Adhesives used in paper conservation: chemical stability and fungal bioreceptivity

I.S. Borges\textsuperscript{a}, M.H. Casimiro\textsuperscript{b}, M. F. Macedo \textsuperscript{a, c}, S. O. Sequeira \textsuperscript{a,c,*}

\textsuperscript{a}Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal

\textsuperscript{b}Centro de Ciências e Tecnologias Nucleares (C\textsuperscript{2}TN), Instituto Superior Técnico, Universidade de Lisboa, EN 10 (km 139.7), 2695-066 Bobadela, LRS, Portugal

\textsuperscript{c}VICARTE, Research Unit Vidro e Cerâmica para as Artes, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa. Campus Caparica, 2829-516 Caparica, Portugal

*Corresponding author:
E-mail address: sos11865@campus.fct.unl.pt

\textbf{SUPPLEMENTARY DATA}

I. Thermal analyses

\textbf{A. TGA}

The thermal stability of the unaged samples was evaluated by thermogravimetric analysis using a TGA Q500 equipment from TA Instruments. The study was performed under a nitrogen atmosphere in the temperature range of 25-500°C at a heating rate of 10°C/min.

\textbf{B. DSC}

Differential scanning calorimetry (DSC) was also used as a complementary technique to identify the composition of \textit{Archibond}\textsuperscript{®} (e.g. polymer blend or copolymer). Glass transition temperature (T\textsubscript{g}) was determined by differential scanning calorimetry (DSC Q2000 from TA Instruments). The samples were scanned from -80 to 200 °C at a rate of 10 °C/min under nitrogen atmosphere. Indium was used to calibrate the calorimeter. Two consecutive DSC runs were performed. In both trials, a change occurred in the baseline near 25°C (Figure A. 1), which corresponds to the glass transition temperature (Tg), in which the polymer has a disordered solid structure (vitreous state) below the said temperature. The fact that only one Tg instead of two was obtained, at a value between the glass transition temperatures of the PMA and the PEMA (9.85°C and 64.85°C respectively [1,2]), suggests that the adhesive may be one copolymer and not a polymer blend.
II. ATR-FTIR

Fourier Transform Infrared (FTIR) spectra were obtained in attenuated total reflectance (ATR) mode with an Agilent Technologies 4300 Handheld Infrared Spectrometer. Triplicate spectra per sample collected on different areas of adhesives in film were acquired with 64 scans per spectrum at a spectral resolution of 4 cm\(^{-1}\) in the wavenumber range from 4000 to 650 cm\(^{-1}\). The results are presented below on Figure A.2.

Starch spectra exhibited identical bands in both unaged and aged samples. The main characteristic bands were identified as: \(\nu\)O-H (stretching; 3600-3200 cm\(^{-1}\)), \(\nu\)C-H (3000-2900 cm\(^{-1}\)), \(\delta\)O-H (bending; 1650 cm\(^{-1}\)), \(\delta\)C-H (1480-1300 cm\(^{-1}\)), \(\nu\)C-O, C-C and C-O-H (1150-1100 cm\(^{-1}\)) and \(\delta\)C-O-H (1100-900 cm\(^{-1}\)) [3,4].

UA spectra contained the characteristic bands of acrylic polymers: \(\nu\)C-H (2981 and 2950 cm\(^{-1}\)), \(\nu\)C=O (1722 cm\(^{-1}\)), \(\nu\)C-O (1232 and 1023 cm\(^{-1}\)) and \(\delta\)C-H (1444, 1385 and 1139 cm \(-1\)) [5]. This is in accordance with the data obtained by DSC analysis presented above, which suggests that the adhesive is a copolymer of ethyl methacrylate and methyl acrylate, P(EMA/MA). The four FTIR spectra of UA show the same characteristic bands, except for the yellow zones 1 and 2 (blue and green) that present a 792 cm\(^{-1}\) band, associated with the C-H rocking (deformation of the CH\(_2\) group). The fact that three different spectra were obtained after artificial ageing suggests that the degradation mechanism of UA is complex. Further research needs to be done to clarify these mechanisms.
CMC characteristic bands were similar in both unaged and aged samples: νO-H (3600-3000 cm⁻¹), νasC-H (2922 cm⁻¹), νCOO- (νs at 1584 cm⁻¹ and νas at 1414 cm⁻¹), δO-H (1323 cm⁻¹), νCH₂O-CH (1052 cm⁻¹) [8–10].

HPC characteristic bands were observed at: νO-H (3600-3200 cm⁻¹), νCH₃ (2972 cm⁻¹), νC-O (1646 cm⁻¹, 1075 cm⁻¹ and ring stretching at 942 cm⁻¹), νC-H (1458 and 1369 cm⁻¹), νC-O-C (1110 cm⁻¹) and symmetric in-plane deformation of the C-H (843 cm⁻¹) [11–15]. After ageing, the obtained HPC spectrum was similar, showing only a slight increase in the intensity in the 3600-3000 cm⁻¹ band.

MC presented the same characteristic bands after ageing although with different intensities: νO-H (3400-3200 cm⁻¹), νC-H (2903 cm⁻¹, νas at 2933 cm⁻¹ and νs at 2838 cm⁻¹), νC-O (1640 cm⁻¹), νC-H (1458 and 1375 cm⁻¹), νC-O-C (1099 and 1052 cm⁻¹) and C-O ring stretching (948 and 895 cm⁻¹) [12–14,16,17]. There was a general decrease in intensity with the exceptions: the band at 1052 cm⁻¹ remained the same; the bands and 3400-3200 cm⁻¹ and 1644 cm⁻¹ had a slight increase.
FTIR contributed to the clarification of UA polymeric composition and revealed molecular alterations in this adhesive after artificial ageing. For the remaining adhesives, no molecular alterations were observed after ageing, within the limits of detection of this technique.

### III. Capillary viscometry (Intrinsic viscosity)

To estimate the viscosity average molecular weight ($M_v$) of the adhesives, their intrinsic viscosity ($[\eta]$) was determined using capillary viscosity and then applying the Mark-Houwink-Sakurada (M-H-S) equation (Eq. (A.1)).

$$[\eta] = k M_v^a$$  \hspace{1cm} (A.1)

Where $k$ and $a$ are constants for a particular polymer-solvent system at a set temperature.

Each adhesive was dissolved in the respective solvent at a 0.001 g/mol concentration (initial solution) under constant stirring for a minimum of 12h. During the experiment, 5 dilutions were analyzed, by consecutively adding 1 ml of solvent to the initial solution, placed in the reservoir of the Übbelohde 1C viscometer. All measurements were carried out with the viscometer immersed in a water bath, with controlled temperature (Nahita blue, Model 692/1, digital magnetic stirrer).

The average flow time of the solvents, initial solutions and respective dilutions was measured, until a minimum of 6 measurements with a maximum interval of 0.1s were obtained. The intrinsic viscosity ($[\eta]$ (dL/g)) was calculated using the average times obtained and using the Huggins equation (Eq. A.2):

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$  \hspace{1cm} (A.2)

where $c$ is the polymer concentration (g/dL) and $\eta_{sp}$ is the specific viscosity calculated by Eq. A.3. In Eq. A.3 $\bar{t}_0$ is the average run time of the pure solvent and $\bar{t}$ the average run time of the solution:

$$\eta_{sp} = (\bar{t} - \bar{t}_0) / \bar{t}_0$$  \hspace{1cm} (A.3)

$M_v$ was calculated using the M-H-S equation, with the parameters $k$ and $a$ for each adhesive obtained from the literature (table A.1). Since there were no specific constants for starch paste and UA, values of similar compounds, namely amylose and Poly (ethyl methacrylate) (P(EMA)) were used, respectively. Finally, the molecular weight of the monomer ($M_o$) and the number-average degree of polymerization (DP) were calculated with Eq. (A.4):

$$DP = \frac{M_v}{M_o}$$  \hspace{1cm} (A.4)

Table A. 1 - Adhesives and associated M-H-S parameters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>T (ºC) ± 1ºC</th>
<th>M.H.S. Constants k (dL/g)</th>
<th>a</th>
<th>Method (1)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amylose (starch)</td>
<td>Aq. KOH (0.5M)</td>
<td>25</td>
<td>0.0000855</td>
<td>0.76</td>
<td>LS (2)</td>
<td>[18]</td>
</tr>
<tr>
<td>P(EMA) (UA)</td>
<td>Ethyl acetate/etanol</td>
<td>35</td>
<td>0.000476</td>
<td>0.53</td>
<td>LS</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>(2/9, v/v)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMC</td>
<td>Aq. NaCl (0.1M)</td>
<td>25</td>
<td>0.000123</td>
<td>0.91</td>
<td>SD (3)</td>
<td>[18]</td>
</tr>
<tr>
<td>HPC</td>
<td>Millipore® water</td>
<td>25</td>
<td>0.0000625</td>
<td>0.84</td>
<td>-</td>
<td>[19]</td>
</tr>
<tr>
<td>MC</td>
<td>Millipore® water</td>
<td>25</td>
<td>0.003166</td>
<td>0.55</td>
<td>LS</td>
<td>[18]</td>
</tr>
</tbody>
</table>

(1) Method used for determination of the absolute molecular weights; (2) Light-Scattering; (3) Sedimentation and diffusion.
IV. Water absorption

The water absorption protocol was adapted from ASTM D280-01 [20]. 0.1g of each adhesive were weighed in weighing bottles (60x40mm, Linex), in triplicate. To determine the initial weight (dry weight), the samples were dried under vacuum (15 ± 5 mbar) for 24 hours. Subsequently, the weight was measured after 24 hours in a desiccator stabilized at 50 ± 5% RH (using a saturated solution of calcium nitrate) and after 24 hours in a desiccator stabilized at 90 ± 5% RH (using a container with distilled water). At all stages, the weighing bottles containing the samples were kept with the lid open inside the desiccators and closed for weighing. The water absorption capability (WAC) was calculated with the equation below (Eq. A.5) based on [21]:

\[
WAC \% = \frac{W\text{\_final} - W\text{\_initial}}{W\text{\_initial}} \times 100
\]  

(A.5)

V. Colourimetry

Colour measurements were carried on samples of adhesives applied on paper (paper with no adhesive was used as control), using a hand-held colourimeter Data Color International® with a D65 Standard Illumination and 10° Standard Observer, according to the Commission Internationale de l’Eclairage (CIE) colourimetry system. The system CIE L*a*b* is defined by the coordinates: L* represents the luminosity, which varies from black (L* = 0) to white (L* = 100); a* is the colour range from red (a* > 0) to green (a* < 0); and b*, is the colour range from yellow (b* > 0) to blue (b* < 0). The variation in the coordinates L*, a* and b* (represented by ∆L*, ∆a* and ∆b*) allowed to calculate the total colour variation (∆E*) (Eq. A.6) [22,23]:

\[
\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\]  

(A.6)

Samples were measured in triplicate at three different points on top of Whatman® paper, using a transparent polyester film template (Melinex®) to guarantee the positioning of the colourimeter in the same points of the samples.

VI. Determination of pH (cold extraction method)

pH measurement of the adhesives applied on paper was performed using the cold extraction method, according to TAPPI 509 [24]. The pH of the paper itself (no adhesive) was used as control. Three replicates were prepared for each adhesive/paper. 36 samples (18 unaged and 18 aged) were prepared, left for one hour in the pH measurement room and then measured with a glass electrode (Docu-pH Meter, Sartorius).

VII. References


