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Lining and Consolidating Adhesives: Some New Developments and Areas of Future Research

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Abstract

This paper focuses on the light aging properties of heat-seal lining adhesives when used as solution-delivered consolidants, an investigation that is the first phase of a long-term research project. Because adhesives may yellow, discolouration related to aging is an important factor to consider when using adhesives as consolidants.

The lining adhesive BEVA 371 is sometimes used for consolidation despite the fact that its photochemical stability does not appear to have been evaluated during its initial testing. In our work, BEVA 371 and 371b, along with alternative formulations with components that have been sourced or synthesized, are in the process of being evaluated qualitatively for their activation behaviour and analytically for their photochemical stability. The alternative tackifiers being considered are urea-aldehyde and hydrogenated hydrocarbon resins. These have low molecular weight and high glass transition temperatures (T_g), and offer improved photochemical resistance compared to the ketone resins found in the two BEVAs. Alternatives for other components, such as amorphous polyolefins and low T_g resins (which affect cohesion), are also being tested. Experimental formulations have been tested in accelerated light aging experiments and are being evaluated using Fourier transform infrared spectroscopy and solvent removability tests. Finally, synthesis of an ethylene vinyl acetate (EVAc) vinyl versatate (VVe) terpolymer is shown as a way to offer improved resistance to hydrolysis over EVAc copolymers used in conservation materials.

Titre et Résumé

Adhésifs pour le rentoilage et la consolidation : nouveautés et futures avenues de recherche

Le présent article porte principalement sur les propriétés relatives au vieillissement à la lumière d'adhésifs de rentoilage thermocollants qui sont employés comme agent de consolidation appliqué en solution. L'étude constitue la première phase d'un projet de recherche à long terme. Comme les adhésifs peuvent subir un jaunissement au fil du temps, l'altération de la couleur par vieillissement est un élément dont il faut toujours tenir compte lorsque des adhésifs servent d'agent de consolidation.

L'adhésif de rentoilage BEVA 371 est parfois utilisé pour des travaux de consolidation, et ce, même si sa stabilité photochimique ne semble pas avoir fait l'objet d'évaluation lors de sa mise à l'essai initiale. Dans le cadre de nos travaux, le BEVA 371 et le BEVA 371b, de même que des formulations de substitution qui ont été acquises ou synthétisées, font présentement l'objet d'évaluations qualitatives, afin de déterminer leur comportement d'activation, et d'analyses qui

visent à établir leur stabilité photochimique. Les agents poisseux de substitution étudiés sont des résines à base d'urée-aldéhyde et d'hydrocarbure hydrogéné. Ces produits, qui ont un bas poids moléculaire et des températures de transition vitreuse (Tg) élevées, possèdent une meilleure résistance à la dégradation photochimique que les résines cétoniques présentes dans les deux adhésifs BEVA. Des essais sont aussi réalisés sur des produits de remplacement pour d'autres composants, par exemple des polyoléfines amorphes et des résines à bas Tg (qui influent sur la cohésion). Des formulations expérimentales ont été mises à l'épreuve dans le cadre d'expériences de vieillissement accéléré à la lumière et leur état final est évalué par spectroscopie infrarouge à transformée de Fourier et à l'aide d'essais d'enlèvement au moyen d'un solvant. Finalement, des données indiquent que la synthèse d'un terpolymère à base de copolymère d'acétate de vinyle et d'éthylène (EVAc) et de versatate de vinyle (Vve) constitue un moyen d'obtenir un produit ayant une résistance accrue à l'hydrolyse, par rapport aux copolymères du type EVAc présents dans les matériaux utilisés en restauration.

Introduction

This new research initiative aims at developing new adhesives and consolidants for the conservation field. Despite a number of important publications on this subject (Brommelle 1984; Down 1996; Down 2003; CESMAR7 2008; Ambers 2009; CESMAR7 2009), a need remains for the development and testing of new products. In this phase of the research we are focusing on designing a light-stable heat-seal adhesive by drawing from new materials developed after 1970 when heat-seal adhesives were first introduced to the conservation field. Our team includes museums that reflect a broad variety of fine art collections and academic institutions experienced in polymer synthesis and characterisation. We also have integrated into this research conservators to help provide feedback as the investigation proceeds. Examples of feedback include solvent recommendations, thoughts on thermal reactivation conditions, and a preliminary qualitative assessment of acceptable adhesive strength for test formulations. This feedback will help guide more thorough analytical characterisation and development of adhesives that will be the subject of future publications.

Heat-activated lining adhesives based on poly(ethylene vinyl acetate) (EVAc) copolymers were first developed for conservation applications in the early 1970s by Berger (Berger 1972a), a decade after the copolymer was first developed commercially (Domine 1977; Satas 1999, p. 399), and marketed under the trade name BEVA® 371. The three classes of compounds in BEVA are EVAc copolymers, a paraffin wax, and tackifier resins. They are distinctly different classes of compounds and our research is considering recent developments for each and will be described below. The EVAc is a semicrystalline thermoplastic copolymer, the wax is a semicrystalline mixture of long-chain hydrocarbons, and the tackifiers are amorphous low molecular weight oligomers. The tackifier resins used in BEVA 371 were Laropal® K80 (BASF), a high glass transition temperature (Tg) ketone resin, and a small quantity of low Tg tackifier resin, Cellolyn™ 21 (Eastman), a phthalate ester of hydroabietyl alcohol. To prevent excessive flow, the crystalline components remain in the solid state at the activation temperature (below the melting point temperature) and since the crystalline portions of the polymers and the wax have not melted, the system can be thought of as a dispersion as long as the crystalline phase, evident by the opaque appearance, remains intact. For activation of the solvent-cast consolidant, joints can be set by heat if the bulk of the solvent is allowed to first evaporate. The benefit of this approach is that a short time later, after the joint has cooled, the pressure can be released. When activation of the bond is accomplished by solvent evaporation, much longer times are required for the joint to set.

Light stability testing does not appear to have been part of the original evaluation process for BEVA 371, possibly because a study indicated that wax interfered with the light-induced cross-linking of EVAc copolymers (Feller 1970). Nevertheless, it was suggested as a consolidant early on (Berger 1970; Berger 1971; Berger 1972b). In a 1994 (Stoner 1994) survey of paintings conservators BEVA 371 was found to be the most commonly used lining adhesive and a 2001 questionnaire found that BEVA 371 was the most commonly used synthetic consolidant (Ackroyd 2002) despite the fact that a few years earlier aging studies indicated that it was found to yellow when exposed to light (Down 1996). In 2010, after production of Laropal K80 was discontinued, BEVA 371 was produced with a different ketone tackifier and renamed BEVA 371b (Chludzinski 2011).

In the last twenty years a number of developments have occurred to suggest alternative materials may be more suitable for heat-seal type adhesives that are light-stable. In 1989 Laropal K80 was shown to oxidize during light ageing leading to embrittlement and solubility changes, and yellow upon subsequent heat ageing in the dark (de la Rie 1989). A following paper discussed more stable commercially available alternatives to Laropal K80 for use in varnishes (de la Rie 1990). All of these resins are low molecular weight high Tg resins and are classified as gloss modifiers in coatings applications and tackifying resins to adhesive formulators (McGlinchey 1990); some are hydrogenated hydrocarbon resins and others are urea aldehyde resins. With respect to the polymer component of heat-seals, there are two advancements that can be considered: first, commercially available amorphous polyolefins which are semicrystalline copolymers of polyethylene (PE) and polypropylene (PP) and second, chemical modification of vinyl acetates (VAc) to a copolymer that is chemically more resistant to deterioration. With regards to the latter, it has been shown that vinyl acetate (VAc) dispersions are resistant to hydrolytic degradation without any major alterations of physical properties when a small percentage of the acetate groups are converted to the more hydrophobic vinyl versate (VVe) group (Smith 1993). The same concept is being considered for EVAc copolymers by making EVAcVVe terpolymers. The influence these more recently developed oligomers, waxes, and polymers have on the behaviour of heat-seal adhesives is the subject of this paper.

Experimental Methods

In this study, scientific analysis falls into two categories. First: evaluating BEVA 371 and 371b and test formulations based on commercial products currently available, and second: synthesis of polymers that are not currently available but may offer improved chemical stability and solubility properties. The test formulations were prepared utilizing EVAc copolymers- Elvax 150 (Dupont) and A-C™ 400 (Honeywell), a urea aldehyde resin- Laropal® A81 (BASF) and a hydrogenated hydrocarbon resin- Regalrez™ 1085 (Eastman) as tackifiers, an amorphous polyolefin (APO) copolymer of PE and PP- Eastoflex™ 1060 (Eastman) as a wax substitute, and Regalrez™ 1018 (Eastman), a low molecular weight low Tg resin. The individual components and their concentrations in the test formulations (samples A-H) are shown in Table 1. The EVAc-VVe terpolymer synthesis is described below and illustrated in Figure 1.

Heat-seal Formulations with Commercially Available Materials

Test adhesive sample preparation

Components requiring aromatic solvents were dissolved in TS-28 (Shell) and other components were dissolved separately in Mineral Spirits 135 (Shell). After both dissolved, the latter solution was added to the former. To help facilitate homogeneity, samples were warmed in a water bath to temperatures between 40°C and 70°C as needed. The amount of solvent used was 2x the weight of solids.

Eight different test formulations (A – H) were prepared and multiple sets of each formulation, along with BEVA 371 (sample I) and BEVA 371b (sample J), were cast onto microscope slides for testing and characterisation. Comments regarding the thermal activation of the unaged test formulation samples are shown in the second column of Table 1; they were tested for their thermal activation conditions relative to those suitable for activation of BEVA 371 (62°C +/- 2°C). BEVA 371b was not studied by this method, but previous tests have indicated that the two BEVAs have similar activation temperatures. Tests were carried out as follows: a heated spatula was warmed to 62°C +/- 2°C and brought in contact with the adhesive and tested for tack by feel and visual examination. Only after all samples had been tested under these conditions was the spatula reset to higher temperatures and the unaffected samples reevaluated.

Table 1: Experimental formulations with qualitative assessment of the dried films when pressed with a tacking iron set at 62°C ± 2°C.

Sample	Feel at 62°C ±2° C	Components and weight percentage in formulations		
		EVA copolymers	Tackifiers	‘Waxes’
A	little effect	Elvax™ 150- 46.1% A-C™ 400- 19.2%	Laropal® A81- 24.4% Cellolyn™ 21- 2.6%	Multiwax® W-835- 7.7%
B	very little effect	Elvax 150- 47.6% A-C 400- 19.9%	Laropal A81- 25.1% Regalrez™ 1018- 0.8%	Multiwax W-835- 6.6%
C	weak tack	Elvax 150- 43.1% A-C 400- 17.9%	Regalrez™ 1085- 32.3% Regalrez 1018- 0.7%	Multiwax W-835- 6.0%
D	good tack	Elvax 150- 38.5% A-C 400- 16.0%	Regalrez 1085- 28.9% Regalrez 1018- 0.6%	Eastoflex™ 1060- 16.0%
E	little effect	Elvax 150- 27.3%	Laropal A81- 18.1% Regalrez 1085- 27.3%	Eastoflex 1060- 27.3%
F	easily activated	Elvax 150- 38.7% AC 400- 16.2%	Regalrez 1085- 29.0%	Eastoflex 1060- 16.1%
G	easily activated	Elvax 150- 42.4% A-C 400- 17.6%	Laropal A81- 22.4%	Eastoflex 1060- 17.6%
H	easily activated	Elvax 150- 37.6% A-C 400- 15.6%	Laropal A81- 15.6% Regalrez 1085- 15.6%	Eastoflex 1060- 15.6%

Transmitted polarized light microscopy (PLM)

A programmable hot-stage (Linkam model LTS 350) was used to characterise and observe the melting behaviour of the unaged experimental formulations and BEVA 371 and 371b. The adhesives were heated at 10°C/min and held at 65°C for 10 minutes then heated to 80°C and cooled.

Accelerated photo-ageing

Samples A-H, BEVA 371, and BEVA 371b were light aged. Four sets of the ten different formulations were placed in the xenon arc Weather-ometer (Atlas) at approximately two-week intervals and were aged for 333, 667, 997, and 1332 hours. The benefit of this approach is that the samples could be analyzed simultaneously, in one day of analysis. The Weather-ometer irradiance was set to 0.9 W/m² at 420nm using a xenon arc lamp (6500 Watt) with an inner soda lime and outer borosilicate filter giving a spectral power distribution that approximates daylight through window glass. The temperature and humidity was maintained at 25°C and 38% RH +/- 6% RH.

Fourier Transform Infrared Spectroscopy (FTIR) and Solubility tests

Micro-attenuated total reflectance (μ ATR) FTIR was performed with a Si crystal μ ATR (Thermo) with an infinity reflectochromat 15X objective and a Nexus 670 bench. FTIR data was collected at 256 scans with a resolution of 8cm⁻¹ for μ ATR measurements and 4cm⁻¹ for data collected in transmission mode. The sampling depth of the μ ATR data is on the order of 0.85 microns. Transmission μ FTIR measurements were performed in an effort to differentiate changes in bulk of the film from oxidation on the surface. Solubility properties were examined using a three-solvent (cyclohexane, toluene and acetone) approach common for assessing the solubility properties of varnishes (de la Rie 1988). The increased oxidation observed in the FTIR spectra can be evidence of changes in the polarity of the films and can be correlated to changes in solubility as the need for a more polar solvent increases as ageing progresses.

Synthesis and Characterisation of EVAc-vinyl versatate (EVAcVVe)

Terpolymer

EVAcVVe synthesis

Vinyl acetate (VAc) groups in Elvax 150 were partially transesterified to vinyl versatate groups (Figure 1). The first transesterification was achieved by dissolving the EVAc copolymer in toluene at 85°C followed by adding potassium hydroxide (KOH), dissolved in isopropanol. The reaction mixture was maintained, with stirring, at 80°C for 1 h. Afterwards, the EVAc-vinyl alcohol (EVAcVAI) terpolymer was precipitated and washed with isopropanol and water, and then filtered. The degree of transformation of acetate groups to hydroxyl was limited to 6% w/w by controlling the reaction time and temperature. The acyl chloride of versatic acid 10 (Hexion) was made by adding oxalyl chloride to a solution of versatic acid in anhydrous tetrahydrofuran (THF). In the second transesterification this product was slowly added to a THF solution of the first terpolymer and stirred under an inert atmosphere for 24 hours. Triethanolamine (TEA) was added to buffer the HCl evolved during the reaction.

The new terpolymer (EVAcVVe) was dissolved in xylene at 70°C, precipitated and washed in methanol, and then filtered and dried at 70°C with a mechanical vacuum.

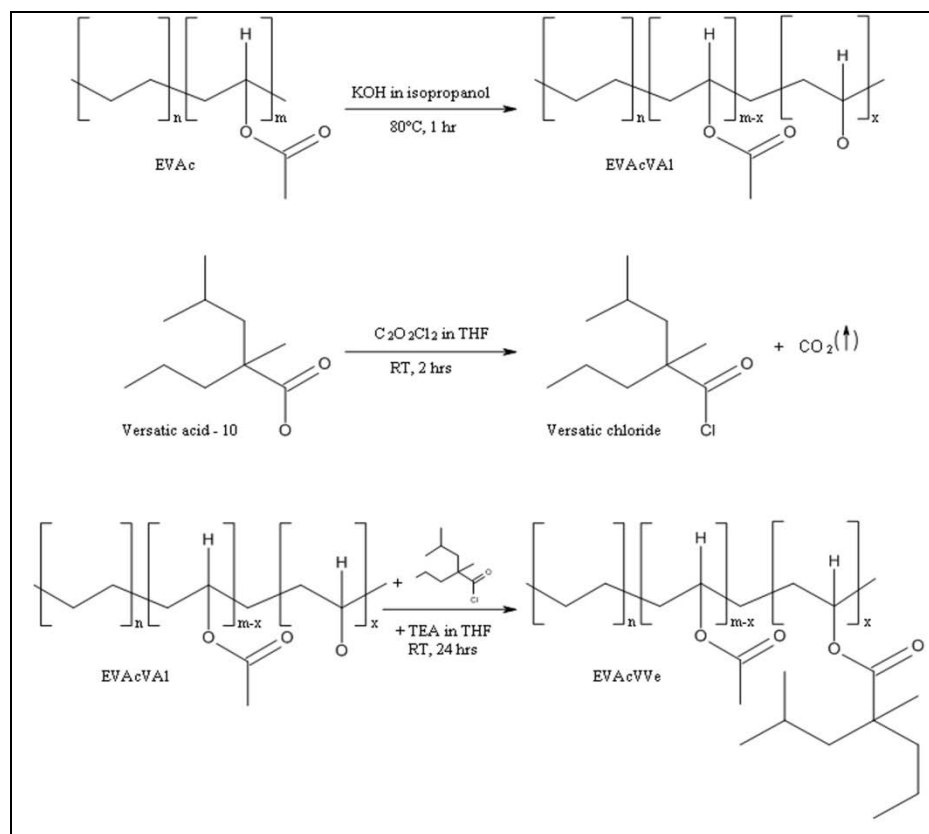


Figure 1: Transesterification reactions converting an EVAc copolymer to a EVAcVVe terpolymer

Nuclear magnetic resonance (NMR)

Terpolymers and intermediates were characterised by ^1H NMR, using a 500 MHz Bruker Avance spectrometer in the normal and $^1\text{H} - ^1\text{H}$ correlation spectroscopy (COSY) modes. Elvax 150 and the first EVAcVAI terpolymer samples were dissolved in CDCl_3 , while the EVAcVVe terpolymer spectrum was obtained by dissolving the sample in orthodichlorobenzene with 10% deuterated tetrachloroethane at 100°C .

Differential scanning calorimetry (DSC)

DSC measurements were performed on a Mettler Toledo DSC821. A double cycle program was used: samples were heated at $10^{\circ}\text{C}/\text{min}$ from -100°C and $+200^{\circ}\text{C}$ and cooled at $-10^{\circ}\text{C}/\text{min}$ from $+200^{\circ}\text{C}$ to -100°C . The data reported are related to the second heating ramp from -100°C to $+200^{\circ}\text{C}$.

Results and Discussion

Evaluation of Experimental Formulations, BEVA 371 and 371b

Transmitted PLM showed that at 65°C, the recommended activation temperature, the crystal structure was evident in crossed polars. Above 75°C, all crystalline character disappeared and samples became amorphous liquids. From a heat-seal perspective maintaining a solid component during activation (i.e. optimal tack) is critical to forming a good bond at the interface.

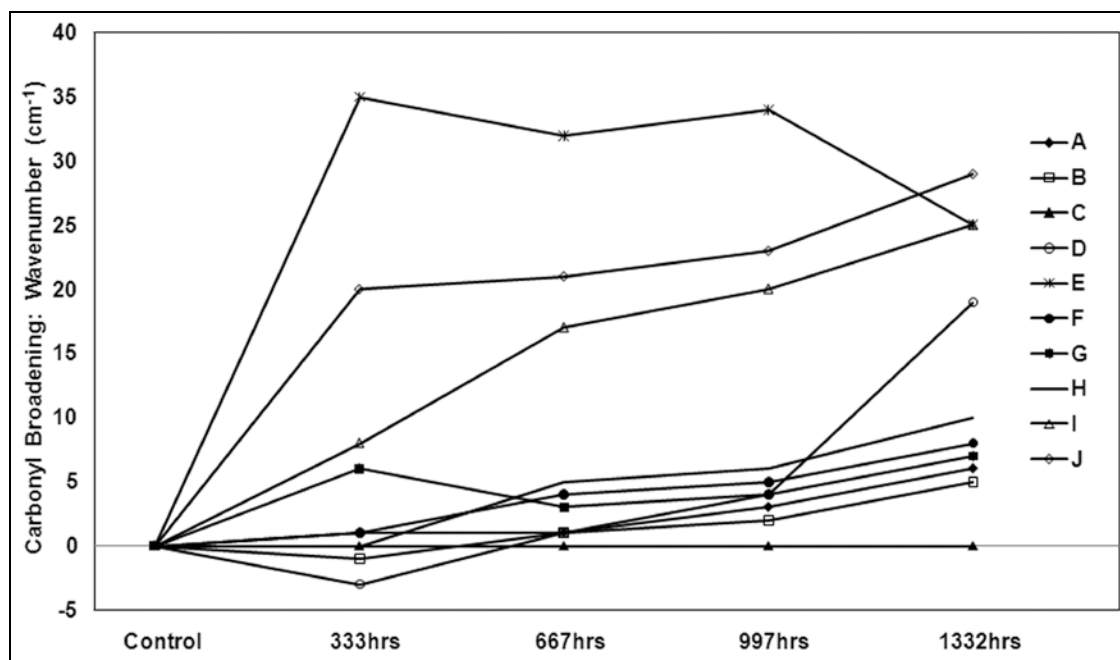


Figure 2: The general assessment of FTIR μ ATR spectra in the C=O region during ageing by looking at the mid-peak broadening; these results clearly show the formation of new oxygen bearing species. A-H are the test formulations and I and J represent BEVA 371 and BEVA 371b respectively.

As seen in Figure 2, BEVA 371 and 371b began to show evidence of oxidation products (in both the μ -ATR and transmission) after 332 hours of light ageing. The carbonyl peak, with a maximum around 1739 cm^{-1} due to the ester groups in the EVAc copolymer and a shoulder around 1711 cm^{-1} (due to the ketone tackifier), broadens significantly. The broadened peak is deconvoluted and illustrated in the detail found in Figure 3. This helps reveal a new shoulder around 1770 cm^{-1} and indicates the formation of lactones. The deconvoluted band also shows broadening towards 1730, 1705 and 1697 cm^{-1} and suggests the formation of aldehydes or esters, other ketones and carboxylic acids respectively. The formation of a peak around 1177 cm^{-1} supports the lactone (CO-O) assignment and the broad hydroxyl peak between 3550 and 3200 cm^{-1} supports the formation of carboxylic acids and possibly hydroperoxides. Peaks

around 1440 cm^{-1} and 962 cm^{-1} develop with photo-ageing and could be linked to the $-\text{COOH}$ stretching plus O-H deformation of the carboxylic acids.

Photo-oxidative degradation in BEVA is likely assigned to the tackifier resin and EVAc copolymer. EVAc copolymers are suggested to undergo a complex set of oxidation reactions which could result in the formation of acids, ketones, aldehydes, esters, lactones, alcohols, hydroperoxides (Allen 2000; Allen 2001; Jin 2010) most of which are observed above. There is also the competition between cross-linking and chain-scission; EVA copolymers with higher vinyl acetate contents are more susceptible to degradation involving chain-scission, since vinyl acetate groups are points of weakness throughout the copolymer (Jin 2010). Ketone groups in the tackifier resin, Laropal K80, undergo Norrish I and II type reactions in UV-light (de la Rie 1989) forming scission products, including aldehydes and alkenes. The tackifier resin in BEVA 371b, is described as a ketone-aldehyde resin (Chludzinski 2011) and based on the spectra, has a structure similar to that of Laropal K 80. In future work EVAcVVe substitutions will be evaluated.

Sample A was modeled after the BEVA formulations, with the substitution of the tackifier with a more stable resin, Laropal A81 (BASF), a urea-aldehyde resin. The exact structure of the resin is unknown; however it is known to contain tertiary amide groups and other functionalities, such as hydroxyl, ether, C-H and esters (de la Rie 2002). The μ -FTIR studies suggest photo-oxidative degradation products such as ketones at 1705cm^{-1} and carboxylic acids with peaks between $1715\text{-}1680\text{ cm}^{-1}$, 1440 cm^{-1} and between $3500\text{-}3200\text{ cm}^{-1}$. These products are likely a combination of the oxidation of the EVAc copolymers and Laropal A81, which has been described to produce species containing hydroxyl, ketone and carboxylic functionality (de la Rie 2002). Urea-aldehyde resins, including Laropal A81 have been shown to have a good resistance to photo-chemical ageing and degradation (de la Rie 1990; de la Rie 2002) and, compared to the BEVA formulations, fewer types of degradation products are observed (see Figures 3 and 4).

Samples prepared with alternative tackifiers only (A-C) show little change in FTIR spectra after light ageing compared to the other samples, which is expected due to the better photo-chemical stability of the individual components. However, preliminary tests indicated that these samples require higher activation temperatures. The higher activation temperature may be irrelevant for a solvent delivered consolidant and may therefore be promising alternatives. However, *reactivation* with heat will likely be difficult using these specific blends.

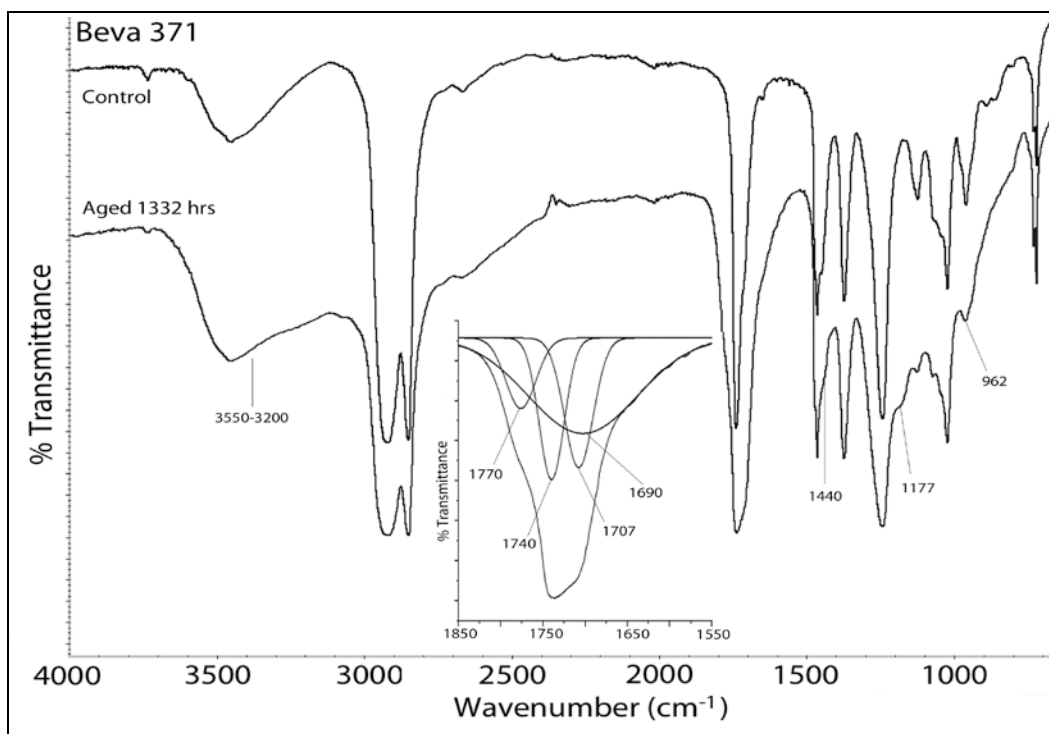


Figure 3: IR μ -transmission spectra of control and light aged BEVA 371. Detail indicates source for carbonyl band broadening.

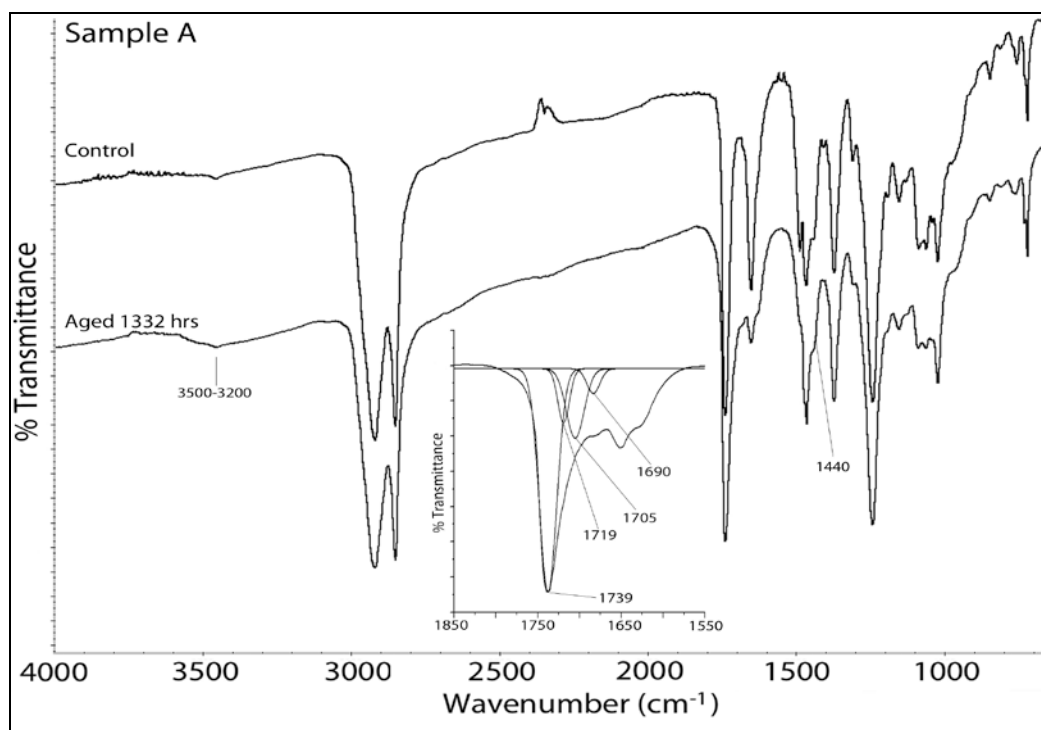


Figure 4 IR μ -transmission spectra of test formulation A with a urea aldehyde resin. Detail indicates source for carbonyl band broadening.

In samples D-H, APO copolymers were used as a substitution for wax. Sample E showed a significant difference between the μ -ATR and transmission, suggesting a phase separation. A non-polar phase was identified along the surface whereas a more polar phase was observed in the bulk. With this sample having the highest concentration of APO, it is believed this separation is a physical phenomenon where the APO with insufficient tack likely settles predominantly on the surface. During photo-ageing there is a dramatic change along the surface of Sample E, where oxidation develops. Carbonyl peaks form and broaden around 1770, 1736, 1718, 1706 and 1682 cm^{-1} representing a range of carbonyl species including lactones, esters and/or aldehydes, ketones and carboxylic acids respectively (Gulmine 2003). Sample H showed many of the same oxidation degradation products along the surface and throughout the bulk. A significant broadening of the carbonyl peak with new peaks forming around 1775, 1718 and 1680 cm^{-1} is observed, as well as the formation of a peak at 1191 cm^{-1} and a broad peak between 3500 and 3200 cm^{-1} . These new oxygenated species are likely a combination of degradation of the EVAc polymer, the tackifier and polyolefin substituted wax component.

At 1332 hrs of light-aging all samples remained soluble in 100% cyclohexane although the ease with which this was accomplished varied with age. Samples A, I and J, after 997 hours of ageing, required a little more time. After more extensive aging some samples become insoluble in cyclohexane. In 2161 hrs, solubility tests show BEVA 371 requires 100% toluene and BEVA 371b requires about 95% toluene with 5% acetone. At the same time interval, the experimental sample that diverges the most from solubility in pure cyclohexane is sample G, requiring about 89% cyclohexane and 11% toluene. Furthermore, after 3127 hrs of light aging BEVA 371 and 371b require 62% toluene with 38% acetone and 52% toluene with 48% acetone, respectively. These results indicate changes in solubility related to light aging is greatest for both samples of BEVA when compared to the experimental formulations.

Characterisation of a Vinyl-acetate Vinyl-versatate Terpolymer.

The degree of transesterification of the samples was determined by ^1H NMR by following the position of the methine protons. ^1H NMR solution spectrum of EVAc shows signals at about 5 ppm corresponding to the methine protons adjacent to the acetate groups, as seen in Figure 5. The magnification in Figure 5 shows the appearance of signals around 3.9-3.5 ppm (in CDCl_3) in the EVAc-vinyl alcohol (EVAcVAI) terpolymer spectrum, and around 3.8 ppm (in *o*-dichlorobenzene) in the EVAcVVe terpolymer spectrum corresponding, respectively, to the methine protons adjacent to hydroxyl groups and versatate groups. The ratio of the integrals of these resonances and the integral of the signal around 5 ppm allows for the estimation of the degree of transesterification. Since the amount of $-\text{OH}$ produced in the first terpolymer can be controlled, different concentrations of versatate groups can be obtained.

^1H - ^1H (COSY) NMR revealed that the final product is a mixture of versatic acids, characterised by different aliphatic side groups. COSY detects interactions between protons no more than a few bonds away and indicates isomeric structures. Pyrolysis Gas Chromatography Mass Spectrometry (Py-C-MS) (not discussed here) has confirmed the product is a mixture of isomers.

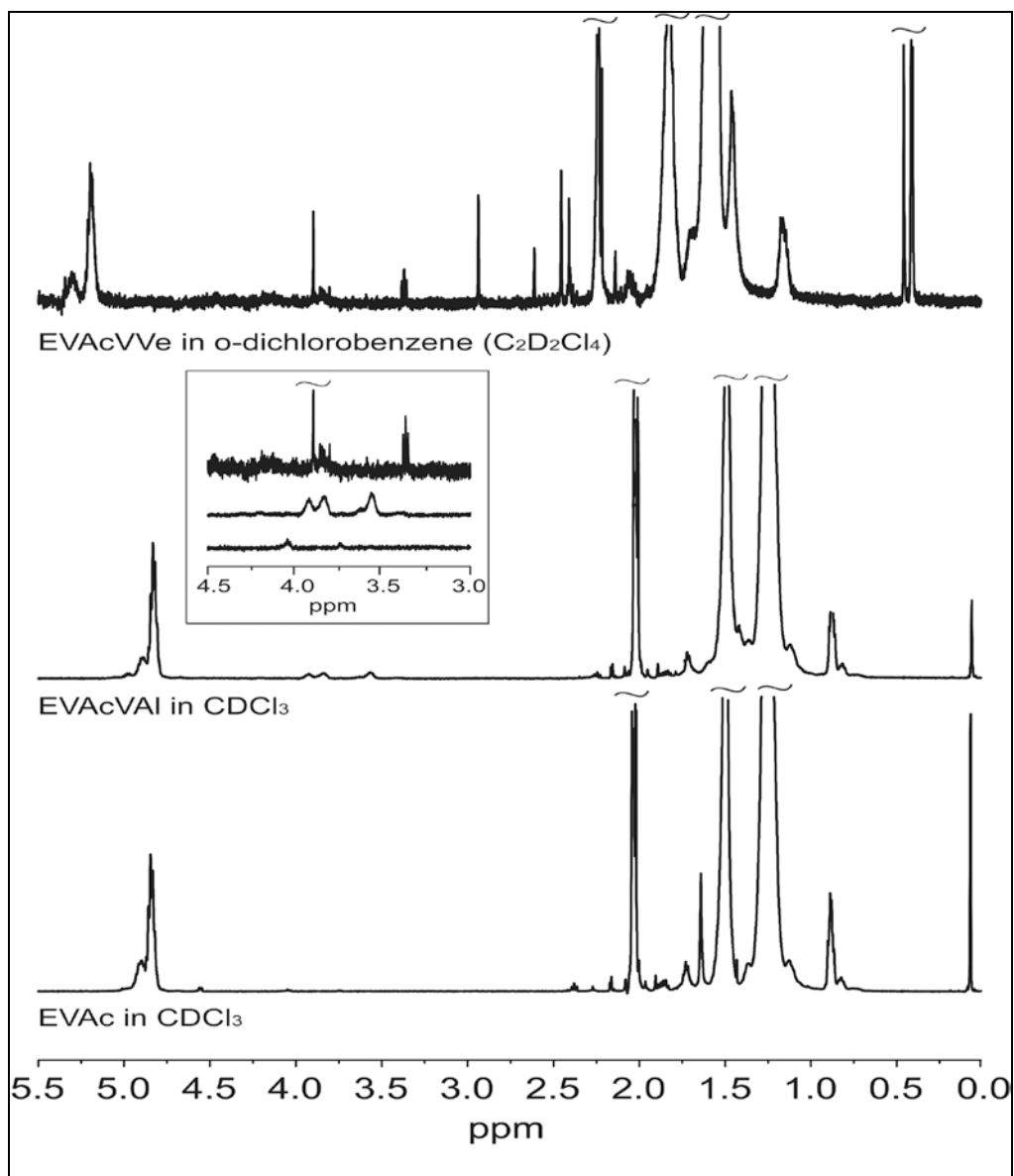


Figure 5: ¹H NMR spectra corresponding to the copolymer EVAc (Elvax 150, Dupont), the terpolymer EVAcVAI, and the terpolymer EVAcVVe. The magnification shows the region among 4.5-3.0 ppm related to methine protons adjacent to a hydroxyl group and a versatate group.

The DSC results of the polymers are reported in Figure 6. There is an increase of the T_g of the versatate terpolymer compared to the EVAc polymer (Elvax 150) from about -29°C to -25°C. This is linked to the fact that the bulky side-groups of the versatate reduce the free volume among the polymeric chains. The melting point increases for the EVAcVAI terpolymer to 68°C, as reported in the literature, but it is the same for EVAc and EVAcVVe (about 63-64°C). On the other hand, we can note a small increase of the enthalpy of melting with the transformation of

the acetate groups into versates. This suggests the degree of conversion as confirmed by NMR is not sufficiently high to dramatically alter the thermal properties.

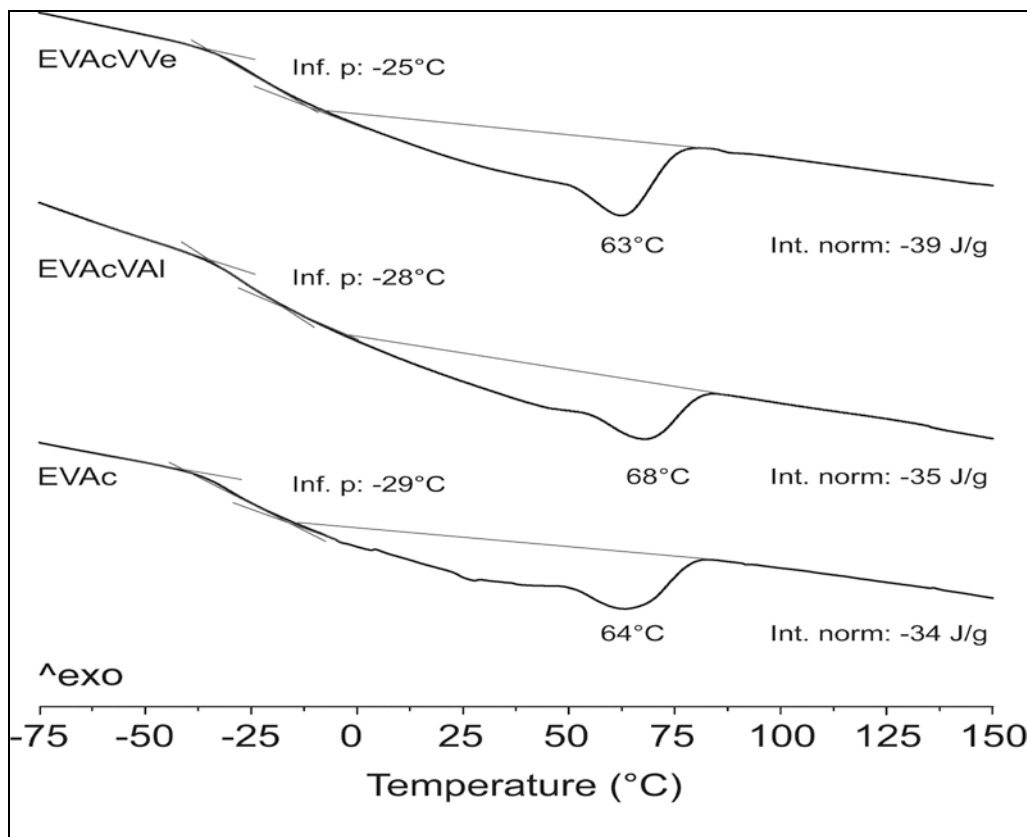


Figure 6: DSC melting curves (3rd scan) of the copolymer EVAc (Elvax 150, Dupont), the terpolymer EVAcVAI, and the terpolymer EVAcVVe.

Conclusions / Future Work

One of the reasons why conservators might prefer a heat-seal type of adhesive is related to these adhesives' gap-filling qualities. This is influenced by the bulking effect some of the components have on the formulation; mainly the dispersed phase of the semi-crystalline component and the low molecular weight tackifier. These features help effectively leverage heat-seals once contact and activation are completed; solvent-based adhesives take longer time to dry and shrink as evaporation proceeds.

Although much work remains, the results show that band broadening of the carbonyl region and changes in solubility for the samples containing Laropal A81 and Regalrez 1085 are significantly lower than what occurs with BEVA 371 and 371b. The findings also suggest that some changes observed with FTIR may be due to the EVAc component, justifying the research in developing and testing what in theory should be more chemically stable polymers via the

versatate process. In addition, the lower polarity of the versatate could influence the solvents these adhesives are delivered in during a treatment. Although some formulations appear to have a higher activation temperature, they may be suitable alternatives when solvent delivery and activation are acceptable. Other formulations are being considered when heat reactivation is necessary.

Future work includes testing of formulations that contain stabilizing additives, and synthesis and characterisation of larger quantities of EVAcVVe containing terpolymer so that additional adhesive blends can be made. The stability of terpolymers will be tested and small angle x-ray scatter (SAXS) will be used to characterise the tack / phase behaviour of both commercial and experimental materials. Formulations that appear to be resistive to light-induced deterioration will be subject to further mechanical testing. Finally, expanded field-testing by conservators will help guide and evaluate these and other experimental formulations.

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Materials & Suppliers

Atlas MTT, LLC 4114 N. Ravenswood Avenue, Chicago, 60613 <http://atlas-mts.com>

BEVA 371, 371b: Conservator's Products Company, P.O. Box 601, Flanders NJ, 07836 <http://www.conservators-products.com/>

Bruker: Bruker Italia S.r.l. Viale v. Lancetti 43, 20158 Milano
<http://www.bruker-biospin.com/nmr.html>

Cellolyn 21; Eastoflex 1060; Regalrez 1085; Regalrez 1018: Eastman, PO Box 431, Kingsport TN.
<http://www.eastman.com/Pages/Home.aspx>

Elvax 150: Dupont 1 800 441 7515 http://www2.dupont.com/Elvax/en_US/products/elvax_industrial_index.html

EVAc AC-400: Honeywell, 101 Columbia Road, Morristown NJ, 07962
<http://www51.honeywell.com/sm/acwax/products.html>

Laropal A81: BASF North America 1 800 526 1072 <http://www.basf.com>

Mettler – Toledo: 1900 Polaris Parkway, Columbus OH, 43240, USA.
http://us.mt.com/us/en/home/products/Laboratory_Analytics_Browse/TA_Family_Browse.html

Linkam Scientific Instruments Unit 8 Epsom Downs Metro Centre, Tadworth, Surrey KT20 5LR UK
<http://www.linkam.co.uk/>

Thermo Scientific: 5225 Verona Road, Fitchburg, WI, USA <http://www.thermofisher.com/global/en/home.asp>

Versatic acid 10: Hexion Specialty Chemical, Inc. Varziner Strasse 49, 47138 Duisburg, Germany
<http://ww2.momentive.com/home.aspx>

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Annalisa Colombo has a Master's in Material Science from the University of Milano-Bicocca in Italy, and is working on a PhD in Nanotechnology and Nanostructure at the same institution. She completed her training as a conservator of wall and easel paintings, works on paper, and library materials in 2003, and has been Project Manager of Cesmar7 (Centre for the Study of Materials for Restoration) since 2006. Her responsibilities include evaluating varnishes, adhesives, and consolidants used in the conservation of paintings, and teaching at the conservation programs in Italy. She is interested in the study of conservation materials and in the development of new materials that utilize nanostructure technology for the benefit of cultural heritage preservation.

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