Journal of Cultural Heritage xxx (2017) xxx–xxx

Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Original article

Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity

Inês da Silva Borges[a], Maria Helena Casimiro[b], Maria Filomena Macedo[a,c], Sílvia Oliveira Sequeira[a,c,*]

[a] Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal
[b] Centro de Ciências e Tecnologias Nucleares (C²TN), Instituto Superior Técnico, Universidade de Lisboa, EN 10 (km 139.7), 2695-066 Bobadela, LRS, Portugal
[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

ARTICLE INFO

Article history:
Received 9 November 2017
Accepted 30 March 2018
Available online xxx

Keywords:
Paper conservation
Adhesive
Bioreceptivity
Fungi
Artificial ageing

ABSTRACT

In paper conservation practice, adhesives are used for several purposes, such as mending tears and gaps, or paper consolidation. The criteria to choose one or another adhesive should be based on the knowledge of the properties and stability of those adhesives. However, the several different adhesives available on the market still lack enough information to help the process of a rational decision-making. In the present work, five adhesives currently used in the paper conservation field (starch paste, unsupported *Archibond*™, carboxymethylcellulose, hydroxypropylcellulose and methylcellulose) were analyzed for their chemical stability and fungal bioreceptivity (the ability of a material to be colonized by fungi). Bioreceptivity of products used in conservation and restoration is a still poorly explored subject, despite its great relevance for the preservation of objects.

The chemical and physical properties of the adhesives, before and after moist heat artificial ageing, were analyzed by thermogravimetry, capillary viscometry, measurement of water absorption capacity, colourimetry, and pH measurement.

Fungal bioreceptivity of the adhesives was tested on two different substrates (paper and glass) against three fungal species: *Aspergillus niger, Aureobasidium pullulans* and *Penicillium pinophilum*. Along 56 days of incubation, the colonization area on the adhesives was measured through digital photo analysis.

Starch paste was the most bioreceptive adhesive, but on other hand was also the most stable adhesive to artificial ageing, regarding colour alteration, degree of polymerization and pH. Carboxymethylcellulose and *Archibond*™ showed chemical deterioration with ageing. Nevertheless, these two adhesives presented only scarce bioreceptivity to the tested fungi. Methylcellulose and hydroxypropylcellulose showed the best relationship between higher chemical stability with artificial ageing and lower fungal bioreceptivity.

1. Introduction

In paper conservation practice, documents and works of art often require the application of external materials, including adhesives, to arrest current damaging processes or reinforce their structure. Adhesives, which are substances capable of maintaining two materials joined by interfacial forces [1], are used in paper conservation for various purposes, such as repair of tears and gaps, consolidation, fixation of soluble inks, sizing, or lamination. In order to be used in cultural heritage conservation, adhesives need specific qualities, such as a compatible pH; chemical inertia with the substrate; a long period of use; colour stability over time; reversibility; and low bioreceptivity [1,2].

One of the most important and less studied characteristics of adhesives is their bioreceptivity – the ability of a material to be colonized by one or more living organisms. Bioreceptivity can be divided into three types: primary bioreceptivity (initial potential of a material to be colonized by living organisms); secondary bioreceptivity (when the material has already undergone processes of

* Corresponding author at: Departamento de Conservação e Restauro Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Campus Caparica, 2829-516 Caparica, Portugal.
E-mail address: sos11865@campus.fct.unl.pt (S.O. Sequeira).

https://doi.org/10.1016/j.culher.2018.03.027
1296-2074/

natural degradation and/or colonization); and tertiary bioreceptivity (when the material has been altered by human practices) [3]. Within microorganisms, filamentous microfungi are considered the main cause of deterioration of paper based cultural heritage [4,5]. Many fungal species can develop on paper under average temperature (20 °C) and relative humidity (RH) conditions (above 65%), causing changes in the paper's physical/chemical structure, and affecting its visual appearance and cultural value [4].

A number of studies have been dedicated to studying the properties of paper conservation adhesives, such as pH, colour, solubility, or reversibility [1,6–9]. However, the adhesives are usually studied in small groups with similar characteristics between them, like cellulose ethers or heat-set adhesives [7,9,10], and using different methodologies [7,9,11], which hinders comparisons between two distinct adhesive types.

The bioreceptivity of adhesives is rarely evaluated or mentioned. On the few investigations that have examined this property [12–14], the available information is not always comparable (adhesives in solution *vs* applied on paper) or coherent among them.

The primary goal of the present study was therefore to provide a consistent comparison between the most common adhesives currently used in paper conservation practice, regarding their chemical stability and fungal bioreceptivity. In order to do so, starch paste, unsupported *Archibond*®, carboxymethylcellulose, hydroxypropylcellulose and methylcellulose were analyzed by thermogravimetry, capillary viscometry, measurement of water absorption capacity, colourimetry, and pH measurement, before and after moist heat artificial ageing. Also, their primary fungal bioreceptivity was evaluated against three fungal species.

1.1. Research aim

This study addresses a major problem for paper conservators: the selection of the most appropriate adhesive to be used in a given paper conservation/restoration work. By providing a comparative study of the chemical properties, ageing stability and fungal bioreceptivity between five of the most common adhesives used in paper conservation practice, this work aims to contribute to a more informed and conscious choice of the adhesive type to be used in a paper conservation and restoration intervention.

2. Materials and methods

2.1. Adhesives selection

Five adhesives, encompassing natural (starch), semi-synthetic (cellulose derivatives) and synthetic (acrylic) polymers were selected, considering their high usage frequency by conservators worldwide [15]. Starch paste, the most used adhesive in paper conservation [15] is a natural polymer composed of two types of molecules: amylose (linear glucose chains) and amylopectin (ramified glucose chains) [1]. Carboxymethylcellulose (CMC) is produced by the reaction of alkali cellulose and chloroacetic acid (Cl–CH_2–COOH) [9]. This adhesive allows viscous solutions at low concentrations and unlike other cellulose derivatives, contains sodium in its composition. Hydroxypropylcellulose (HPC), resulting from the reaction of alkali cellulose with propylene oxide [9], can either be dissolved in water or ethanol, being a very useful option for non-aqueous treatments. Methylcellulose (MC), produced by the reaction of alkali cellulose and methyl chloride (CH_3Cl) [9], is the second most used adhesive in paper conservation [15] and is usually prepared in aqueous solutions. *Archibond*®, an acrylic adhesive (PMA and PEMA copolymer, according to our analyses provided as Supplementary Data (Section I-B and II, Appendix A), is one of the most common heat set adhesives used on solvent sensible objects [14]. Most heat set adhesives are sold impregnated on paper tissue, however, to eliminate the paper tissue variable, which was not included in the other adhesives being studied, an unsupported *Archibond*® (UA) version was used instead.

2.2. Substrates

Whatman #1 paper was chosen as the paper substrate due to its high cellulose content (98%, w/w), and absence of additives, to simulate the application of adhesives on site without adding more variables. To evaluate the bioreceptivity without the influence of paper, the adhesives were also applied in glass Petri dishes (150 mm × 25 mm, Normax), three samples per dish.

2.2.1. Application of adhesives on substrates

The adhesives' solutions were prepared in distilled water, except HPC, prepared in ethanol, and UA, which did not require preparation. Starch paste (Starch from wheat, unmodified, Sigma-Aldrich), was prepared at a 10% (w/v) concentration [16]. Dried starch was pre-soaked in distilled water for 30 min and cooked under constant stirring in a double boiler. After being cooled to room temperature, the paste was sieved through a plastic mesh four times until a creamy texture was obtained. All cellulose ethers were prepared at a 4% (w/v) concentration, according to the manufacturers and the literature [6,2]. CMC powder (Blanose™ GS 7H4F, Ashland), was progressively added to hot distilled water under constant stirring. HPC powder (Klucel G, Arte & Memoria) was added to absolute ethanol and stirred until total dissolution was obtained. MC powder (Culminal™ MC 2000S, Ashland) was added to heated distilled water (half of the total volume) under constant stirring. After dissolution, water at room temperature (the other half of the total volume) was added to the mixture.

The weight of UA film samples (75 mm Ø for paper and 55 mm Ø for glass) was taken as a reference for the dry weight of the remaining adhesives, to guarantee a similar quantity of adhesive on every sample. Starch and cellulose ethers were applied and evenly spread on silicone coated polyester film circles (75 mm Ø) with a plastic spatula. Each paper substrate (75 mm Ø) was placed over the respective adhesive and air dried. After drying, the polyester film was easily detached, leaving a film of adhesive on the paper. In glass Petri dishes, the adhesives were evenly spread with a plastic spatula in circular areas (55 mm Ø) and left to dry inside a vertical laminar flow cabinet to prevent dust deposition. For the application of unsupported *Archibond*™ (Arte & Memoria) on paper and glass substrates, a hot spatula (80 ± 5 °C) was used to activate the adhesive.

2.3. Artificial ageing

Moist heat artificial ageing was performed at 80 °C and 65% RH (ISO 5630/3:1986) [17] for 504 h in a FITOCLIMA 150 EDTU, Cimaplus IV climate chamber. Artificial ageing tests do not allow a direct correspondence with natural degradation processes [17] only allowing a relative comparison between samples.

2.4. Adhesives characterization

Samples were analyzed by capillary viscometry, water absorption measurement, colourimetry, pH measurement and thermogravimetry (TGA). Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was also performed to analyze the composition of the studied adhesive formulations and evaluate the changes occurred after artificial ageing. Unsupported

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027

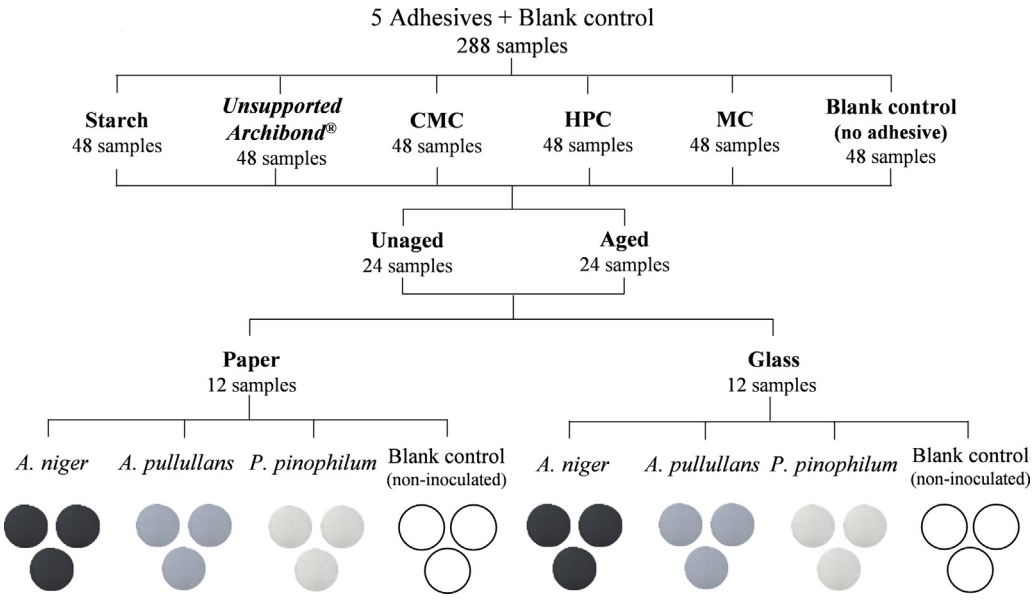

Fig. 1. Experimental design of the fungal bioreceptivity assay.

Archibond™ was analyzed by Differential Scanning Calorimetry (DSC) as a complementary technique to identify its composition (polymer blend or copolymer. The methods used for all the analyses and the results obtained with DSC and ATR-FTIR are presented as Supplementary Data, in Appendix A. The adhesives were studied in solution (capillary viscometry), film (ATR-FTIR, water absorption capacity, TGA, DSC), and applied on paper (colourimetry, pH, bioreceptivity) or glass substrates (bioreceptivity).

2.5. Fungal bioreceptivity test

Three fungal species, *Aspergillus niger, Aureobasidium pullulans* and *Penicillium pinophilum*, known to colonize natural and synthetic polymers were selected according to standards ASTM G21-96 and ASTM D4300-01 [18,19], which are used to assess the capacity of film adhesives and synthetic polymers to support or resist fungal growth. *A. niger* was obtained from National Institute of Health Doutor Ricardo Jorge, IP (Lisbon, Portugal). The remaining strains were obtained from the mycological collection of Universidade do Minho (Braga, Portugal).

2.5.1. Sterilization of samples

Adhesive samples applied on paper substrates were individually wrapped in aluminium foil and autoclaved (120 °C for 20 min). After sterilization and inside a vertical laminar flow chamber, each sample was placed in an individual polystyrene petri dish (90 mm × 14 mm, Deltalab) using sterile tweezers. Glass Petri dishes with applied adhesives were closed, wrapped in aluminium foil and autoclaved under the same conditions.

2.5.2. Inoculation and incubation

A. niger was cultured in Potato Dextrose Agar (PDA) and the remaining two species in Malt Extract Agar (MEA) at 25 °C for 7–20 days. Different culture media and incubation times were used to stimulate conidia formation. Spores were harvested in sterile 0.05% Tween80 (Panreac), and the inoculum prepared at a 1×10^6 spores/ml concentration, using a haemocytometer. Sterilized samples were inoculated with a 10 μl drop of the inoculum placed at the centre of each sample. Each species was applied individually. Non-inoculated samples were used as controls. The experimental design is presented in Fig. 1. The samples in the respective Petri dishes were incubated inside an acrylic box with distilled water in the bottom (RH ≈ 100%, $T \approx 22$ °C), for 56 days.

2.5.3. Evaluation of fungal growth

To evaluate fungal growth, the samples were analyzed under a stereomicroscope (Leica MZ16) and recorded with a digital camera (Leica ICD). Colonization areas were calculated with ImageJ 1.51j8

Table 1
Rating system of fungal growth.

Observed growth on samples	Colonized area (%)	Rating
None	0	0
Traces of growth within the inoculum stain	≤2	1
Traces of growth	2-10	2
Light growth	10-30	3
Medium growth	30-60	4
Heavy growth	60-100	5

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027

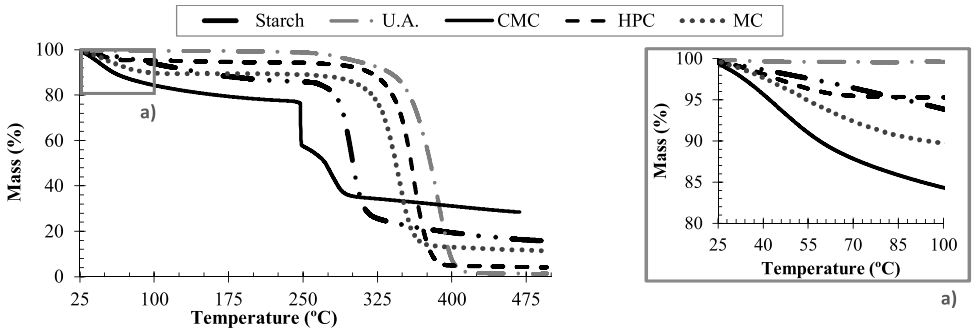

Fig. 2. TGA curves of the adhesives.

software (National Institutes of Health, Bethesda, Maryland, USA) [20]. The colonization rating system used is based on the literature [18] and presented in Table 1.

3. Results and discussion

3.1. Evaluation of chemical stability with ageing

3.1.1. Thermogravimetric analysis

To ensure whether the adhesives would not undergo structural changes during test and sterilization conditions, thermogravimetric analyses (TGA) were conducted. TGA, a tool to investigate materials' thermal stability, shows variations of mass as a function of temperature. According to TGA curves displayed in Fig. 2, up to 100 °C all adhesives, except for UA, present a slight decrease in mass. This decrease is most likely related to the loss of water which would still be present in the film. This is in accordance with the results obtained by water absorption measurement (see Section 3.1.3). At 80 °C (temperature used for artificial ageing) the adhesives with the greatest mass loss were: CMC > MC > HPC and Starch > UA, which corresponds to the order of adhesives with higher affinity for water absorption.

TGA curves also show that, with exception of CMC, all studied adhesives had a one-step thermal degradation pattern. All samples showed a significant mass loss for higher temperature values, and at 400 °C one can observe mass loss of HPC > MC > CMC and UA > Starch. Therefore, higher values of weight loss indicate the existence of a chemical degradation process resulting from degradation of side chain and from bond scission (carbon–carbon bonds) in the polymeric backbone. However, despite not being the most stable adhesive, CMC is the one that shows the highest mass residue due to the presence of Na^+ in its unit structure.

3.1.2. Capillary viscometry

Intrinsic viscosity ([η]) decreased after artificial ageing for all adhesives, except for starch (Table 2). Some insoluble particles were observed in the aged starch solution, indicating that part of the adhesive has crosslinked. Also, the increase of viscosity-average molecular weight (M_v) and degree of polymerization (DP) in aged starch suggests this adhesive did not undergo chain scission with ageing, but instead its polymeric chains may have formed new branches.

Whilst unaged UA required at least 48 h under constant stirring for a complete dissolution in the selected solvent, it was not possible to completely dissolve aged UA. Particles of UA remained in suspension, indicating that cross-linking has occurred on the polymer. Due to the presence of those particles, it was not possible to know the exact concentration of the solution, which would be lower than the one used in the calculations. This associated error is reflected in the low correlation observed in the UA linear regressions (Table 2). The [η], M_v and DP decrease indicates the ocurrence of chain scission on the polymer.

CMC showed the greatest [η] decrease after ageing and the highest depolymerization (ΔDP). Unaged CMC adhesive was transparent and colourless, but after ageing it became yellow, with thicker and more rigid zones that did not completely dissolve in the solvent, indicating the formation of cross-linking in the polymer. The observed [η], M_v and DP decrease also indicates the occurrence of chain scission.

HPC and MC had a slight [η], M_v and DP decrease after ageing, which illustrates minor chain scission on these polymers.

3.1.3. Water absorption capacity (WAC)

Fig. 3 shows the hygroscopic behaviour of the adhesives' films at RH levels generally found in museums and archives (50% RH) and at high humidity levels (90% RH).

Table 2
Capillary viscosimetry results.

Adhesive		M_o (g/mol)	Linear regression equation	R^2	t (s)	[η] (dL/g)	M_v (kg/mol)	DP	ΔDP (%)
Starch	Unaged	180	$y = 8.643x + 0.517$	0.943	20.74	0.52	95,240	529	+23%
	Aged		$y = 6.880x + 0.606$	0.993	20.44	0.61	117,438	652	
UA	Unaged	114	$y = -4.814x + 0.881$	0.563	18.62	0.88	1,461,036	12,816	−27%
	Aged		$y = -4.707x + 0.743$	0.488	18.46	0.74	1,058,515	9285	
CMC	Unaged	540	$y = 91.053x + 12.404$	0.955	57.63	12.40	315,155	584	−84%
	Aged		$y = 15.656x + 2.2468$	0.979	25.16	2.25	48,211	89	
HPC	Unaged	618	$y = 17.834x + 2.1005$	0.986	25.77	2.10	244,693	396	−33%
	Aged		$y = 22.165x + 1.4929$	0.999	25.44	1.49	162,961	264	
MC	Unaged	190	$y = 28.207x + 3.9931$	0.998	30.43	3.99	435,828	2294	−48%
	Aged		$y = 29.445x + 2.7652$	0.971	28.01	2.77	223,441	1176	

M_0: Molecular weight of the monomer; t(s): Flow time of the initial solution; [η] = Intrinsic viscosity; M_v = viscosity-average molecular weight; DP: degree of polymerization; ΔDP: Depolymerization occurred with artificial ageing.

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027

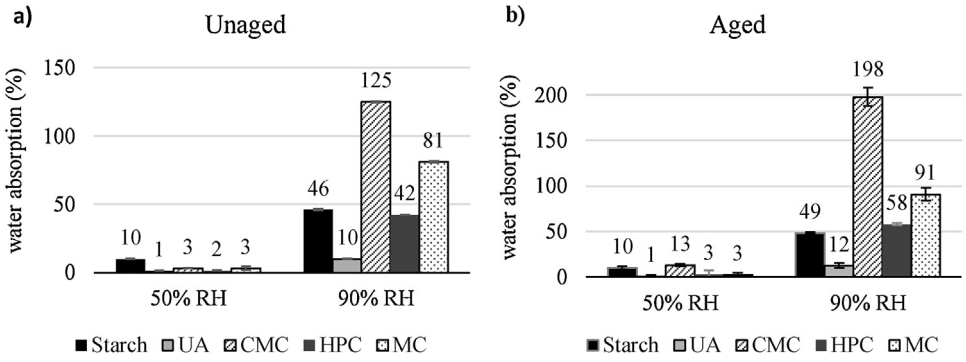

Fig. 3. Water absorption (%) of unaged (a) and aged (b) adhesives.

At 50% RH, starch is the most absorbent adhesive regarding unaged samples, showing values in accordance with the literature (10–17%) [21]. However, at 90% RH, the cellulose ethers significantly increase their WAC, with CMC and MC largely surpassing starch. The water absorption of cellulose ethers is dependent on the hydrogen bonds that are established between the hydrogen atoms in the water and the available oxygen atoms in their chemical structure, therefore MC has a higher absorption than HPC [9]. The considerably high WAC observed in CMC, which was able to absorb two times its initial weight in water on aged samples (Fig. 3), is largely due to this adhesive's ionic character [9]. UA, as an acrylic polymer, has shown to be poorly hygroscopic, with its WAC not exceeding 12% in aged samples at 90% RH.

When comparing unaged and aged samples, an increase in WAC with ageing is observed for all adhesives at 90% RH. At 50% RH, there are no significant alterations with ageing, except for CMC, which becomes the most absorbent adhesive, exceeding starch.

The information regarding the WAC of adhesives is of importance to the conservator. A highly moisture-holding adhesive may be used as a poultice and has a higher working time. Nevertheless, such type of adhesives, after being applied on paper can become tacky at high RH, and may increase the fading rate of organic pigments [9].

3.1.4. pH measurement

Adhesives used in paper conservation treatments should have a pH compatible with the substrate and not cause its acidification along time. In this work, the pH of the adhesives was measured while applied on paper to evaluate their reaction with the substrate, before and after artificial ageing.

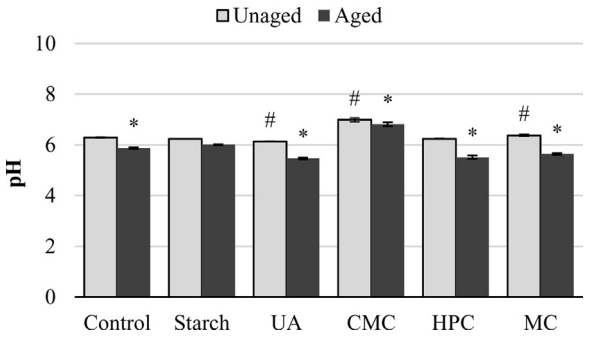

Fig. 4. pH of adhesive samples applied on paper substrates. Control stands for paper without adhesive. Unaged adhesives statistically different ($P < 0.05$) from unaged control samples are marked with "#". Aged adhesives statistically different ($P < 0.05$) from aged control samples are marked with "*".

Unaged adhesives applied on paper showed a close to neutral pH (pH = 6–7) (Fig. 4). CMC exhibited the highest pH probably due to the presence of Na^+ ions [9]. After ageing, all adhesives suffered a pH decrease, and except starch, have lower pH values than paper without adhesive (controls). This indicates there will be a slight acidification of the documents on which these adhesives are applied to, in the long term. Aged UA had the lowest pH, below pH = 5.5, followed by HPC and MC, with pH lower than 6, values close to those found in the literature [10,22].

3.1.5. Colourimetry

Colourimetric coordinates (L^*, a^*, b^*) of the unaged paper substrate without adhesive were used as a reference for colour measurements. The differences between the reference and the adhesives applied on paper are presented in Table 3.

On unaged samples, the colour differences between starch or CMC samples and control paper are not detectable ($\Delta E < 1$) [23]. The colour alteration on paper caused by the application of UA, HPC and MC is minor, being only discernible by an experienced observer ($1 < \Delta E < 2$) [23].

After ageing, the colour of starch samples was still not distinguishable from reference samples ($\Delta E < 1$). Smith et al. (1989) agree that starch does not undergo any colour change after ageing if it is of good quality [6]. HPC and MC maintained the minor colour variation ($1 < \Delta E < 2$) after ageing, which indicates a good colour stability on the long term.

UA samples, on the other hand, having a $2 < \Delta E < 3.5$, already showed a discernible colour difference after ageing, which is mainly manifested by yellowing ($+\Delta b^*$). These results are in agreement with a previous study [8].

CMC suffered a high discoloration after ageing ($\Delta E > 10$). From $\Delta E > 5$ two different colours can already be distinguished [23]. This alteration is mainly a result of darkening ($-\Delta L^*$) and yellowing ($+\Delta b^*$). Adhesives to be applied to cultural heritage should have colour stability over time, which was clearly not observed for CMC.

Cellulose ethers have previously shown to only scarcely yellow after artificial ageing [9]. The obtained intense CMC discoloration could not be compared with previous studies [6,7,9,12], since none of them used the CIE $L^*a^*b^*$ system, and different CMC brands with different degrees of substitution and viscosity were analyzed. Nevertheless, Feller and Wilt (1990) observed that different CMC samples discoloured in decreasing order of degree of substitution, and Strnadová (1994) [12] concluded that CMC had the highest loss of whiteness (%) when compared with HPC and MC.

3.2. Evaluation of fungal bioreceptivity

The evaluation of fungal bioreceptivity of the adhesives applied on paper pretended to test/simulate a real situation of application

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027

Table 3
L^*, a^*, b^* coordinates (average ± S.D) of control samples (paper substrate) and calculated differences obtained on the adhesives applied on paper. Colour differences discernible by an unexperienced observer ($\Delta E > 2$) are underlined.

		L^*	a^*	b^*	
Paper substrate	Unaged	94.17 ± 0.02	−0.45 ± 0.03	1.32 ± 0.07	
		ΔL^*	Δa^*	Δb^*	ΔE
Paper substrate	Aged	0.07 ± 0.04	0.02 ± 0.02	−0.01 ± 0.06	0.09 ± 0.02
Starch	Unaged	−0.12 ± 0.11	−0.09 ± 0.03	−0.81 ± 0.04	0.83 ± 0.06
	Aged	−0.95 ± 0.04	0.02 ± 0.03	0.03 ± 0.05	0.95 ± 0.04
UA	Unaged	0.55 ± 0.12	−0.17 ± 0.03	−1.27 ± 0.06	1.40 ± 0.02
	Aged	−1.00 ± 0.09	0.09 ± 0.07	1.77 ± 0.07	2.03 ± 0.04
CMC	Unaged	−0.78 ± 0.11	−0.24 ± 0.15	0.15 ± 0.28	0.86 ± 0.16
	Aged	−6.70 ± 0.89	1.46 ± 0.24	9.17 ± 0.94	11.45 ± 1.28
HPC	Unaged	0.05 ± 0.01	−0.27 ± 0.03	−1.07 ± 0.04	1.10 ± 0.03
	Aged	−1.11 ± 0.19	−0.11 ± 0.03	0.91 ± 0.21	1.44 ± 0.27
MC	Unaged	−0.31 ± 0.41	−0.20 ± 0.03	−1.24 ± 0.04	1.34 ± 0.15
	Aged	−1.37 ± 0.09	−0.15 ± 0.05	0.58 ± 0.11	1.49 ± 0.12

Table 4
Rating of fungal growth on the adhesives applied on paper and glass: 0 (none); 1 (traces of growth within the inoculum stain); 2 (traces of growth); 3 (light growth); 4 (medium growth); 5 (heavy growth).

		Paper						Glass					
	days	Paper substrate	Starch	UA	CMC	HPC	MC	Glass substrate	Starch	UA	CMC	HPC	MC
A. niger	0	0	0	0	0	0	0	0	0	0	0	0	0
	7	0	1	0	0	0	1	0	1	0	0	0	0
	14	0	1	0	0	0	1	0	1	0	0	0	0
	28	2	3	0	0	1	2	0	3	0	0	0	0
	56	2	5	0	1	2	3	0	5	0	0	0	0
	days	Paper substrate	Starch	UA	CMC	HPC	MC	Glass substrate	Starch	UA	CMC	HPC	MC
A. pullulans	0	0	0	0	0	0	0	0	0	0	0	0	0
	7	0	0	0	0	0	0	0	1	0	0	0	0
	14	0	0	0	0	0	1	0	1	0	0	0	0
	28	0	0	0	0	1	1	0	2	0	0	0	0
	56	1	3	1	1	2	1	0	4	0	0	0	0
	days	Paper substrate	Starch	UA	CMC	HPC	MC	Glass substrate	Starch	UA	CMC	HPC	MC
P. pinophilum	0	0	0	0	0	0	0	0	0	0	0	0	0
	7	0	0	0	0	0	0	0	2	0	0	0	0
	14	0	1	0	0	0	0	0	2	0	0	0	0
	21	0	1	0	0	0	0	0	2	0	0	0	0
	56	0	2	0	1	0	0	0	4	0	0	0	0

in documents. The glass substrate allowed for a bioreceptivity evaluation without the influence of a paper support.

Starch showed the highest fungal bioreceptivity, considering all three fungal species tested, surpassing the colonization observed in control paper samples (without adhesive) (Table 4). It was also the only adhesive exhibiting colonization by the three tested fungi on the glass substrate. These results indicate starch may increase the bioreceptivity of the papers where it is applied to.

UA revealed the lowest fungal bioreceptivity. This acrylic adhesive even inhibited *A. niger* growth on paper, probably due to its lower water absorption, unfavourable to fungal growth.

Although all cellulose ethers have a cellulosic structure as a base, differences in their chemical arrangement may turn them more or less accessible to the degrading cellulases excreted by fungi, and therefore more or less bioreceptive. MC showed fungal growth traces earlier than control paper samples for *A. niger* and *A. pullulans*, and was, therefore, the most bioreceptive cellulose ether. HPC was only slightly more bioreceptive than control paper samples regarding one fungal species, *A. pullulans.* CMC was the least bioreceptive cellulose ether to *A. niger* and *A. pullulans*, even though, it was the only one showing, although only minor, colonization by *P. pinophilum*. Although the most hygroscopic adhesive by far, as shown in Section 3.1.3, CMC was not the most bioreceptive cellulose ether. Its unique ionic character probably influences its biodegradation susceptibility.

Summarizing, the fungal bioreceptivity of the adhesives followed the decreasing order: Starch ≫ MC > HPC > CMC > UA.

Fungal growth on paper was faster and more intense than in glass, possibly due to the bioreceptivity of the paper itself, its hygroscopic nature and texture/thickness, which creates a larger specific area available for colonization. Whatman filter paper was used instead of writing/printing/artwork paper, which would be a better approximation to paper used in "real" paper objects. However, the composition of these papers with several additives varies enormously, which would influence the bioreceptivity results [24]. In the present work, a neutral substrate was intended, so that the adhesives' characteristics could be clearly observed.

The high fungal bioreceptivity of starch is common knowledge and has been mentioned in previous articles [6,12], but it was here systematically analyzed and simultaneously compared with

other paper conservation adhesives for the first time, to our knowledge. Fungi produce enzymes to degrade the materials and obtain the chemicals needed for their nutrition [25,26], like amylases to degrade starch [27–29]. Starch is a natural polymer, contrarily to the other adhesives studied here, and its degradation by fungi has been subject to millions of years of natural selection and evolution. Nonetheless, the majority of paper conservators still use this adhesive on paper objects already affected by fungi [30].

4. Conclusion

The current study affords an opportunity to transversely examine five of the most commonly used paper conservation adhesives, including natural, semi-synthetic and synthetic polymers, regarding their chemical properties, ageing stability and fungal bioreceptivity.

Our main goal was to provide a valuable tool for paper conservators, for a more conscious choice of an adhesive to be used in an intervention and thus contribute to the extension of the existence of our documentary memory.

Starch paste was, as expected, the most bioreceptive adhesive to the tested fungi. Nevertheless, it also showed to be the most chemically stable adhesive towards artificial ageing, with the lowest colour alteration, depolymerization and pH variation. The purity of starch should be taken into account when evaluating these results, since less pure formulation may render poorer results. Due to starch's high fungal bioreceptivity, paper objects treated with this adhesive should be preserved under conditions that are unfavourable to fungal growth (RH < 65% and $T < 20\,^{\circ}C$) and be regularly monitored. The use of starch in paper objects already contaminated/colonized by fungi is totally discouraged.

On the opposite side of the scale, CMC and UA revealed the lowest chemical stability with ageing, regarding colour (CMC; UA), degree of depolymerization (CMC) and pH (UA), but on the other hand, these two were the least bioreceptive adhesives. MC and HPC showed the best relationship between higher chemical stability with artificial ageing and lower fungal bioreceptivity. After ageing, both adhesives presented only minor colour change, depolymerization, and pH decrease. Their bioreceptivity varied with fungal species, being generally lower for HPC. As with starch, the obtained results have to be analyzed taking into account the used formulations. Formulations currently sold by retailers of conservation products were used in this study, to better approximate to a real situation. Regardless, different formulations with different purity degrees may lead to different results regarding chemical and biological stability.

Acknowledgments

This work was supported by Fundação para a Ciência e Tecnologia–Ministério da Educação, Ciencia, Tecnologia e Ensino Superior (FCT-MCTES), through the projects PTDC/EPHPAT/0224/2014 (UNL); UID/EAT/00729/2013 (UNL); and UID/Multi/04349/2013 (C2TN/IST). The authors would like to acknowledge the following researchers/entities for making available the respective techniques and instruments and for all the support in using them: Dr Miguel Silva and Dr J. L. Ferreira for the FTIR analysis; Professor Ana Ramos for the viscometry; and Laboratório José de Figueiredo, Direcção-Geral do Património Cultural, Portugal, with the accelerated degradation climate chamber. We also thank Arte & Memoria (Barcelona, Spain) for offering part of the adhesives used in this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.culher.2018.03.027.

References

[1] V. Horie, Materials for Conservation: Organic Consolidants, Adhesives and Coatings, second ed., Elsevier Ltd, 2010.
[2] S. Zervos, I. Alexopoulou, Paper conservation methods: a literature review, Cellulose 22 (2015) 2859–2897, http://dx.doi.org/10.1007/s10570-015-0699-7.
[3] O. Guillitte, Bioreceptivity: a new concept for building ecology studies, Sci. Total Environ. 167 (1995) 215–220, http://dx.doi.org/10.1016/0048-9697(95)04582-L.
[4] F. Pinzari, G. Pasquariello, A. De Mico, Biodeterioration of paper: a SEM study of fungal spoilage reproduced under controlled conditions, Macromol. Symp. 238 (2006) 57–66, http://dx.doi.org/10.1002/masy.200650609.
[5] A. Sandak, A. Jaszczur, J. Sandak, I. Modzelewska, Near infrared assessment of biodegradability and mechanical properties of paper made of cellulose sulfate bleached coniferous pulp with addition of cationic starch and resinous adhesive, Int. Biodeterior. Biodegrad. 97 (2014) 31–39, http://dx.doi.org/10.1016/j.ibiod.2014.09.019.
[6] C. Smith, S. Bertalan, A. Dwan, J. English, C. Nicholson, S.R. Albro, K. Schenck, L. Stiber, S. Wagner, 46. Adhesives, B. Pap. Conserv. Cat, 1989, pp. 128.
[7] C.A. Baker, Ethylcellulose and sodium carboxymethylcellulose: an evaluation for use in paper conservation through accelerated aging, in: Adhes. Consolidants Prepr. Contrib. to Paris Congr. 2–8 Sept. 1984, 1984, pp. 55–59, http://dx.doi.org/10.1179/sic.1984.29.Supplement-1.55.
[8] C. Gonçalves, A.M. Ramos, C. Casanova, L.M. Alberto, Study on the application of heat set adhesives in conservation of tracing paper, in: J. Bridgland (Ed.), ICOM-CC Lisbon 2011 Sixt. Trienn. Conf., International Council of Museums – Committee for Conservation, Lisbon, 2011, CD-ROM.
[9] R. Feller, M. Wilt, Evaluation of Cellulose Ethers for Conservation, The Getty Conservation Institute, 1990, Second pri.
[10] A.C. Gonçalves, Estudo da Aplicação de Materiais Adesivos Termofusíveis na Conservação de Papel Vegetal, Universidade Nova de Lisboa, 2010.
[11] M. Seki, N. Sonoda, T. Morita, T. Okayama, A new technique for strengthening book papers using cellulose derivatives, Restaurator 26 (2005) 239–249, http://dx.doi.org/10.1515/REST.2005.239.
[12] J. Strnadová, M. Ďurovič, The cellulose ethers in paper conservation, Restaurator 15 (1994) 220–241, http://dx.doi.org/10.1515/rest.1994.15.4.220.
[13] J.D. Gu, Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances, Int. Biodeterior. Biodegrad. 52 (2003) 69–91, http://dx.doi.org/10.1016/S0964-8305(02)00177-4.
[14] R. Stevens, P. Garside, E. Russell, A review of current and recent practice in the use of adhesives by the conservation department at the british library, in: Adhes Consolidants Conserv. Reasearch Appl. Symp., 2011, p. 2011.
[15] I. Alexopoulou, S. Zervos, Paper conservation methods: an international survey, J. Cult. Herit. 21 (2016) 922–930, http://dx.doi.org/10.1016/j.culher.2016.04.001.
[16] C. Maitland, Microscopy for paper conservation: comparing various adhesives and examining wheat starch paste preparation methods, in: B. Pap. Gr. Annu. Vol. 29, 2010, pp. 129–138.
[17] H. Bansa, Accelerated ageing of paper: some ideas on its practical benefit, Restaurator 23 (2002) 106–117, http://dx.doi.org/10.1515/REST.2002.106.
[18] ASTM G 21-96, Standard practice for determining resistance of synthetic polymeric materials to fungi, in: ASTM Int. (2013)., 2002, http://www.astm.org/cgi-bin/resolver.cgi?G21.
[19] ASTM D 4300-01, Standard test methods for ability of adhesive films to support or resist the growth of fungi, Cultures 57 (2001) (2013) 1–10, http://dx.doi.org/10.1520/D4300.
[20] C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH image to ImageJ: 25 years of image analysis, Nat. Methods 9 (2012) 671–675, http://dx.doi.org/10.1038/nmeth.2089.
[21] H. Musa, A. Gambo, P.G. Bhatia, Studies on some physicochemical properties of native and modified starches from digitaria iburua and Zea mays, Int. J. Pharm. Pharm. Sci. 3 (2011) 28–31.
[22] J.L. Down, S. Guild, G. Hill, D. St-Jacques, K. Westbury, E.O. Loug, E. Kaminska, R.S. Williams, J. Iraci, S. Tse, Update on the CCI adhesive tape and heat-set tissues project, in: Adhes. Consolidants Conserv. Reasearch Appl. Symp., 2011, pp. 1–29, http://dx.doi.org/10.1520/D2244-05.
[23] W.S. Mokrzycki, M. Tatol, Color difference delta E – a survey, Mach. Graph. Vis. 20 (2011) 383–411.
[24] A.A. Reis-Menezes, W. Gambale, M.C. Giudice, M.A. Shirakawa, Accelerated testing of mold growth on traditional and recycled book paper, Int. Biodeterior. Biodegrad. 65 (2011) 423–428, http://www.sciencedirect.com/science/article/pii/S0964830511000102.
[25] R.I. Nielsen, K. Oxenbøll, Enzymes from fungi: their technology and uses, Mycologist 12 (1998) 69–71, http://dx.doi.org/10.1016/S0269-915X(98)80048-7.
[26] Z. Abbasi, Water resistance, weight loss and enzymatic degradation of blends starch/polyvinyl alcohol containing SiO_2 nanoparticle, J. Taiwan Inst. Chem. Eng. 43 (2012) 264–268, http://dx.doi.org/10.1016/j.jtice.2011.10.007.

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027

[27] C.L. Blaxland, Adhesives in an historic library – a conservator's view, Int. J. Adhes. Adhes. 14 (1994) 123–129, http://dx.doi.org/10.1016/0143-7496(94)90007-8.
[28] A.A. Storey, J.M. Ramirez, D. Quiroz, D.V. Burley, D.J. Addison, R. Walter, A.J. Anderson, T.L. Hunt, J.S. Athens, L. Huynen, E.A. Matisoo-Smith, Handbook of Adhesives, Springer US, Boston, MA, 1990, http://dx.doi.org/10.1007/978-1-4613-0671-9.
[29] V.H. Sunitha, A. Ramesha, J. Savitha, C. Srinivas, Amylase production by endophytic fungi *Cylindrocephalum* sp. isolated from medicinal plant *Alpinia calcarata* (Haw.) Roscoe, Braz. J. Microbiol. 43 (2012) 1213–1221, http://dx.doi.org/10.1590/S1517-83822012000300049.
[30] S.O. Sequeira, E.J. Cabrita, M.F. Macedo, Fungal biodeterioration of paper: how are paper and book conservators dealing with it? An international survey, Restaurator 35 (2014) 181–199, http://dx.doi.org/10.1515/res-2014-0005.

Please cite this article in press as: I.d.S. Borges, et al., Adhesives used in paper conservation: Chemical stability and fungal bioreceptivity, Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.027