during the heating process.
- After that allowing to the extract to be cooled and then filtering the extract many times in order to get a clear solution of colored.

Dyeing procedure

Dyeing procedure of wool fabrics was done according to the exhaustion method [16] a liquor ratio of dyeing bath (LR) of 1:20 (for each 1 g of natural dye the bath volume is 20 ml). The dyeing procedure was performed in a beaker. In the step of dyeing procedure some mordants, 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. After finishing the dyeing procedure, removing the unfixed dyestuff was done by rinsing the dyed samples three times in cold water baths (for 5 min at room temperature, LR 1:20) [17-19]

Samples preparation

Wool fabric samples were cut into 25 x 5 cm (length x width) in warp test specimens direction. The warp strips were prepared by reveling away the yarns on each side forming 1.5 cm wide strips with a 2.5 mm fringe down each side. In this test five samples were used for each test.

Preparation of nano-animal glue

Gelatin nanoparticles were prepared by a two-step desolvation method, previously described by Coester et al [20]. In brief: 1.25 g gelatin was dissolved in 25 mL distilled water under constant heating temperature range at 27 °C. 25 mL acetone was added to the gelatin solution as a desolvating agent to precipitate the high molecular weight (HMW) gelatin. The supernatant was discarded and the HMW gelatin re-dissolved by adding 25 mL distilled water and stirring at 600 rpm under constant heating. The pH of the gelatin solution was adjusted to values between 4.0 and 5.5. Acetone (75 mL) were added drop-wise to form nanoparticles. At the end of the process, 250 μL of 25% glutaraldehyde solution was used for preparing nanoparticles as a cross-linking agent, and stirred for 12h at 600 rpm. The remaining organic solvent was evaporated using a rotary evaporator. Figure 2 show they are TEM images of the prepared nano-animal glue.
Dyed wool fabrics were treated with the animal glue adhesives and Nano animal glue adhesives in 5% concentration according to the standard method of conservation [8-11].

Accelerated ageing

Feller presented a possible thermal testing times for different classes of thermal stability based on the deterioration rate that will double for a rise of 100°C and on the statement that heating textiles or paper for 72 h (3 days) at 100 °C is equivalent around 25 years of natural ageing under normal condition of ageing. Wool dyeing fabrics ware hanged in a temperature-controlled oven “Herous-Germany” on special frames. The dyed wool samples were thermally aged at 100 °C for different times such as 3, 6, days [21-23].

Examinations and analysis

Morphological study of wool samples

The surface morphology of the dyed wool fabrics (untreated and treated by glue adhesive or nano glue adhesive) were investigated by using Scanning Electron Microscope module (Quanta 200 ESEM FEG from FEI). Very small samples were cut and taken from the treated and untreated wool dyed fabric from different areas. Then the samples were investigated under SEM in order to show any changes of fibers resulting the damage by thermal ageing [24-25].

Morphological study of glue and nano glue

The particle size of the prepared nano-animal glu was measured using transmission electron microscope (TEM), where the TEM images were obtained by 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 [26].

Color measurement

The CIE-Lab values of dyed wool fabrics (untreated and treated by glue adhesive or nano glue adhesive) were measured by using a double beam Optimatch spectrophotometer (Datacolor international Spectraflash SF450-UK). When the color in different formulae desirable to express color specifications in terms of such correlates. The colors that given in CIE Lab coordinates are , L value corresponding to the brightness (100 = white, and 0 = black), while a* value to the red–green coordinate (positive sign = red, and negative sign = green), and b* value to the yellow–blue coordinate (positive sign = yellow, and negative sign = blue). The total difference of color $\Delta E^*$ between two color stimuli $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ [27-29].

Tensile strength and elongation

Elongation and tensile strength test of the dyed wool fabrics (untreated and treated by glue adhesive or nano glue adhesive) before and after thermal ageing were measured by using a Lloyd Tensile Testing Machine Type T5K. Elongation and tensile strength test were 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% [30].
Fig. 3. Show the TEM images of the normal animal glue. From the figure, it is obvious that, the glue particles have no regular shape and also were not regularly dispersed, with particle size reached to 197 nm.

Fourier transform infrared spectral analysis (FTIR)

The chemical structural changes that occurring in dyed wool fabrics (untreated and treated by glue adhesive or nano glue adhesive) before and after thermal ageing were measured by using FTIR. Vibrational bands of wool fabrics that appear in the infrared spectra will provide more information about the chemical functional groups of a wool sample. This information will leads to a general characterization of the treated and untreated wool fabrics. Also this bands will help in the identification of specific compounds [31-32]. FTIR analysis of wool fabrics was carried out by using BRUKER – FTIR- TENSOR

Results and discussions

The effect of ageing on mechanical parameters of treated samples

Strength and elongation of coated wool fabrics by animal glue and Nano animal glue before and after ageing are presented in Tables 1 and 2. It is noticed that animal glue and Nano glue adhesive increase the tensile strength of treated wool samples. For examples wool dyed by safflower mordanted by alum show increase in the tensile strength from 25.13 to 27.72 after applying animal glue adhesive. By other words the using animal glue improves the strength of treated wool fabrics. It is clear that the treated wool fabrics with animal glue adhesive became more rigid as the elongation of the sample is decreased. While the Nano glue adhesive improves both of the strength and elongation of coated wool fabrics. While the treated wool fabrics with Nano glue adhesive more elastic as the elongation of the wool sample is increased. The results indicate that the percent of the increase in the tensile strength depends on type of the adhesives.

The effect of ageing on mechanical parameters of treated samples

Table 1 show that there are slightly decrease in strength and elongation of coated wool fabrics with animal glue adhesive after thermal ageing. While Table 2 show that there are slightly increase in tensile strength and elongation of treated wool fabrics with Nano glue adhesive after thermal ageing. By comparing different results in Tables 1 and 2 of both strength and elongation of treated wool fabrics before and after thermal ageing it is noticed that the most effective adhesive is Nano glue adhesive. It is clear that Nano glue adhesive is suitable for conservation of wool fabrics more than animal glue adhesive.

The effect of ageing on optical parameters of treated samples

Color change such as K/S and Lab value of treated samples by animal glue and nano animal glue before and after thermal ageing are presented in Tables 3 and 4. From Tables 3 and 4 it is observed that there is decrease of treated samples by animal glue in the brightness index L after ageing. For example wool dyed by safflower mordanted by alum show decrease in the brightness, index L from 66.06 to 65.61. While there is an increase of treated samples in the value to red-green, coordinate. One can see that wool dyed by safflower mordanted by alum show very slight increase in the value to red-green coordinate from 16.5 to 16.75. While there is a increase in b*
value yellow–blue coordinate of treated samples after ageing. For example, wool dyed by safflower mordanted by alum show increase in value yellow–blue coordinates from 32.9 to 34.8. By other hand, there are no noticeable changes in the color of treated wool textile by nano glue adhesive samples before and after the thermal ageing.

Furthermore, Table 3 and 4 show the different color change ΔE of the wool fabrics dyed with safflower or madder mordented with different type of mordents that treated with animal glue or nano glue before and after ageing. The tables showing increasing of ΔE when increase the time of ageing for all the samples. Also, one can see that the total color change different of treated wool with nano glue after ageing less than treated wool fabrics with animal glue after ageing. This is mean that the nano glue is more stable than animal glue.

**TABLE 1.** The elongation and force of samples after applying Glue and ageing.

<table>
<thead>
<tr>
<th>Wool Samples</th>
<th>Samples after dyeing</th>
<th>Samples after applying Glue</th>
<th>Samples + Glue + ageing 100C for 72 h</th>
<th>Samples + Glue + ageing 100C for 144 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elongation %</td>
<td>Max Force N</td>
<td>Elongation %</td>
<td>Max Force N</td>
</tr>
<tr>
<td>Saff + Alum</td>
<td>27.57</td>
<td>25.13</td>
<td>27.45</td>
<td>27.10</td>
</tr>
<tr>
<td>Saff + Iron</td>
<td>36.27</td>
<td>24.21</td>
<td>25.95</td>
<td>24.92</td>
</tr>
<tr>
<td>Saff without</td>
<td>31.88</td>
<td>23.42</td>
<td>23.03</td>
<td>26.77</td>
</tr>
<tr>
<td>Mad + Alum</td>
<td>36.45</td>
<td>24.53</td>
<td>28.92</td>
<td>28.61</td>
</tr>
<tr>
<td>Mad + Iron</td>
<td>35.25</td>
<td>24.35</td>
<td>29.85</td>
<td>27.71</td>
</tr>
<tr>
<td>Mad without</td>
<td>23.59</td>
<td>23.59</td>
<td>27.33</td>
<td>27.98</td>
</tr>
</tbody>
</table>

**TABLE 2.** The elongation and force of samples after applying Nano Glue and ageing.

<table>
<thead>
<tr>
<th>Wool Samples</th>
<th>Samples after dyeing</th>
<th>Samples after applying Nano glue</th>
<th>Samples + Glue + ageing 100C for 72 h</th>
<th>Samples + Glue + ageing 100C for 144 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elongation %</td>
<td>Max Force N</td>
<td>Elongation %</td>
<td>Max Force N</td>
</tr>
<tr>
<td>Saff + Alum</td>
<td>27.57</td>
<td>25.13</td>
<td>27.45</td>
<td>27.10</td>
</tr>
<tr>
<td>Saff + Iron</td>
<td>36.27</td>
<td>24.21</td>
<td>25.95</td>
<td>24.92</td>
</tr>
<tr>
<td>Saff without</td>
<td>31.88</td>
<td>23.42</td>
<td>23.03</td>
<td>26.77</td>
</tr>
<tr>
<td>Mad + Alum</td>
<td>36.45</td>
<td>24.53</td>
<td>28.92</td>
<td>28.61</td>
</tr>
<tr>
<td>Mad + Iron</td>
<td>35.25</td>
<td>24.35</td>
<td>29.85</td>
<td>27.71</td>
</tr>
<tr>
<td>Mad without</td>
<td>23.59</td>
<td>23.59</td>
<td>27.33</td>
<td>27.98</td>
</tr>
</tbody>
</table>
The effect of ageing on fiber morphology of treated samples

SEM show that the fine undamaged flat scales with even, smooth surface and sharp scale edges were visible before treated wool fabrics surface. In addition, after applying the glue or nano glue still the undamaged flat scales are visible nut less than nan treated fabrics. It is noticed by SEM image that the undamaged flat scales of treated wool with nano glue are clearer and visible than wool fabrics treated with animal glue. Fig 4 and 5 show SEM of wool fiber morphology after glue and nano glue adhesive application. One can see that nano glue adhesive do not cause noticeable changes in the fiber morphology of treated samples. One can see that nano glue adhesive do not cause noticeable changes in the fiber morphology of treated samples. It is noticed that the characteristic of fiber morphology surface is too clear. By other words, the results indicate that the coating layer by using nano glue adhesive on the fiber surface is not disappearing the fiber surface and the layer is very thin.
SEM images show that the changes in morphology of treated fiber by using nano glue adhesive are less than the changes in the surface morphology of treated fiber by using glue adhesive after thermal aging. These results are confirmed that the nano glue adhesive enhance the durability of surface morphology of sample against the thermal deterioration. By comparing SEM images in Figures 4 and 5. It is clear that Nano glue adhesive is suitable for conservation of wool fabrics more than animal glue adhesive.

**The effect of ageing on fiber chemical structure**

From the Fig 6 and 7 it is clear for the reader that typical bands of wool fabrics are assigned to the peptide bond, the fundamental structural unit of the polypeptide chain on wool fabrics, were visible on FTIR spectra. Furthermore, FTIR spectroscopy show the changes in chemical structure of the treated wool fabrics by using animal glue and nano glue adhesive under artificial thermal ageing were assessed by ATR-FTIR spectroscopy. The FTIR spectroscopy is including difference
spectra obtained by subtracting the spectrum of a control wool sample from the spectrum of the thermally aged samples. By other words, the absorption spectra of wool fabric by using Fourier-transform infrared spectroscopy show characteristic absorption bands of the peptide bonds (-CONH-) that establish different bands that known as the strong amide I, amide II, and amide III. One can notice that the amide I is very useful to investigate the secondary structure of the wool proteins that is mainly related with the C=O stretching and it appear in the range of 1700–1600 cm\(^{-1}\) of spectra. On the other side, the amide II, that appear in 1540–1520 cm\(^{-1}\) range, is related to the C-N stretching and N-H bending vibration. While, the amide III occurs in the range of 1430–1450 cm\(^{-1}\), and it results from C-H bending vibration. In addition, the positions of these bands indicate the conformations of the protein materials: 1650 cm\(^{-1}\) (random coil) and 1630 cm\(^{-1}\) (β-sheet) for amide I, 1540 cm\(^{-1}\) (random coil) and 1520 cm\(^{-1}\) (β-sheet) for amide II. By noticed the Figures (6 and 7) the results are showed that all the amide I and amide II accour at ≈1620 cm\(^{-1}\) and ≈1513 cm\(^{-1}\) indicating that all the wool samples present mainly in β-sheet structure. One can see that ageing make a slight hydrolysis of the polypeptide chain that are apparent as an increase in the OH stretching or bending frequencies found at ≈ 3400 and ≈1650 cm\(^{-1}\) [33-34].

The result referee that the treated wool fabrics without ageing show the bands associated with the peptide bonds were well resolved and possessed high intensity. For the same treated wool, fabrics after ageing the position of the amide bands did slight change and slight change of their intensity was observed. Also, it is noticed increasing of the reduction in the density of different amide bands were observed when increase the ageing time and ageing intensity.

Fig. 6. Show FTIR of wool dyed with safflower mordanted by alum (black color), and FTIR FTIR of wool dyed with safflower mordanted by alum treated with animal glue adhesive after ageing for 144h.
DEGRADATION BEHAVIOR OF NANO-GLUE ADHESIVE

Fig. 7. Show FTIR of wool dyed with safflower mordanted by alum (black color), and FTIR of wool dyed with safflower mordanted by alum treated with Nano animal glue adhesive after ageing for 144h.

Conclusion

This research provided interesting results of using Nano glue adhesive. These results of this work are confirmed that the nano glue adhesive enhance the durability of surface morphology of sample against the thermal deterioration. Furthermore, there are no noticeable changes in the color of treated wool textile by nano glue adhesive samples before and after the thermal ageing. FTIR show that there are new characteristic bands due to application by animal glue adhesive and Nano glue adhesive. By this study, it is clear that Nano glue adhesive is suitable for conservation of wool fabrics more than animal glue adhesive. The next step of this work that applying Nano animal glue adhesive in order to conserve and consolidate the fragile textiles in the museum.

References


*Egypt.J.Chem. 60*, No.6 (2017)
DEGRADATION BEHAVIOR OF NANO-GLUE ADHESIVE


سلوك تلف لاصق الغراء في حجم النانو وذلك لأعمال ترميم وصيانة المنسوجات التاريخية

حربى عزالدين, هناء نصر, محمد مرسي, نجلاء محمود
1 قسم الترميم - كلية الآثار - جامعة القاهرة, مصر 2قسم المبادرات والتحديات - المركز القومي للبحوث - مصر
3 قسم الترميم - كلية الآثار - جامعة الفيوم, مصر

تتعرض المنسوجات التاريخية لمبادرات تلف مختلفة مثل التلف البيولوجي بأنواعه والظروف البيئية المختلفة غير المحتملة في بيئة الدفن أو العرض المتحف والتخزين. لذلك تحتاج هذه المنسوجات التاريخية إلى عمليات ترميم وصيانة باستخدام البوليمرات واللواصق المختلفة. وقد استخدم قديما لاصق الغراء الحيواني كأحد البوليمرات الطبيعية التي تتواجد بكثرة في تلك الفترة في تقوية المنسوجات التاريخية، وقد لوحظ أن لاصق الغراء الحيواني يتعرض بدوره إلى تلف وتحلل وقد في خواص اللصق وقوته الشد يحدث لونه أصفر وتقصف. مما استدعى البحث عن تحسين خصائص هذا البوليمر ليكون أكثر مناسبة لأعمال الترميم والصيانة

ركزت هذه الدراسة على إنتاج لاصق غراء حيواني في حجم النانو قبل استخدامه. ثم تم تطبيق هذا اللصق على عينات موالية من الصوف الحديث والمنسوجات الطبيعية بصورة مشابهة المنسوجات التاريخية في المتاحف المصرية. وقد تم قياس قوة الشد والاستطالة والخصائص الكيميائية والفيزائية للمنسوجات الصوفية المستأنسة بالبوليمر النانو والبوليمر في الحجم العادي للمقارنة بين الخصائص المختلفة. لم تكن النتائج كافية لتطبيق البوليمرات في أنباع أخرى تم تطويرها آلات اختبار للручية المتاحة التي تم ققية لها بالبوليمر في حجم النانو والبوليمر في حجم العادي للمقارنة بين خصائص المنسوجات التي تم تقويتها بالبوليمرات على المدى الزمني البعيد.

وقد أثبتت الدراسة أساليب علمي عديدة للفحص والتحليل للاستفادة في حجم النانو والبوليمر الطبيعي قبل ومع استخدامها على المنسوجات التاريخية الحديثة. ومن هذه الفحوص فحص قوة الشد والاستطالة، فحص التغير الزمني للعينات النسيجية المعقوفة، إضافة فحص قوة الشد وتحمل المحمول للفيبريات، فحص الضغط والتمدد والتكيف الميكروسكوبي للفيبريات سعياً لتحديد مختلف الضغوط Fiscal معالجة النقاط المجهولة لل鹧ابة على الشكل المورفولوجي للفيبريات النسيجية للموقع.

وقد أثبتت الدراسة تقدمها واعدة أن لاصق غراء الحيواني في حجم النانو كان أكثر فاعلية ويكفاء من نفس البوليمر في الحجم العادي. وقد أثر أكثر بكثير من الظروف المتغلبة في الدراسة استخدامه لاستخدامه في تقوية المنسوجات التاريخية الضعيفة والتي تحتاج إلى تدخل بالعلاج والترميم والصيانة.

Egypt.J.Chem. 60 , No.6 (2017)