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The long-term stability of a popular heat-seal adhesive for the conservation of painted cultural objects

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(Article begins on next page)

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Title: The long-term stability of a popular heat-seal adhesive for the conservation of painted cultural objects

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Keywords: poly(ethylene vinyl acetate) adhesive; poly(cyclohexanone) tackifier; photo-chemical stability; heat-seal adhesive; paint layers consolidation

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Abstract: A large number of products, both natural and synthetic, have been and are used for the consolidation of flaking or fragile paint layers occurring on paintings, polychrome sculpture, furniture and other cultural objects. Most products in use, which include natural as well as synthetic materials, remain untested. Most synthetic materials used for consolidation of paint layers consist of a solution or dispersion of a single polymeric component, and may not have the proper physical and mechanical properties, as well they have not been formulated using knowledge and expertise from the field of adhesion science. The only material that has been specifically formulated as an adhesive for the conservation field is BEVA® 371, which contains several components. It was designed as a hot-melt adhesive for the lining of canvas paintings in the early 1970s, but has since then become a popular adhesive for paint layers in need of consolidation. Its stability, an important parameter for this application, was however never fully investigated. This paper investigates the photo-chemical stability of BEVA® 371 as a whole, and each of its components independently using Fourier transform infrared spectroscopy, size exclusion chromatography and solubility tests.



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Dear Prof. Gardette,

it has been a long revision of the paper "The long-term stability of a popular heat-seal adhesive for the conservation of painted cultural objects" (Ms. Ref No.: PDST -D-13-00677) in order to take into proper account the changes and suggestions received by the referees, and I am submitting now the copy.

The responses to the specific reviewer indications are in particular reported in the following.

With many thanks for your help, and for the useful reviewers suggestions.

Yours sincerely,
Oscar Chiantore

Response to reviewers

Reviewer #2:

My major concerns are related to the fact that relevant experimental data is not presented and that molecular structures for the five existing compounds in BEVA are not given. Although P(E-VA) and wax structures may be considered trivial the "takifiers" are not; and it would be helpful for the reader to access it within the paper. Taking into account that a relevant part of the work is based in IR analysis, I strongly suggest to present this information in a table as bellow.

please see table in the attached pdf file

This table was drawn for personal use, to enable this reviewer to follow the introduction. An historic overview and important information is carefully presented in this section, but it lacks a concise and accurate description of the BEVA@371 formulation, which should, at least, be summarized and its end.

- In Table 1 a column with chemical composition of BEVA components has been added.

Concerning, the "new" formulation, BEVA 371b, it was not possible for this reader to precisely understand in which it consisted. If the authors cannot disclose it, please just state so in the introduction

- The sentence was changed accordingly:

"...manufacturers of BEVA® 371 were forced to make a formulation change, since the ketone resin tackifier component was discontinued by its chemical manufacturer [26]. The new formulation contains an alternative ketone resin, which gives the product a more yellow appearance (the new tackifier was not disclosed)".

Relevant experimental data that the authors could easily display are the full infrared spectra (4000-400 cm⁻¹) for the 5 compounds of BEVA@271 and 271b (if different), before ageing and after the 8 weeks irradiation time.

- Spectra are supplied as Supplementary Material

Taking into account that SEC was performed for all BEVA 371 (371b?) components, it is necessary to present it in Table 2, together with the data for Elvax and Laropal.

- The description of SEC results has been slightly changed in Section 3.2.

A-C 400 was not measured because it was not completely soluble. Cellolyn is a minor component of the mixture, with MW much lower than the polymeric constituents.

SUGGESTED COMMENTS/CHANGES:

Introduction

1) As it stands now, the abstract misleads the reader to consider BEVA as an adhesive to be used to consolidate all kind of artworks. It should be made clear that BEVA was developed as an adhesive to be applied in the conservation of paintings, textiles and paper, but has been popular mainly in paintings conservation. It would be even better if in the abstract the author would restrict their field of study to the conservation of paintings. This would help in defining a consolidating treatment in this field. Taking in consideration the number of times



that the word is used thorough the text, a definition should be offered (in the main text or as a footnote).

- Abstract revised

2) p 5: " In the end, Berger designed an adhesive following a standard recipe for hot-melt adhesives based on an EVA copolymer: polymer, tackifier and wax". This sentence is not clear: authors should describe the compounds existing in the "standard recipe" as: two EVA copolymers, two "takifiers" and one wax; or similar. Otherwise, readers will be surprised, or confused, when in p7 they will read "containing two EVA co- polymers, a ketone resin tackifier, a phthalate ester of hydroabietyl alcohol secondary tackifier".

- Corrected

3) In p5, it is described when Berger proposed BEVA formulation "for consolidation of paint layers", but not when it was suggested /tested for lining treatments.

- This point is already in the text:

"BEVA 371® was specifically formulated as an alternative to wax-resin lining adhesives. In 1967, Gustav Berger began a research program.... During its development, the mechanical properties were evaluated for lining applications [10, 11]..... Berger suggested using BEVA® 371 for consolidation of paint layers in the first years after its development [12],...."

4) p7: " UV accelerated ageing tests", please, add the irradiation conditions, irradiation for wavelengths > 300 nm?, 310 nm? other?

- Added

5) p8: At this point" This paper will investigate the photo-chemical stability of BEVA® 371, and its reformulated version 371b", please summarize the composition of the formulation, and refer to an updated table 1. Until now there is no single paragraph in which all the compounds present are described nor what is different in the "new" BEVA371b.

- Table 1 updated

Also, and considering that BEVA is usually not exposed to light and that interested reader may be not an expert in polymers degradation, explain why a photo-degradation study will contribute to a better understanding of the formulation stability.

- Additional considerations about photostability of polymeric materials are not necessary to PDST readers, neither to people dealing with conservation treatments.

Materials and methods

6) p9: " The BEVA® 371 and 371b solution samples examined were produced by C.P.C. (Conservator's Products Company), Flanders, NJ, USA. These formulations were based on Berger's original formulation described in Table 1". The samples were produced by the only producers of BEVA? if yes, it would be best to write acquired? In Table 1, only the "original" BEVA formulation is present, not the "new" BEVA371b. Please, provide this information and respective references that are also missing in this sentence.

- Done

7) p9: "CellolynT 21-E (Eastman) was not aged as a pure film as it has a low glass transition temperature and can flow at ambient temperatures." This is not a reason for not being able to irradiate this compound, therefore this is not correct - please, see above- and rewrite this sentence.

- Rewritten

8) p10: "The BEVA® 371 used was characterized using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) and solid phase micro-extraction gas chromatography-



mass spectrometry (SPME GC/MS) and the only difference observed was higher than expected xylene content."

The only difference compared to what??

- Specification added

9) p11, 2.2: "Transmission μ -FTIR measurements were performed in an effort to differentiate changes in bulk of the film from oxidation on the surface." No results from transmission measurements are shown or discussed in the paper. So, I would suggest removing this description. If authors will prefer to discuss these results in the paper, then they should describe how they obtained the infrared spectra: after compressing the films in a diamond anvil cell? or films in KBr windows were also irradiated? other?

- OK. Diamond anvil cell.

Results and discussion

10) For "3.Results and discussion section" please provide, in the main text or appendix, the full infrared spectra for all compounds present in the BEVA formulation ("original" and "new").

- See above

11) p13, section 3.1: "Both BEVA® 371 and 371b began (...), as seen in Figure 1". No results are shown for 371b in Figure 1. This reviewer would suggest to represent its trend (in e.g Fig 1B) for at least the t0 and t8 weeks for BEVA371b. Also, it would be important to comment on the changes observed in the 1300-1000 cm⁻¹ window. Could they result from a change in the Tg due to the P(E-VA) scission? or to the loss of one or more components, e.g., the phthalate derivative, Cellolyn?

- We introduced in the section, and in the caption to Figure 1, that BEVA 371b gave the same results as BEVA 371. It is difficult to comment changes in the fingerprint region, due to the overlapping of many different contributions. We mention the peak formation at 1180 cm⁻¹, coming from the oxidation of the polymeric structures. On the other hand the scission reactions cannot produce enough new structural features as to influence this spectral region.

12) p13: "Films of Elvax® 150, A-C® 400 and Laropal® K 80 were aged individually" The authors do not show the infrared spectra evolution for P(E-VA) copolymer A-C400 nor the corresponding SEC data is displayed in Table 2. This is important information that should be shared with the reader

- Differences between Elvax and A-C400 were small, and the main feature is mentioned: "A-C® 400 shows slight broadening at the base of the carbonyl peak, around 1720 cm⁻¹."

13) In p13, the paragraph starting with "One can infer the photo-oxidative stability and reactions of CellolynT 21-E", speculates over the photo-degradation of Cellolyn, and as such is misplaced in the "Results and discussion section". In this long speculative paragraph, it would be advisable to maintain only the final sentence, " Since CellolynT 21-E is present in a low concentration (...) not contribute significantly to the new peaks observed in the IR-spectra of aged BEVA® 371", and to add, if justified, that a loss of this phthalate derivative is expected over time.

- We prefer this part on Cellolyn chemical stability be maintained here, in the "discussion" section, in order to facilitate the reader in the comprehension of the chemical stability characteristics of this compound.

14) p15: "Elvax® 150, showed a small decrease in molecular weight after ageing", in agreement with what described in the literature, e.g.: Polym. Degrad. Stab., 95 (2010) 453-461.

- O.K.

15) In the conclusions and taking into account that the authors mention it in their abstract, comments and suggestions for future research that would integrate the physical / mechanical properties should be addressed - "(BEVA) may not have the proper physical and mechanical properties".



- Final sentence has been reformulated

Reviewer #3: This is a great paper and I only have a few minor comments:

1. Introduction: "Ageing reactions"; why not just "Ageing"?
2. Introduction: "a research program financed by the Samuel H. Kress Foundation"; how this was financed is irrelevant. Please delete.
3. Introduction: For the benefit of PDSt readers, please explain what is "activation temperature".

4. Introduction: "Conservation ethics and obligations restrict ..." please add a reference for this paragraph.

- Done, all points.

5. Introduction: "Under strong UV oxidative conditions (unfiltered UV light, including wavelengths below 315 nm)..." please explain why this would be relevant to paintings usually exhibited indoors in environments with filtered light, or delete.

- We are reporting the results from the Literature. A sentence was added.

6. Materials and Methods: "Films of Elvax® 150 (DuPontT), A-C® 400 (Honeywell) and Laropal® K 80 (BASF) were prepared in a similar fashion"; please provide the details about the composition of these products.
7. Materials and Methods (and elsewhere): "photo-ageing"; please use the term "degradation" for any accelerated degradation experiments, and not ageing, to avoid confusion with natural ageing. Instead of photo-ageing, please use photodegradation.

- Changes and additions inserted.

8. Materials and Methods: "The BEVA® 371 used was characterised using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) and solid phase micro-extraction gas chromatography-mass spectrometry (SPME GC/MS) and the only difference observed was higher than expected xylene content" Please provide experimental details and results of these analyses.

- The sentence was canceled, as not relevant in this context.

9. 2.4: "...polystyrene standards with weight-average molecular weights ranging between 580 and 377,400." Please specify exactly which molar masses were used and if mixed standard solutions were prepared.

- MW of PS standards are shown on the calibration curve in Fig. 4. Easical prepared kits were used, as indicated in 2.4

10. 2.4: "As the calibration curve is logarithmic, looking exclusively at the chromatograms can be misleading when estimating weight average and number molecular weights; large changes in molecular weight of high molecular weight materials appear as less dramatic shifts compared to lower molecular weight materials." Please delete; PDSt readers will be very aware of this.

- Deleted.

The long-term stability of a popular heat-seal adhesive for the conservation of painted cultural objects

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Abstract

A large number of products, both natural and synthetic, have been and are used for the consolidation of flaking or fragile paint layers occurring on paintings, polychrome sculpture, furniture and other cultural objects. Most products in use, which include natural as well as synthetic materials, remain untested. Most synthetic materials used for consolidation of paint layers consist of a solution or dispersion of a single polymeric component, and may not have the proper physical and mechanical properties, as well they have not been formulated using knowledge and expertise from the field of adhesion science. The only material that has been specifically formulated as an adhesive for the conservation field is BEVA® 371, which contains several components. It was designed as a hot-melt adhesive for the lining of canvas paintings in the early 1970s, but has since then become a popular adhesive for paint layers in need of consolidation. Its stability, an important parameter for this application, was however never fully investigated. This paper investigates the photo-chemical stability of BEVA® 371 as a whole, and each of its components independently using Fourier transform infrared spectroscopy, size exclusion chromatography and solubility tests.

Key words

poly(ethylene vinyl acetate) adhesive; poly(cyclohexanone) tackifier; photo-chemical stability; heat-seal adhesive; paint layers consolidation.

1. Introduction

“Paintings are complex structures and differ in composition both over the visible area of their design and in the cross-section” [1]. Paintings conservators are faced with a broad array of conservation-related challenges that require an adhesive, ranging from cuts and tears in the canvas to the delamination and incompatibilities of paint layers. Degradation reactions can change the chemical and mechanical properties of the paint layers and their cohesion and effective interlayer adhesion. As a result, they are less resilient to both internal and external stresses, and delamination, cracking and powdering may occur, among a list of many issues. The intrinsic properties of the work of art guide or restrict the choice of the consolidating adhesive and it is the conservator’s training, experience and intuition that influences one course of action over another. One of the most popular synthetic conservation adhesives, BEVA® 371 (original formulation) [2,3] and its variations under other trade names¹, is a complex multi-component synthetic mixture developed by Gustav A. Berger in the late 1960s and early 1970s.

BEVA® 371 was specifically formulated as an alternative to wax-resin lining adhesives. In 1967, Gustav Berger began a research program to investigate new adhesives for paintings [5, 6]. One of the main problems with wax hot-melt systems was the potentially hazardous temperatures required to activate them. This drove Berger’s research into the development of a new adhesive and approach to the problem. His first experiments looked at increasing the structural strength of waxes by adding resins of greater elasticity and rigidity, using, in particular, poly(ethylene-vinyl acetate) (EVA), which offered a range of properties and possibilities [7]. In the end, Berger

¹ The original BEVA 371 formulation was published during its time of invention allowing conservators and conservation materials manufacturers to duplicate it. Only in the mid-1980s was BEVA® officially trademarked in the United States by Gustav Berger and is now officially manufactured by C.P.C. (USA) and C.T.S. (Italy). A similar conservation heat-seal adhesive, based on Berger’s original formulation, is Lascaux heat-seal adhesive 375 [4].

designed an adhesive following a standard recipe for hot-melt adhesives based on two EVA copolymers, two tackifiers and a wax [8, 9], but with an added component- a solvent carrier- thus, making it more accurately described as a “heat-seal” adhesive (Table 1, [7]). The solvent both facilitated delivery of the adhesive into the painting and reduced the heat-activation temperature [7]; that is the temperature where the system can flow and wet the surface of the substrate, which is essential in creating a good bond. The recommended activation temperature for BEVA® 371 is 65°C. During its development, the mechanical properties were evaluated for lining applications [10, 11]; however, little research has been published on its long-term chemical stability, which is of particular concern when it is used for a consolidation treatment. A lining treatment involves the application, using an adhesive, of a new support canvas to an original degraded or damaged canvas; whereas, a consolidation treatment involves the stabilization of weak, damaged or degraded paint layers using a suitable adhesive. Berger suggested using BEVA® 371 for consolidation of paint layers in the first years after its development [12], and later it was adopted by many conservators for that purpose despite the lack of full stability testing. Berger [7] describes cross-linking tests on a number of BEVA® test formulations, including 371. He found the 371 formulation to be stable against cross-linking and refers to Feller and Curran’s [13] studies on EVA co-polymers. Berger also claimed that the presence of paraffin wax ensured ‘that [the formulation] will stay removable forever’. Details of this claim are not offered, but it can be thought that Berger is referring to the relative chemical inertness of paraffin wax, which will not chemically interact with the other components. Feller and Curran [13] briefly address this ‘resistance-to-crosslink’ claim; however, no satisfactory conclusion is offered for EVA/wax systems.

Conservation ethics and obligations² restrict the range of materials that can be used in treatments; consolidation treatments may affect or be needed for every layer of a painting, so the delivery of the materials, mechanical properties, optical properties and chemical stability are important factors. The consolidating materials must best match the original mechanical properties of the painting to prevent the introduction of new stresses and strains in the paint films, and they cannot optically modify the work of art, eg. they cannot change the gloss and colours, including colour saturation. Also, the treatment must remain “reversible” – i.e. the consolidants must remain soluble in solvents that are safe for the painted layers; although, it is generally realized that once a consolidating material is introduced into a painting it may be difficult to remove all of it.

Berger was aware of these unique conservation requirements during the development of BEVA® 371, whose formulation was chosen as the best combination in terms of optical properties, stability and adhesive properties [7]. However, some conservators, after using the material, have reservations about its removability and yellowing over time [3, 14-19]. Work done by Down [15], also showed that BEVA® 371 (original formulation) performed poorly in terms of colour stability and yellowed significantly, but still maintained its mechanical properties. In the early 1970s, Feller and Curran [13], in response to Berger’s new development, tested the stability of several EVA co-polymers, including Elvax® 150, the major component of BEVA® 371, and were satisfied by their performances. EVA co-polymers, upon thermal degradation, can first undergo a deacetylation step resulting in the formation of free acetic acid and unsaturation in the polymer backbone, as well as various carbonyl species, followed by chain scission [20, 21].

² Principles of conservation are formalized in: C. Brandi, *Theory of Restoration*, Nardini, Firenze, 2005. Codes of Ethics for Art Conservators have been formulated by a number of national and international professional organizations. Among others, the E.C.C.O. Professional Guidelines issued in 2002 by the European Confederation of Conservator-Restorers' Organisations (www.ecco-eu.org/about-e.c.c.o./professional-guidelines.html).

Using unfiltered UV light, including wavelengths below 315 nm (the typical cut-off for window glass), it has been suggested that EVA can undergo photolysis, resulting in acetic acid evolution and the formation of carbon-carbon double bonds along the polymer backbone, or ketones may evolve from hydroperoxide formation/degradation reactions and aldehydes via chain scission reactions [22, 23]. However, it is unlikely that these reactions will occur in a museum climate. During both thermal and UV-ageing cross-linking can also occur; however, chain scission appears to be dominant. Down [15] detected negligible traces of acetic acid during the ageing of BEVA® 371, suggesting that many of the reactions listed above occur primarily under more harsh ageing conditions, such as high temperature and unfiltered UV radiation. de la Rie et al. [24, 25] has looked at a number of different resins for painting varnishes, including Ketone Resin N, later sold under the tradename Laropal® K 80, the polycyclohexanone tackifier resin used in BEVA® 371. He found that it photo-oxidized relatively rapidly during UV accelerated ageing tests (simulated daylight filtered through glass), and it was difficult to stabilize with a hindered amine light stabilizer (HALS), specifically Tinuvin® 292. These optical and chemical stability concerns were compounded in 2010, when the manufacturers of BEVA® 371 were forced to make a formulation change, since the ketone resin tackifier component was discontinued by its chemical manufacturer [26]. The new formulation contains an alternative ketone resin, which gives the product a more yellow appearance (the new tackifier was not disclosed). The manufacturers of BEVA® 371 assured conservators that the mechanical performance of the new formulation was comparable to the original formulation [26]; however, the material was no longer ‘colourless’ or ‘translucent to transparent’ as Berger originally specified [7].

As mentioned previously, BEVA® 371 is a heat-seal adhesive, containing two EVA co-polymers, a ketone resin tackifier, a phthalate ester of a technical grade hydroabietyl alcohol secondary tackifier and paraffin wax (Table 1). Berger never specified in his publications why he used two different types of EVA co-polymers (Elvax® 150 and A-C® 400) in BEVA® 371; however, several reasons can be speculated. The first is that the addition of AC-400®, which only has a vinyl acetate (VA) content of 12-13wt% would offer better compatibility with the paraffin wax. The poly(ethylene) (PE) blocks and wax can co-crystallize [27] and promote adhesion to more non-polar surfaces. Since BEVA® 371 came about as an alternative to wax-resin linings, this property is important if one were re-lining a canvas that had been previously wax-lined. A second possibility, since A-C® 400 has a higher melting point than Elvax® 150 (VA content of 32wt%) and the paraffin wax, is that it served as a solid organic crystalline phase during the heating step to keep the adhesive as a 'tacky solid' because full penetration into all the layers is not always desirable. The balancing of properties is employed in commercial hot-melt adhesive formulations and can yield final materials with better elevated temperature properties and low temperature flexibility [9]. The incorporation of tackifiers allows one to improve the structural performance of the final material. In the case of BEVA® 371, Laropal® K 80, the ketone resin, helps increase the glass transition temperature (T_g) of the system (governed by the EVA co-polymer), as well as acts as a diluent to lower the polymer chain entanglement density resulting in a decreased plateau modulus [28]. The tackifier modifies the viscoelastic, thermal, and adhesion properties of the system, as well as substrate wetting [9, 28], thus facilitating plastic deformation to ensure a good contact. It makes the system 'tacky' under the desired conditions. The softening point of Laropal® K 80 is 75-85°C, which Berger [7] noted as being too high for lining application. He found that the softening point could be successfully lowered,

without showing detrimental effects, by the addition of a second resin, Cellolyn™ 21 with a softening point of 68°C.

This paper will investigate the photo-chemical stability of BEVA® 371, and its reformulated version 371b, and the consequences of photo-oxidation for conservation treatments. Understanding the degradation of the formulation and the individual components will help in the development of improved formulations in the future.

2. Materials and Methods

The BEVA® 371 and 371b solution samples examined were produced by and acquired from C.P.C. (Conservator's Products Company), Flanders, NJ, USA. These formulations were based on Berger's original formulation described in Table 1, noting that the Laropal K® 80 tackifier was replaced by a comparable ketone tackifier resin in 2010. The ratios of the components could have also changed slightly during the reformulation. BEVA® 371 and 371b solution come pre-mixed in a 40 weight percent (wt%) solids in solvent mixture. The solvents used are a combination of aliphatics and aromatics, including toluene, octane and isomers, naphtha petroleum (also known as benzine or VM&P naphtha) and petroleum.

Samples of BEVA® 371 and 371b, diluted with toluene to 20 wt% solids were prepared on a magnetic stirring hot-plate (temperature approximately 55°C), and cast onto glass microscope slides. Films of Elvax® 150 (DuPont™), A-C® 400 (Honeywell) and Laropal® K 80 (BASF) were prepared in a similar fashion. Cellolyn™ 21-E (Eastman) was not aged as a pure film as it has a low glass transition temperature and can flow under its own weight at ambient

temperatures. Ageing using a different type of set-up was not attempted. To evaluate the efficacy of a hindered amine light stabilizer (HALS) in the new BEVA® formulation, 371b, samples were prepared with approximately 2wt% (of solids) Tinuvin® 292 (BASF) and cast onto glass microscope slides as described above. The films were allowed to dry for at least one week before accelerated photodegradation tests.

The drying of BEVA® 371 and 371b solution samples in a vacuum oven revealed that both were approximately 60 wt% solvent mixtures.

2.1 Accelerated photodegradation

Five sample sets were prepared on glass slides and aged in an Atlas Ci4000 Xenon arc Weather-ometer®. The samples were introduced into the chamber at two-week intervals corresponding to total ageing times of: 0 (reference), 333, 667, 997, and 1332 hours (0, 2, 4, 6 and 8 weeks). The benefit of this approach is that the samples could be analyzed simultaneously, during one day of analysis. The Weather-ometer® irradiance was set to 0.9 W/m^2 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 (that is, it eliminates UV radiation below ca. 315 nm). The temperature and humidity was maintained at 25°C and 38% RH +/- 6% RH. An Envirotronics 1-3-WC condensing unit (supplied by Atlas) was fitted to refrigeration lines located on the exterior walls of the sample chamber. This system provided the capability to maintain a desired temperature set point within the chamber by offsetting the heat load of the xenon burner. Additionally, maintaining the chamber temperature thusly enhanced the efficiency of the onboard chamber RH control system. These temperature and RH conditions mimic typical

indoor conditions; wavelengths below 315-310nm should rarely be involved if the tests are to speed up the types of photo-chemical degradation that might occur indoors in museums [29]. Using a simple approximation and the ageing conditions above, 8 weeks of accelerated ageing represents 25 years of natural ageing.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Micro-attenuated total reflectance (μ -ATR) FTIR was performed with a Si crystal μ -ATR (Thermo) with an infinity reflachromat 15X objective and a Nexus 670 bench. FTIR data were collected at 256 scans with a resolution of 8cm^{-1} for μ -ATR measurements, and 4cm^{-1} for data collected in transmission mode using a diamond anvil cell. 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: no difference was observed between the two sampling modes. Data were collected and analysed with Thermo Fisher Scientific OMNIC (v. 7.4.127) software. Carbonyl broadening data are calculated using mid-peak values.

2.3 Solubility tests

Solubility properties were examined using a three-solvent system (cyclohexane, toluene and acetone) previously described for assessing the solubility properties of varnishes [30]. The increased oxidation observed in the FTIR spectra can be evidence of changes in the polarity of the films and can be correlated to an increased need for a more polar solvent mixture as ageing progresses.

2.4 Size-exclusion chromatography (SEC)

Solutions (1wt%) in stabilized tetrahydrofuran (THF) were analysed on a Polymer Laboratories PL-GPC 20 liquid chromatography system consisting of two Polymer Laboratories PL-gel 5 μm mixed-D columns (300mm x 7.5mm) and an refractive index detector. The instrument was maintained at 30°C, and THF was used as the eluant. The instrument was calibrated daily using ten Polymer Laboratories EasiCal polystyrene standards with weight-average molecular weights ranging between 580 and 377,400. Polymer Laboratories CIRRUS™ (v. 2.0) software was used to collect and analyse data. It should be noted that the molecular weights reported were calculated from a calibration curve constructed from polystyrene standards, which are not the same as the materials studied in this paper; thus the values reported are not true molecular weights.

3. Results and discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Both BEVA® 371 began to show evidence of oxidation (in both the μ -ATR and transmission) spectra after two weeks of light ageing, as seen in Figure 1. The carbonyl peak in the unaged BEVA® 371 formulation, with a maximum around 1736 cm^{-1} , is due to the ester groups in the EVA co-polymers, Elvax® 150 and A-C® 400, the predominant materials representing approximately 60wt% of the dry film. The shoulder around 1705 cm^{-1} is assigned to the ketone resin tackifier, Laropal® K 80, which makes up approximately 27wt% of the dry film. The ester group carbonyl band of the secondary tackifier, Cellolyn™ 21, which is around 1728 cm^{-1} , cannot be observed due to its low percentage in the dry film. As accelerated ageing proceeded, the carbonyl band broadened indicating a significant amount of photo-oxidation. After eight

weeks of ageing, the deconvoluted carbonyl peak shows the development of new peaks around 1775, 1705 and 1695 cm^{-1} suggesting the formation of lactones, new ketones and carboxylic acids respectively. The formation of a peak around 1180 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. Peak development around 1640 cm^{-1} is also present suggesting the formation of unsaturation. BEVA 371b showed the same results.

Films of Elvax® 150, A-C® 400 and Laropal® K 80 were aged individually. The paraffin wax and Cellolyn™ 21-E were not aged; paraffin wax, as fully saturated un-branched hydrocarbon, is known to be a relatively stable material, and the low glass transition temperature (T_g) of Cellolyn™ 21-E made it incompatible with the instrumental set-up.

One can infer the photo-oxidative stability and reactions of Cellolyn™ 21-E from its chemical structure: a phthalate ester of a technical grade of hydroabietyl alcohol as indicated on the product data sheets from Eastman. Technical grade hydroabietyl alcohol is partially hydrogenated and can potentially contain traces of abietyl alcohol and other impurities. The sites of possible oxidation in hydroabietyl alcohol are the tertiary carbon atoms and allylic hydrogen atoms. If abietyl alcohol is present as an impurity, another potential site of oxidative attack is along the conjugated double bonds. In abietic acid, the conjugated double bonds are suggested to be the principle point of oxidation [31]. Hydrogenation, even if partial, results in a more stable material, but it still remains susceptible to oxidative degradation. The oxidation reaction of rosin materials is not yet well understood due to difficulties in separating and identifying reaction intermediates; however, there is evidence of hydroperoxide formation and degradation

into hydroxyl and carbonyl species [31]. Since Cellolyn™ 21-E is present in a low concentration in BEVA 371, it is reasonable to assume that its oxidation products will not contribute significantly to the new peaks observed in the IR-spectra of aged BEVA® 371.

Figure 2 illustrates the results of the photodegradation of Elvax® 150 and Laropal® K 80 in the carbonyl region of the FTIR spectra. The Elvax® 150 appears to be stable, showing no evidence of photo-oxidation. Laropal® K 80 performed poorly, resulting in the formation of multiple photo-oxidation products. The ketone groups in the tackifier resin undergo Norrish I reactions in UV-light [24] forming free radical scission products, which react to form further products, including aldehydes and alkenes. The deconvolution of the carbonyl area shows peaks around 1770, 1730 1695 and 1640 (broad) cm^{-1} suggesting the formation of lactones, aldehydes, carboxylic acids and alkenes. The broad hydroxyl peak between 3550 and 3200 cm^{-1} supports the formation of carboxylic acids. A-C® 400 shows slight broadening at the base of the carbonyl peak, around 1720 cm^{-1} . This can be evidence of chain scission and the formation of carbonyl oxidation products.

The degradation of each component may take place separately or synergistically [32]; however, results point towards the ketone resin as the least stable component in BEVA® 371 and the cause of most of the new photo-degradation species formed during accelerated ageing.

Tinuvin® 292 was added to BEVA® 371b to assess its stabilization potentiality. However, it was shown to only marginally stabilize the new BEVA® formulation. The photo-oxidation of the unstabilized and stabilized formulations are summarized as mid-peak carbonyl broadening data

in Figure 3. Until approximately four weeks of ageing, the HALS appears to effectively stabilize material, but after this point Tinuvin® 292 loses its efficacy and photo-oxidative degradation begins. These results were expected, as the literature has demonstrated that Laropal® K 80 cannot be effectively stabilized with Tinuvin® 292 [25, 33]. This is also further evidence that the ketone resin tackifier is the least stable material in the BEVA® formulations.

3.2 Size Exclusion Chromatography (SEC)

Size exclusion chromatography was performed on aged and unaged BEVA® 371 and 371b, and on individual components to compliment the FTIR data. Figure 4 describes the shifts in molecular weight for Laropal® K 80 and Elvax® 150. The molecular weight calculations are in Table 2. A-C® 400, which is predominantly composed of poly(ethylene) units, was not completely soluble in THF and could not be analysed. Laropal® K 80 behaved as expected, showing an increase in molecular weight after ageing [33]. As observed in the FTIR spectra, during photo-degradation, a large number of new oxidative species are formed in Laropal® K 80. Despite the Norrish I scission reactions of the cyclohexanone ring structures, the oligomeric linkages remain intact. As oxidative degradation proceeds, there is a large up-take of oxygen into the resin and an increase in molecular weight. Elvax® 150, showed a small decrease in molecular weight after ageing. This could be due to the start of chain scission, in agreement with what is described in the literature [34]. Very few chain scissions have a strong effect on the molecular weight. At this point, no changes in chemical structure can be observed with FTIR.

3.3 Conservation treatment consequences

A consequence of oxidation is a change in the solubility of the material. An important consideration for all conservation materials is that they must remain safely reversible. Chemical changes may not manifest themselves on a mechanical or optical level, thus they may go undetected until a conservator comes to remove the material. The solubility of Laropal® K 80 has shown to rapidly change during photodegradation because of the formation of new polar oxidation products [24]. At eight weeks of light-ageing BEVA® 371 and 371b remained soluble in 100% cyclohexane, while after more extensive ageing some samples become insoluble in cyclohexane. After 12 weeks of ageing, solubility tests showed that BEVA® 371 required 100% toluene, and BEVA 371b required about 95% toluene with 5% acetone. Furthermore, after 18 weeks of light ageing BEVA® 371 and 371b required approximately 62% toluene with 38% acetone and 52% toluene with 48% acetone, respectively.

It has been suggested that BEVA® 371 can separate into its individual components [4, 16, 35]. The compatibility and miscibility of the ingredients is beyond the scope of this paper; however, it should be noted, that the removability of BEVA® 371 with solvents may vary in practice. Also worth mentioning, but also beyond the scope of this paper, is the activation temperature of BEVA® 371 and 371b which is believed not to change significantly over the eight weeks ageing period. The melting temperature is governed by the EVA co-polymers and paraffin wax, which have been shown to be the more stable materials in the formulation.

Another important consequence of oxidation is the development of chromophores causing yellowing. Down [15] showed that BEVA® 371 performed poorly in terms of colour stability, yellowing in both dark and light ageing conditions. During photodegradation Laropal® K 80 has

been reported to develop chromophores [24], and, although not studied in this project, Cellolyn™ 21-E, as a rosin derivative is susceptible to colour change [31]. EVA co-polymers have been reported to discolour under more aggressive ageing conditions involving high temperatures [20, 21]. The yellowing of BEVA® 371 and 371b observed during the photodegradation was likely due predominantly to Laropal® K 80 and possibly also to Cellolyn™ 21-E, which is present in a much lower concentration.

4. Conclusions

The polycyclohexanone tackifying resin appears to be the least stable component in BEVA® 371 and 371b. Many of the oxidation products identified in the aged BEVA® 371 IR-spectra can be attributed to the ketone resin. SEC also shows an increase in molecular weight of the ketone resin component. The EVA co-polymers were more stable, showing little to no evidence of oxidation in the IR-spectra. SEC data showed a shift to a slightly lower molecular weight for Elvax® 150 after ageing, suggesting that chain-scission is occurring in the degradation process. The oxidation of the ketone resin can result in yellowing and shifts in polarity and solubility.

BEVA® 371 was originally designed as a lining adhesive to be used exclusively on the back of paintings. It should be noted that degradation reaction rates may vary depending on whether BEVA® 371 or 371b has been applied to the back or the front of a painting, since exposure to ambient conditions will be different. Residue of the BEVA® formulation applied to the front of a painting, as a consolidant, could show yellowing and shifts in solubility, requiring polar solvent mixtures, within a number of years depending on storage and display conditions. These changes may introduce complications to future conservation treatments.

BEVA® 371 (now 371b) is an important material for the conservation field. It has a range of material properties which makes it suitable for a wide variety of treatments, and a go-to material for many conservators. However, BEVA® 371b could benefit from some appropriate formulation change, and it is suggested that the ketone resin tackifier be replaced with a more stable tackifier or one that can be stabilized. Work is currently being done to test alternative tackifiers that are more photo-chemically stable and capable of giving the adhesive formulation the optimal physical and mechanical properties. The results will be presented in future publications.

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Figure Captions

Figure 1: FTIR spectra using μ -ATR of BEVA® 371 over eight weeks accelerated photodegradation. There is evidence of the formation of oxidative degradation products, as highlighted in the carbonyl region inset (approximately $1850\text{-}1550\text{ cm}^{-1}$). BEVA® 371b showed a similar trend.

Figure 2: FTIR spectra using μ -ATR in the carbonyl region (approximately $1850\text{-}1550\text{ cm}^{-1}$) of a) Laropal® K 80 and b) Elvax® 150. Laropal® K 80 shows significant formation of new oxidation degradation species, whereas the Elvax® 150 remains stable over the eight weeks of accelerated photodegradation.

Figure 3: Carbonyl peak broadening (mid-peak) of BEVA 371b and BEVA 371b with 2wt% Tinuvin® 292. The HALS provides only a moderate stabilization and after four weeks of photodegradation oxidation becomes evident.

Figure 4: Changes in molecular weight distribution, using SEC, of Elvax® 150 and Laropal® K 80; overlaid is the calibration curve (right axis- logarithmic scale of peak average molecular weight (Da)). A to d are representative points along the calibration curve corresponding to the M_p values of a) 377,400; b) 46,500; c) 2360 and d) 580.

Tables

Table 1: BEVA® 371, original formulation recipe [7]

Component	Composition	Weight (g)	Weight % solids	Comments
Elvax® 150 (DuPont™)	Ethylene-Vinylacetate copolymer (VA 32%)	500	45	Dissolve in Toluene (1000g) and Naphtha (250g) in water-bath
Ketone Resin N* (BASF)	Polycyclohexanone low molecular weight resin	300	27	
Cellolyn™21 (Eastman)	Phthalate ester of technical grade hydroabietyl alcohol	40	4	
A-C® 400 (Honeywell)	Ethylene-Vinylacetate copolymer (VA 13%)	170	15	Dissolve in Naphtha (300g) in water-bath, add to above mixture
Paraffin wax (oil free, mp 65°C)**		100	9	Dissolve in Naphtha (250g) in water-bath, add to above mixtures
Activation temperature: 65°C				

*Ketone Resin N was later sold under the tradename Laropal® K 80 (BASF)

** original material called 'Essowax 4610', from Humble Oil and Refining Company, NY

Table 2: Molecular weight averages of unaged and aged bulk BEVA® 371 components (in Da)

Component	M_P	M_W	M_N	M_W/M_N	M_Z
Laropal® K 80, 0wk	530	650	400	1.63	1030
Laropal® K 80, 8wk	990	1950	670	2.91	4500
Elvax® 150, 0wk	70300	110700	17900	6.18	275500
Elvax® 150, 8wk	39850	100500	13100	7.60	330100

Figure 1
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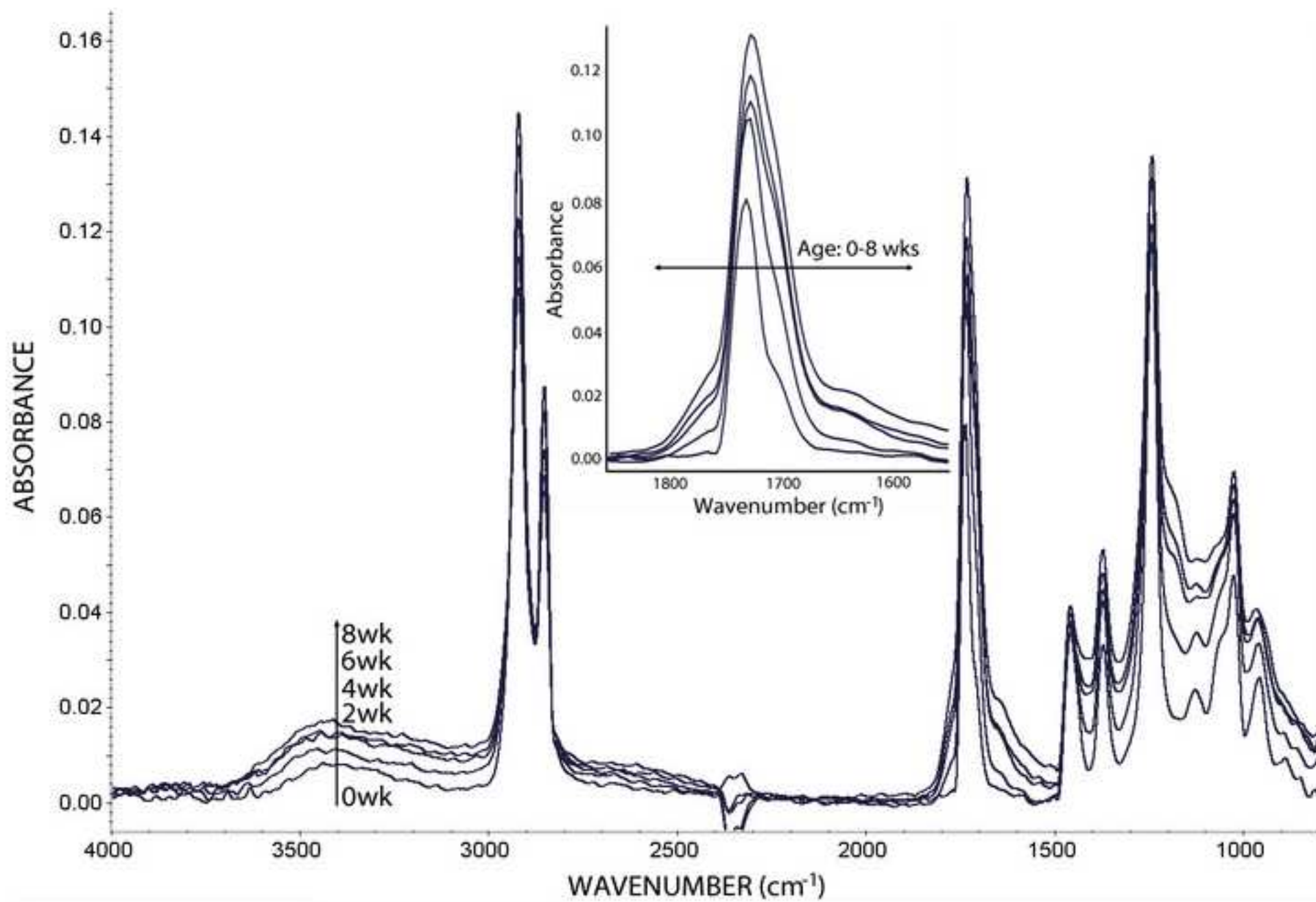


Figure 2
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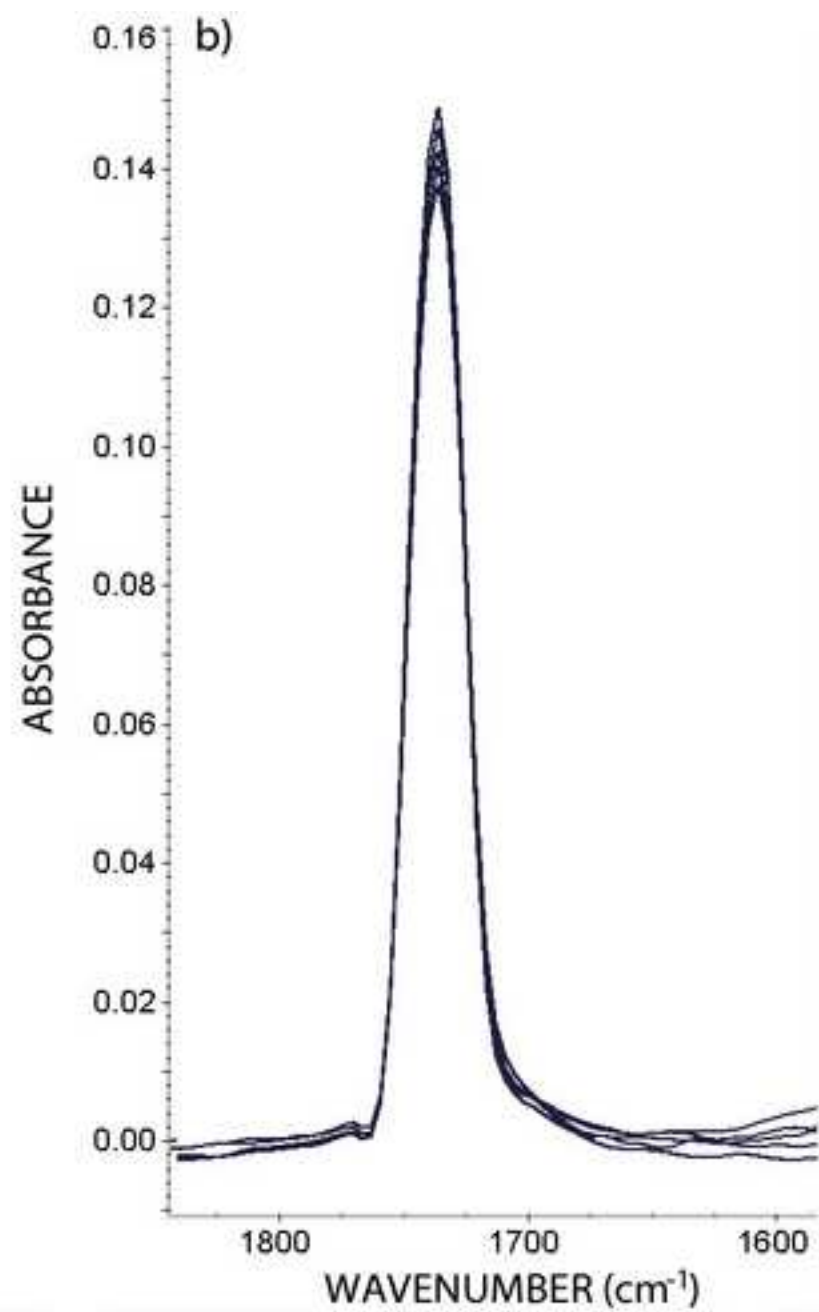
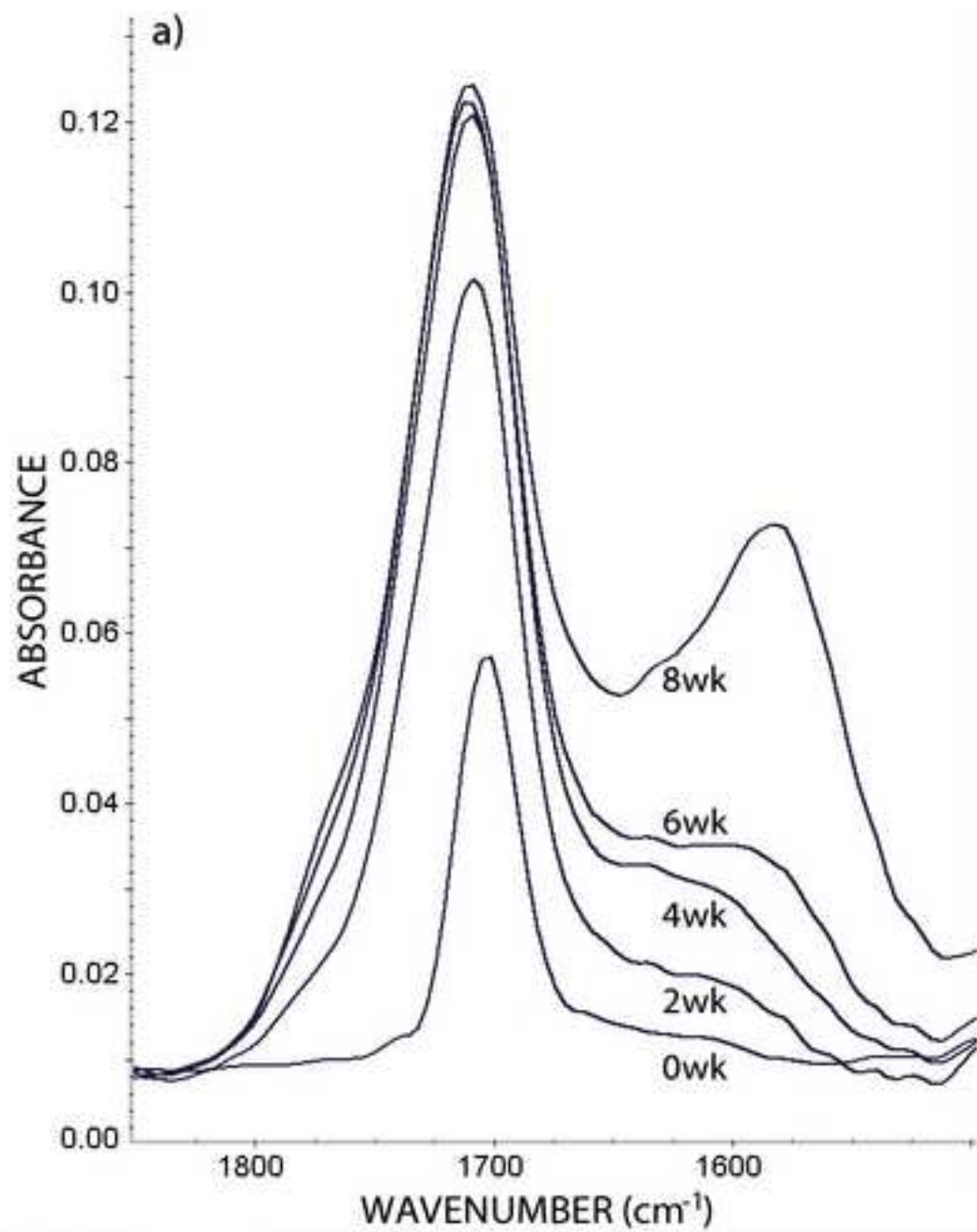


Figure 3
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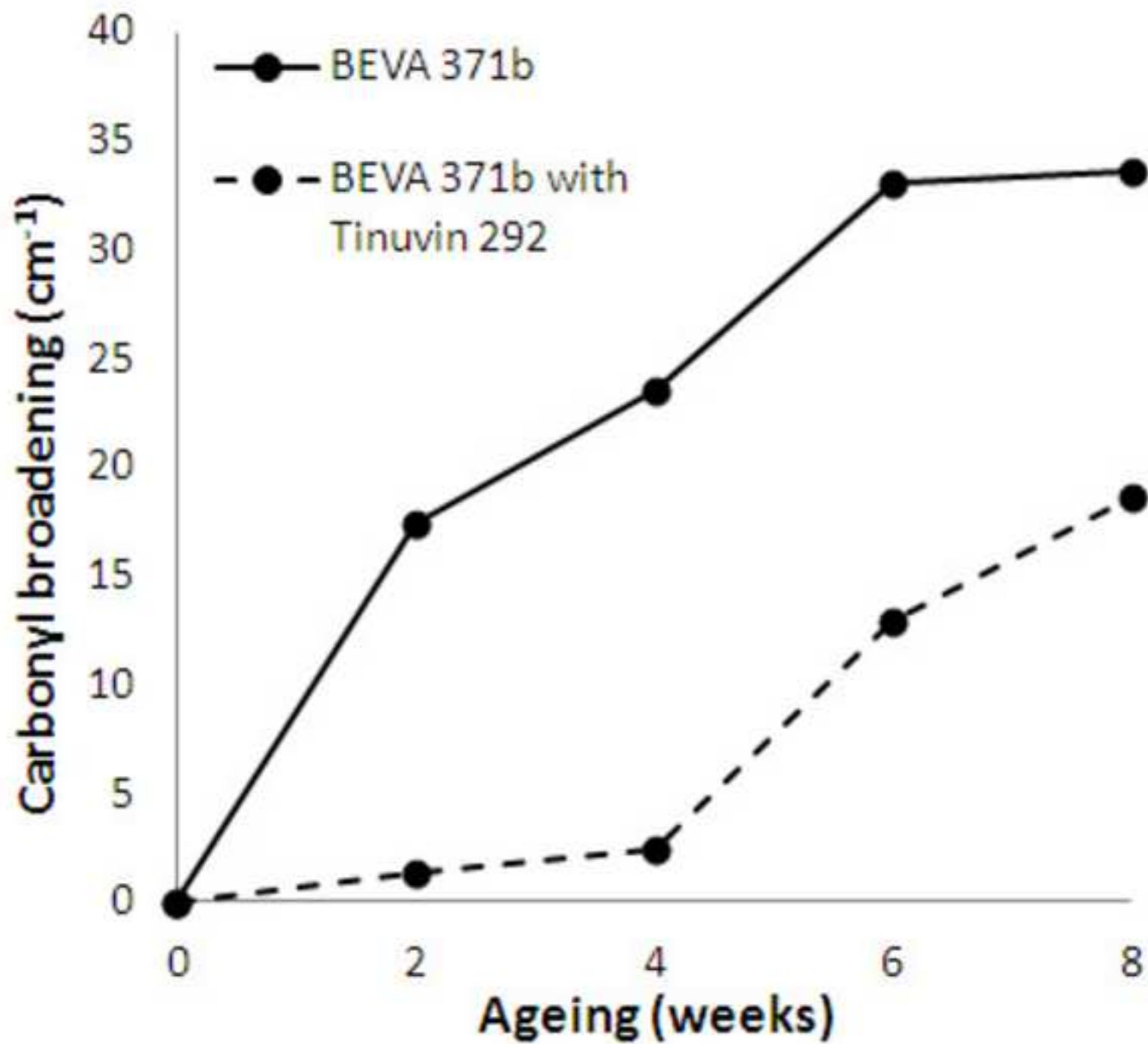
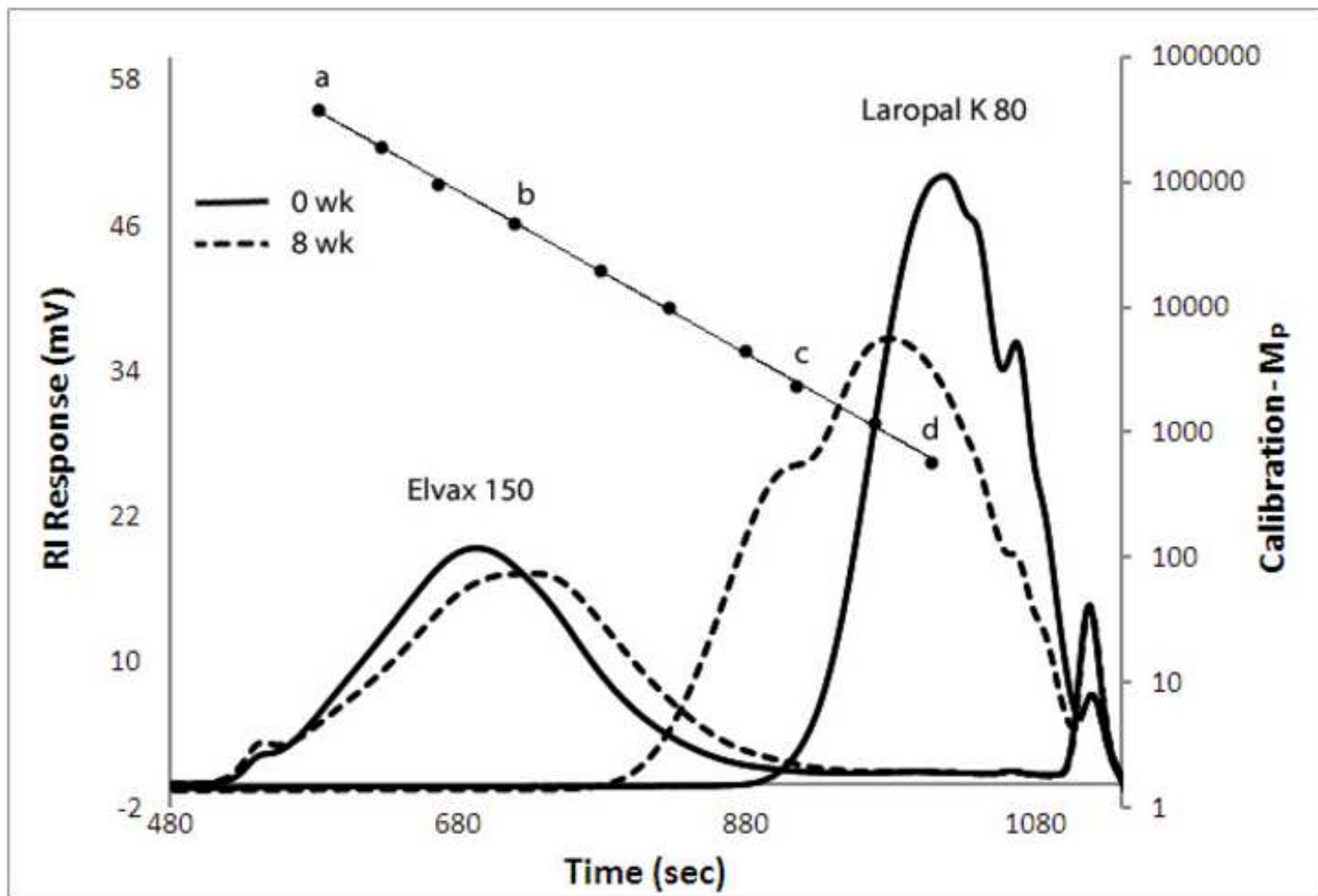
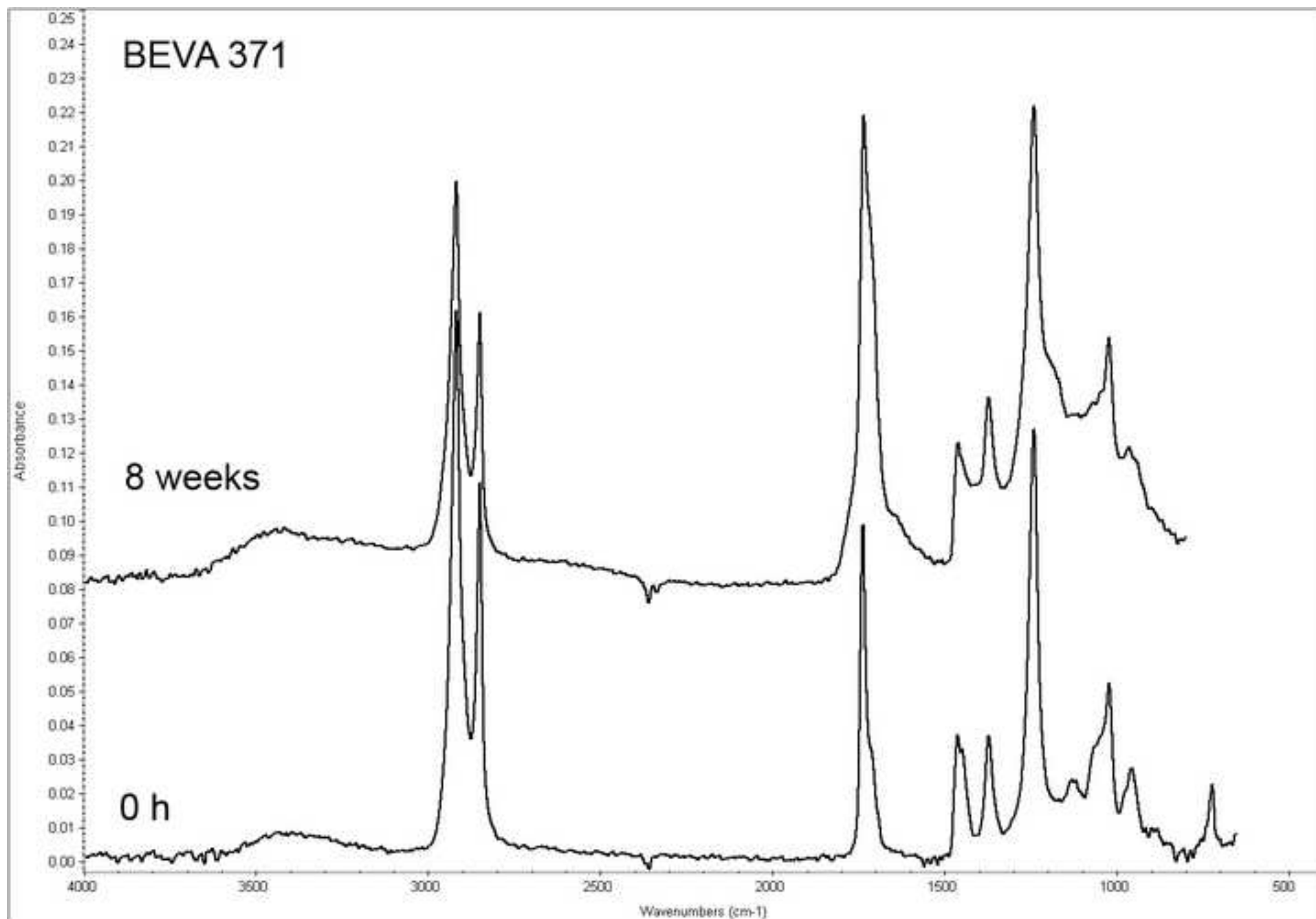
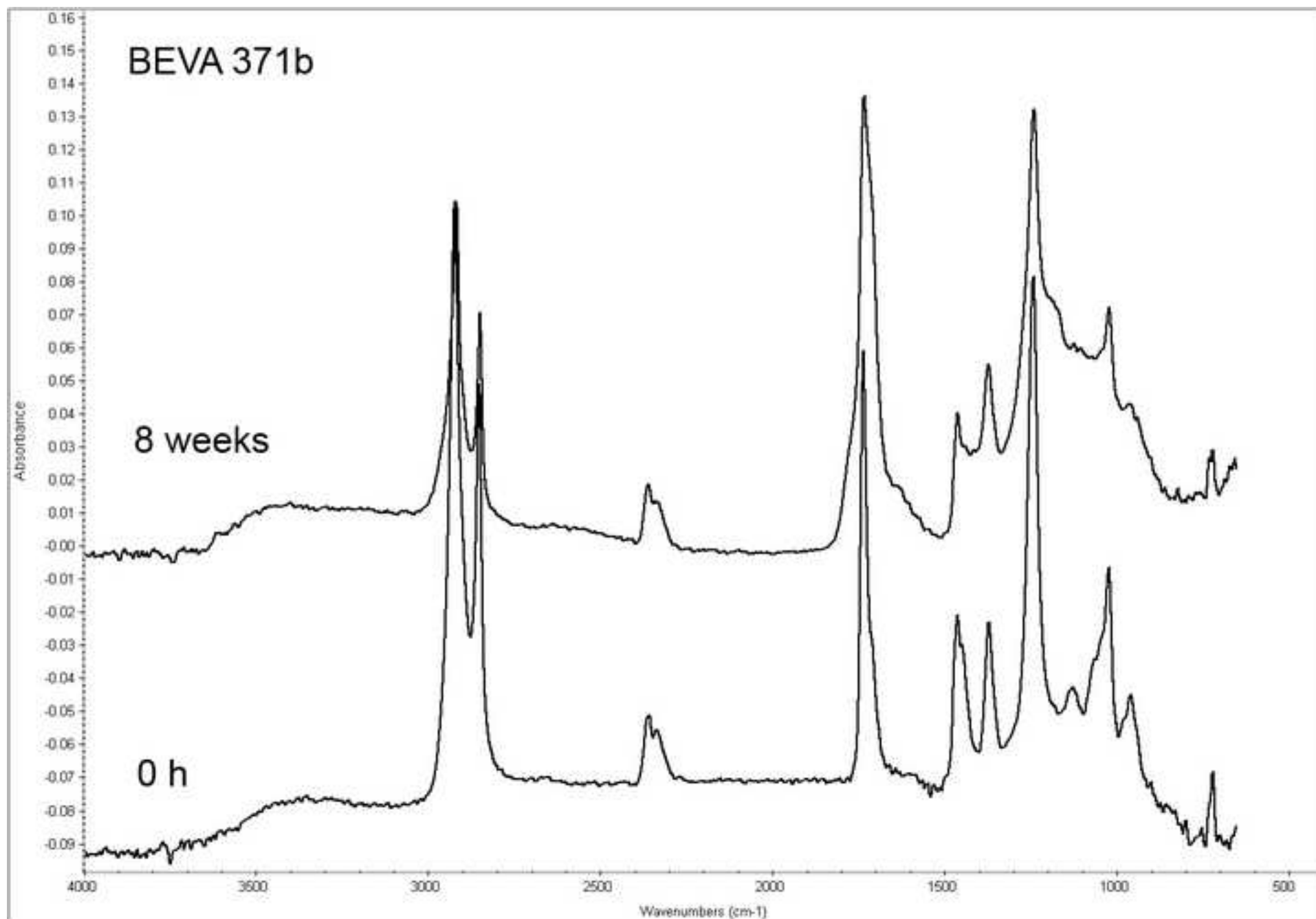
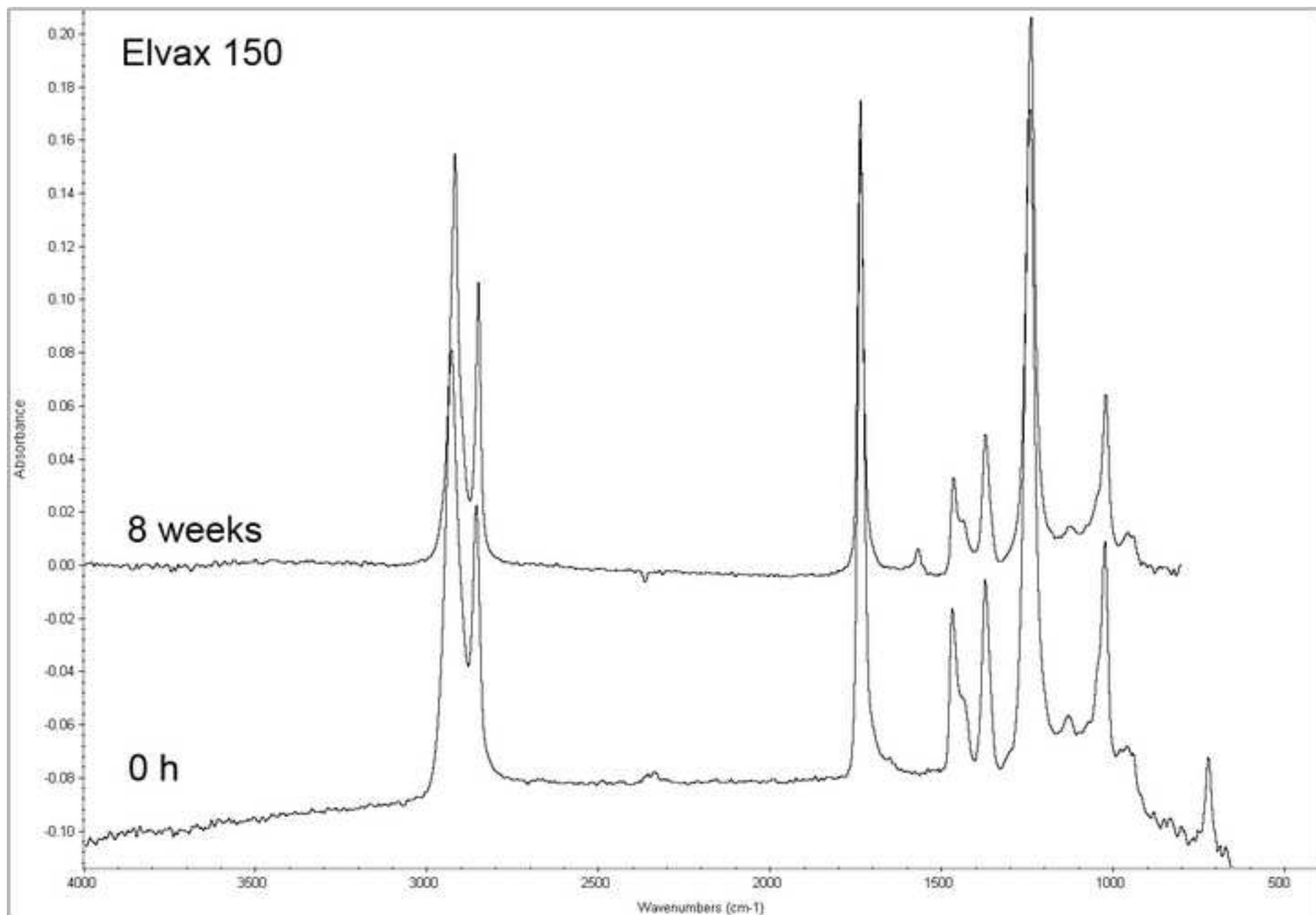


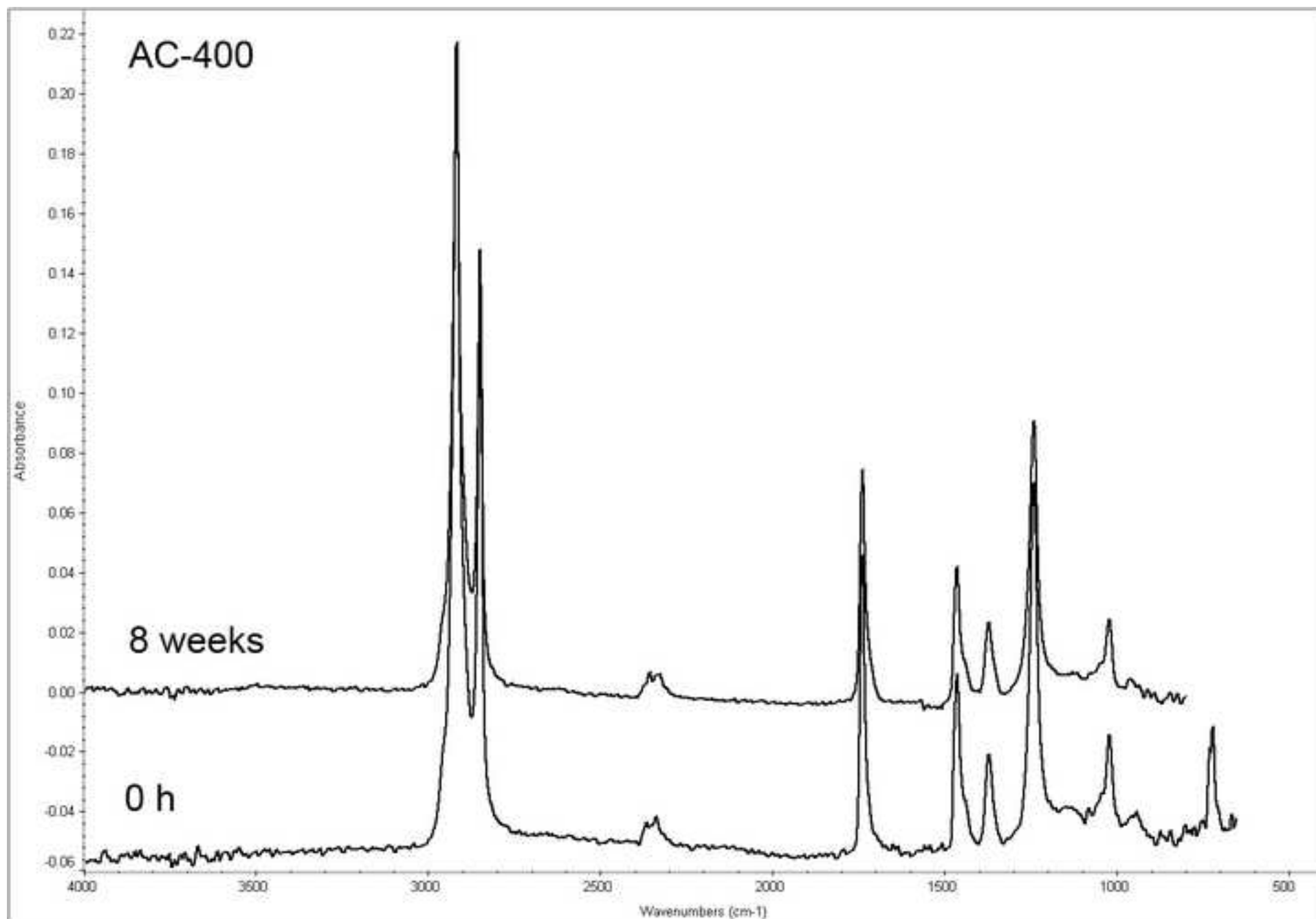
Figure 4
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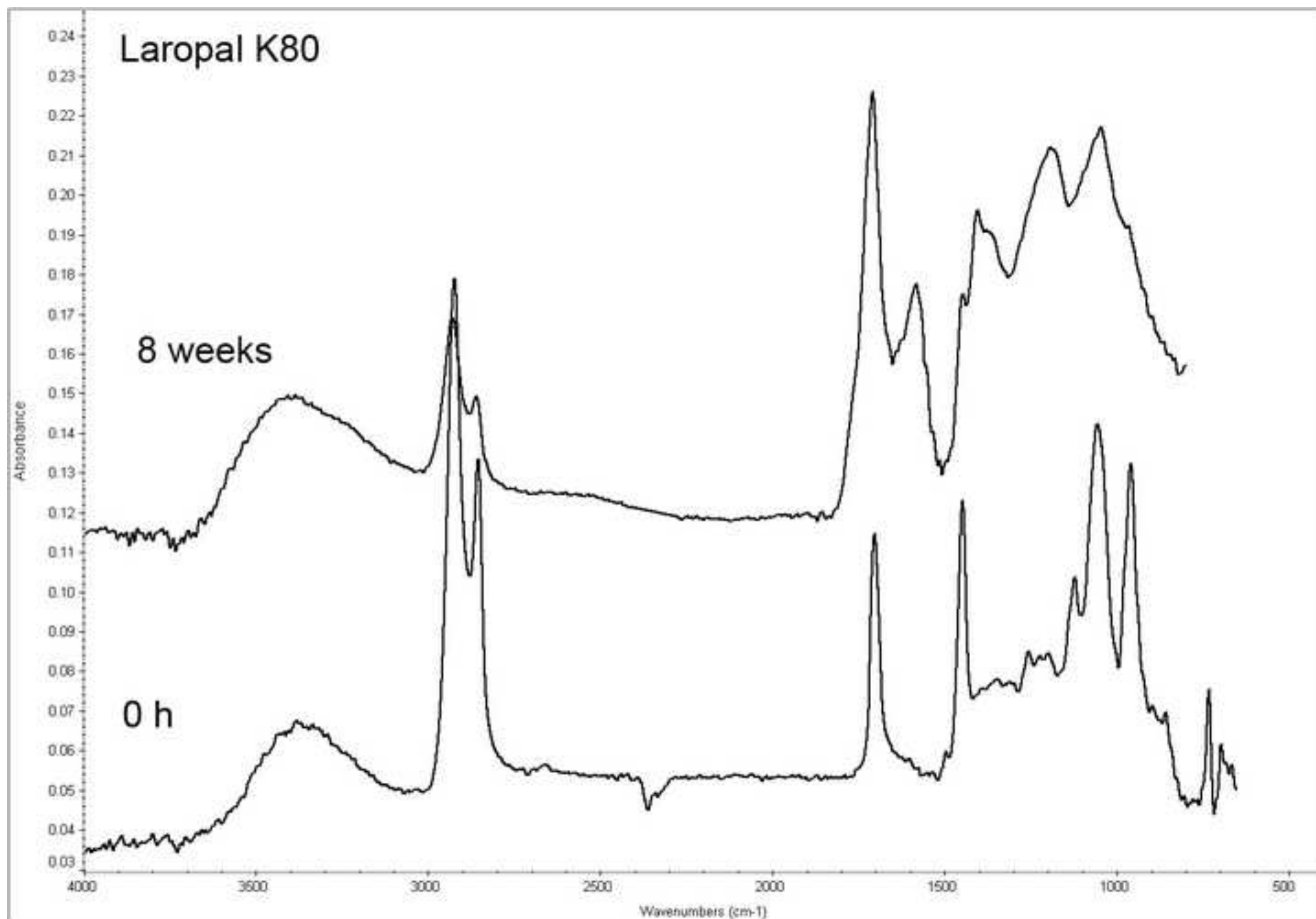












Supplementary Material to the paper:

The long-term stability of a popular heat-seal adhesive for the conservation of painted cultural objects

Rebecca Ploeger, E. René de la Rie, Christopher W. McGlinchey, Michael Palmer, Christopher A. Maines and Oscar Chiantore

FTIR spectra of BEVA 371, BEVA 371b, Elvax 150, AC-400, Laropal K80, before (0h) and after 8 weeks of accelerated photodegradation.