Kjartan Slettemark's *Time Zero*

Adhesion and Consolidation of Plastics in Art

Anja Sandtrø

Project Based Masters Dissertation

Conservation Studies

UiO **Department of Archaeology, Conservation and History**
University of Oslo

Spring 2016

Kjartan Slettemark's *Time Zero* – Adhesion and Consolidation of Plastics in Art

Anja Sandtrø

2016

Kjartan Slettemark's *Time Zero* - Adhesion and Consolidation of Plastics in Art

Author: Anja Sandtrø

http://www.duo.uio.no

Print: Reprosentralen, Universitetet i Oslo

Frontpage: *Time Zero* detail. Photo: Anja Sandtrø/2012

Abstract

Plasticised PVC is known to have less longevity than certain other plastics in a museum environment. Pressure-sensitive adhesives are also not durable. In the object of study, *Time Zero* (1982) by the Norwegian-born artist Kjartan Slettemark, both are used. The first part of this study investigates the artistic context and the current condition of the plastic collage, and reflects upon common degradation patterns in PVC and pressure-sensitive adhesives. The second part of this project is devoted to an experimental study designed to test different conservation-grade consolidants in an environment of PVC and pressure-sensitive adhesive, by artificially ageing a series of mock-ups, followed by the evaluation of ageing properties

The experiment aims to elucidate questions related to ageing properties of PVC and pressure-sensitive adhesive in conjunction with conservation grade adhesives, while exploring the suitability of this approach in order to support conservation treatment to stabilise the plastic collage *Time Zero.*

Acknowledgements

This project has fortunately been surrounded by knowledgable and willing people, and there are many to be thanked. Firstly, the National Museum for the opportunity, and head of Conservation, Kari Greve, for giving me work space and insistently encouraging me to proceed. Many thanks to Tate and not least Principal Conservation Scientist Bronwyn Ormsby, Tate, for supervision, advice and for letting me visit the Tate conservation science lab facilities and patiently helping with the FTIR and light ageing. Thanks to Senior Conservation Scientist Joyce Townsend, Tate, for guidance with the colour measurements. Thank you to the Gabo Trust for supporting the project with a travelling grant. Many thanks to Principal Engenieer Calin Constantin Steindal and the Saving Oseberg lab for running the SEM imaging. Slettemarks partner Karin Grönlund and Slettemarks assistant Marie Grönlund are to be thanked for letting me get to know the works by Kjartan Slettemark through looking and asking questions. Thanks to Jan Åke Pettersson, Director at the Haugar Vestfold Art Museum for invaluable information about Slettemark. Thanks to INEOS for providing samples of plasticisers. Thanks to Paintings Conservator Laura Homer for proof reading. Thanks to Associate Professor Nöelle Streeton for constructive feedback and supervision, and positively encouraging me to continue. Last but not the least: Tengel, Klara and Aurora - Thank you.

Table of contents

1

Images and tables

1 Introduction

Research on synthetic polymers (plastics) in museum collections was only appreciated as late as 1991 (Shashoua, 2001b: 4). In the field of conservation, the focus has been mainly on how to prevent or inhibit degradation in plastics. Thus we are still missing guidelines on how to execute invasive conservation treatments on plastics.

Due to the relatively brief shift from an induction phase following manufacture, to degradation and irreversible damage (Shashoua, 2008a: 9), the poor state of plastic objects in collections may come suddenly and slightly unexpected to the collector or custodian. One way to identify the degradation and destabilisation of the artwork is to look at the environmental conditions in which it has been stored and displayed, and to adjust the environment and handling accordingly – a subject which has been in the attention of conservators for a while. The next step of action, when the improvement of environmental factors alone is not adequate to save the object, invasive techniques may be introduced. Adhesion, consolidation and cleaning are regarded as high-risk activities when applied on plastics (Shashoua, 2008b: 15). This rather passive approach has resulted in poor development of practices in this field (Shashoua, 2008b: 12). This is supported by Horie (Horie, 2011: 4 - 5), stating consolidation to be one of the most invasive and irreversible treatments, and also the least understood, calling for advances in this field. This study will contribute to the development of guidelines, as well as pointing at risks involved in the process of joining plastics.

The object in focus for this study, *Time Zero (1982)* (Image 1 and Image 2) by Kjartan Slettemark (1932–2008), has been a museum collection in Norway since 1982. The collage is made out of several types of plastic film glued together by a self-adhesive backing and by various tapes. The overall impression when examining *Time Zero* is that there is a lot of excess adhesive around the films. In some areas the adhesive 'tide-lines' are as wide as approximately 2 cm. The films are buckling and have tears and splits. In areas of buckling the films have lost contact with each other, creating lacunae. Some of the tapes have completely lost their contact with the rest of the artwork, and are only attached at the ends. When examining the adhesive layer of the films under the microscope, the adhesive has a jelly-like consistency, almost liquefied.

Searches in publication databases produce no evidence of material examination or conservation of Slettemark's plastic art, except on *Trappan* and *Soul Food* (Moderna Museet, Stockholm) in 2007 (Nord and Tonner, 2008). This examination led to a series of tests in which the polystyrene parts were tested for adhesion (Winther et al., 2013). The study concluded that there is a need for more research in the area of adhesion of plastics. When the National Museum for Art, Architecture and Design (National Museum) in Oslo scheduled a retrospective exhibition of the works of Kjartan Slettemark in 2013, it provided the opportunity to study his plastic-art as a whole, and to interview the people closest to the artist. For the National Museum, this project was the first step towards a directed awareness of preservation needs for plastics in the ever-growing collection.

Image 1. Front view of Time Zero (MS-02789-1988) (1982) by Kjartan Slettemark. Photo: Frode Larsen, National Museum of Art, Architecture and Design/ ©Slettemark, Kjartan/BONO

Image 2. Verso of Time Zero (MS-02789-1988) (1982) by Kjartan Slettemark. (Photo: Frode Larsen, National Museum of Art, Architecture and Design/2012)

1.1 Objectives

Studying *Time Zero* and its context may be beneficial for further research on Slettemark's plastic artworks. Prior to the 1980s, Slettemark made a significant number of polyester artworks that also need stabilising to inhibit further degradation. The study may also contribute to guidelines for preservation of other plastic collages similar to *Time Zero*. Research into conservation methods and materials applied on flexible synthetic polymers may be valuable to custodians of such art. One of these materials, poly (vinyl chloride) (PVC), has been identified as one of the most problematic polymers in collections, due to the process of degradation (Quye and Keneghan, 1999: 127; Shashoua, 2008a: 15). Furthermore, the polymer has several challenges when it comes to adhesion due to secondary plasticisers migrating out to create a sticky surface

(Skeist, 1977: 657 ; Shashoua, 2008a). To establish the situation in this field, Waentig states: 'The active restoration on poly vinyl chloride is still in its infancy' (Waentig, 2008: 254). This project aims to address the challenges in this field by focusing on adhesion and stabilisation of PVC and pressure-sensitive adhesives (PSA), and the interaction of adhered materials. Furthermore, the project aims to elucidate aspects of the following question: What are the optimum means to stabilise *Time Zero*?

To get a better understanding of the materials, the degradation processes, the weak areas, and some indication of why the degradation processes occur in the way they do, the project identified and characterised the materials in *Time Zero* by implementing interviews, literature review, visual examination and documentation of the films, descriptive information of each film, as well as both simple and advanced analytical techniques.

1.2 Dissertation structure

The first chapter presents an overview of examination methods applied on *Time Zero*, as well as a strategy for the experiment. Research questions are outlined at the end of this first chapter. In the second chapter, the study-object, *Time Zero*, is described in terms of materials, historical context and condition. Chapter 3 gives an overview of the properties of plasticised PVC and pressure-sensitive adhesives (PSA). Aspects of re-joining delaminated plastic films have been explored in Chapter 4, presenting an overview of some principles in designing and evaluating ageing studies of polymers. By aiming for a simple experimental design, the possibilities, but also some of the limitations within such research are discussed. The fifth chapter describes the experimental design of this project, while in the sixth chapter the results from the experiment are presented. Chapter seven discusses the results in relation to research questions and adhesive requirements. The final chapter is a conclusion from the project, also looking at topics to be further explored.

The scope of this project includes identifying both degradation challenges in the study object *Time Zero*, and methods to test and evaluate adhesives to be used to adhere plastic art. As far as possible, advanced analytical techniques are avoided in order to keep the interpretation of results at a level not requiring deep scientific understanding, and to explore the possibilities that may lie within an average conservation department when it comes to laboratorial facilities. The scope does not include discussions of results in relation to significance, artist intent and methods of application. Nor does it explore rheology and bonding physics.

1.3 Method

This project was divided into three main sections: Investigations of the garbage-collage *Time Zero*; experimental design into the ageing properties of plasticised poly (vinyl chloride) and pressure-sensitive adhesive (PSA) in conjunction with a conservation grade adhesive; evaluation and discussion of results from the experiment, related to the conservation challenges and possible paths for conservation treatment of *Time Zero*.

1.4 Project overview

1.4.1 Interviews, photographs, films, literature – Time Zero

Slettemark´s assistants and friends were interviewed to learn about the artist's materials, working methods and intent, such as preference of materials and views on display and conservation issues. The interviews have been supported by a literature review on the artist, with particular focus on *Time Zero* and the period around the early 1980s. Film footage by Jørn Hole and Pierre Stahre gives a valuable historic context to the materials and techniques in the art of Kjartan Slettemark. Early documentary photographs of *Time Zero*, exhibition catalogues, 'sop-collage' in other collections and conservation reports are important supplements to describe the condition and process of degradation. Finally, the Kjartan Slettemark official web-page (www.kjartan.se) is a great resource, and has several images of other 'sop-collage'.

1.4.2 1.4.2 Examination of Time Zero

The aim of the documentation is to try to understand the artist's working processes and the work's layer structure in order to detect any flaws or weaknesses within the structure. *Time Zero* was examined visually in direct light, raking light and UV-light with the naked eye and by stereomicroscope. Furthermore, *Time Zero* was photographed, front and reverse, in studio lighting and UV-lighting. The plastic film cuts that constitutes the surface face and reverse were all given an individual ID, described and characterised based on terminology developed during the POPART-project (Lavédrine et al., 2012, p. 296). The purpose of describing the characteristics and damages is, apart from documentation, to give an overview of the severity of damages, and to assess if any damages are more frequent than others. The class of damages, as in accordance with the POPART damage atlas (POPART, 2012), may indicate whether the material or the handling and storage are the main threats to its stability. The most prominent characteristics are presented in Appendix 1.

1.4.3 Sampling – from Time Zero

In order to obtain a deeper understanding of the material composition and chemistry, A total number of 13 micro-samples were removed from the front face and the verso of the collage, using a scalpel. The samples were labelled and kept between two microscope glass slides, closed with phthalate-free tape. The selection was based on the criteria of obtaining a wide variety of sample material, but also from the materials most widely represented in the artwork. Particularly weak or unstable areas of materials were also selected for sampling. In addition, three coloured micro-samples were collected for the destructive Beilstein test. A table of the micro-samples and results is presented in Appendix 3.

1.4.4 Microscopy – on samples from Time Zero

A selection of micro-samples of transparent contact films were viewed in an Olympus BX51 polarising light microscope at the Conservation department at the National Museum, Oslo. Polarising light microscopy was used to compare the part component (carrier side) of the micro-samples to find if some samples are of similar manufacture. Further, crystallinity has been explored to establish refractive orientation (biaxial or monoaxial orientation of the carrier film). Finally, attempts were made to differentiate the samples by mode of manufacture, i.e. cast or rolled by calendering. The difference in crystal orientation may also affect the ageing properties with regards to how tearing occurs as well as optical properties.

1.4.5 Simple testing – on samples from Time Zero

A simple, yet destructive technique, the Beilstein test, was explored to get a preliminary impression on whether the plastic films in *Time Zero* are PVC. A sample was placed on the tip of a red hot copper wire and put into the flame of a Bunsen burner. The presence of chlorine is indicated by a green flame when a sample is burned, thus confirming PVC. The test was performed as described in the CCI-notes 17/1, Waentig (2008: 396) and Shashoua (2008a: 127).

Image 3: Beilstein test. Green flame indicates the presence of chlorine. (Photo: Anja Sandtrø/2014)

1.4.6 Advanced analytical techniques – on samples from Time Zero

To give a more precise characterisation of polymers and additives present in the *Time Zero* films, the micro-samples were analysed using a Perkin Elmer bench top Fourier Transform Infrared Spectrometer with an ATR attachment at the University of Oslo, and a Thermoscientific Nicolet iN10 MX microscope with a single diamond cell at Tate, London. 64 scans were collected at a resolution of 4 cm^{-1} across a wavenumber range of 4000 to 600 cm^{-1}. Data was processed using Omnic 8 software. Both film and adhesive was analysed, and the functional groups were compared in both scans. FTIR has long been the preferred method of identifying plastics (Mills and White, 1999: 138-139) and has become one of the common and more available instruments in conservation laboratories. The method is suitable for identifying the polymer, fillers, plasticisers, and some additives. The minimum sample size required is 0.1-1mm^3 (Lavéndrine et al., 2012: 105). FTIR in combination with Differential Scanning Calorimetry (DSC) or Pyrolysis-Gas Chromatography Mass Spectrometry (Py-GCMS), may give an even more specific characterisation of the synthetic polymer (Lavéndrine et al., 2012: 105). However, this study has focused on exploring the possibilities and limitations in FTIR. The results are presented in Appendix 2 and 3.

1.5 Experimental on mock-ups

Based on the finds from the preliminary research, an experimental set-up was designed to understand the physical and chemical processes in both the carrier and the pressure-sensitive adhesive during ageing, and to evaluate if the addition of a consolidant acts as a stabilising agent to the material. The experimental is designed to explore some commonly used methods of examination and testing on plastic composites. A series of mock-up samples were created, aged and tested to simulate the ageing and possible treatments of *Time Zero*. A further description of the preparation of the samples is given in chapter 5.

The main purpose of the experiment is to test the adhesive compatibility with the pressure-sensitive products of book-protective films and window-decoration films by mimicking a museum environment. By studying the deterioration process mimicking deterioration after the work has been acquisitioned into the museum, the conservation treatment decision making may be supported. Another aim is to study the effect of introducing a second adhesive to an aged adhesive sandwiched in between two impermeable plastic films.

The experiments were performed in the following stages:

- Measuring contact angle of samples prior to ageing
- Ageing of mock-up samples, in UV-free lighting, and in a natural, dark environment
- FTIR characterisation of mock-up samples before and after ageing
- Measurement of surface pH before and after ageing [1]
- Measuring colour before and after ageing
- Mechanical testing after ageing
- SEM imaging of aged mock-ups

Initially, the experiments were designed to compare ageing properties in consolidated samples on a PVC carrier to a poly propylene (PP) carrier. However, as FTIR analysis of samples removed from *Time Zero* does not reveal any poly propylene present as a surface film, the results from this part of the study are not presented. Furthermore, the

---

[1] The inconsistencies of surface pH measurements are recognised.

difference in ageing in the two carrier materials lead to more questions. A brief summary of the results from the PP film carrier is presented in chapter 6. The results are tabulated in Appendix 5, Appendix 7, Appendix 9 and Appendix 13.

1.6 Research questions

In order to make informed decisions about the means by which to stabilise the artwork, the following needs to be further investigated:

- What are the driving forces behind the degradation process that cause loss of adhesion?

One of the aims was to elucidate the intrinsic processes and external factors affecting the degradation of *Time Zero*.

- What is the effect on the original bond when introducing a new adhesive to the degraded material?

The methods of evaluating accelerated ageing were meant to reveal some aspects of interaction between the adhesives and the PVC carrier.

- Can the addition of a consolidant stop or slow down further cold flow of the adhesive?

One main objective was to determine whether it is possible to consolidate the existing pressure-sensitive adhesive between two films of plasticised PVC.

- What are acceptable changes of materials introduced to *Time Zero*?

The project will attempt to work through the research questions with the following hypothesis in mind: ***Migration of plasticisers from the plastic films into the adhesive layer can be causing creep and deformation of plastic films, and cold flow of adhesive.***

2 Research object: Kjartan Slettemark and *Time Zero*

The Norwegian-born artist Kjartan Slettemark (1932–2008) has an extensive body of work, as he dedicated his life to art – eventually embodying *Art, being Art* (Slöör, 2009: 184). Slettemark started experimenting with plastics in his art after attending a plastics-course in 1964 at the Kungliga akademien för de fria konstnerna (the Royal Art Academy) in Stockholm (Grönlund and Grönlund, 2012b).

2.1 *Time Zero*: Materials and construction

The plastic art of Kjartan Slettemark may roughly be divided into two eras. In the early period – in the 1960s and 70s –he explored casting and modelling of plastic resin (polyester). He mixed the plastic material and the colours himself, and the period is thoroughly described by Stina Högkvist in *KjARTan the Art of being Art* (Högkvist, 2013). In the later period – from the late 1970s – Slettemark had a focus on plastic films, collages, assemblages and found objects. This is the period – represented by *Time Zer*o - where he used found materials and readymade products which he processed.

Time Zero (Image 1 and Image 2) is a collage (200x227cm) made of mixed materials. Slettemark called this type of collage ‘sop-collage’ (garbage-collage), as he used leftovers from posters, window-stickers, signs and various items found in garbage-skips and leftovers from his studio. The ‘sop-collage’ in the National Museum collection was produced in 1981-82, made from scrapped materials from his solo-exhibition *TITTA JAG SER* in Norrköping Art Museum in 1980 (Grönlund and Grönlund, 2012b). The backing is mainly coloured window-film, and the face-side is made of lettered window-foil, cut out strips from posters and test-prints, NCS colour-samples, film-negatives, cassette-tape ribbon, hair, wallpaper, bottle protection sleeves, vacuum-cleaner bag, paper cut-outs, mini paper-collages, various types of sticky tape, coloured lamp-filters. All these items are adhered to the backing foil and laminated with different qualities of transparent self-adhesive book-film. In the period 1980–1982 several ‘sop-collage’ were made. However only a few are known to remain (The National Museum: one, Trondheim Art Museum: one; Karin and Marie Grönlund: four–five) (Grönlund and Grönlund, 2012b).

The collage was on display in Oslo, at Kunstnernes hus, in 1982, when he finally made his artistic break-through in Norway. *Time Zero* was purchased by the National Gallery in 1982, together with the controversial *Av rapport fra Vietnam. Barn overskylles av napalm, deres hud brenner og de dør* (1964), also known as 'The Vietnam Painting', and six enamels portraying Nixon (Nasjonalgalleriet, 1982). *Time Zero* was transferred to the Museum of Contemporary Art in 1988, and is now part of the National Museum collection in Oslo. The purchase marks the long-awaited acceptance and acknowledgement of Slettemark's art in Norway.

2.1.1 Theme

Time Zero was created in a period in which Slettemark was very interested in video-art, and represent objects and themes appealing to him at the time: a dolls' head, eyes, paper strips, letters, text without a beginning or ending, strong colours, shiny surfaces, botanical forms, collages, Polaroids. Even the title 'Time Zero' represents a new era ('year nil'), underlining the significant shift in his artist career at the time. Slettemark often used the concept 'time zero' in connection to Polaroid imaging, video and techniques for reproduction (Pettersson, 2013). The title may even be inspired by a new Polaroid format introduced in 1980: 'SX-70 Time-Zero Supercolor'.

2.1.2 Process

Several sources claim that the process –creating the art –was a very important part of the art itself (Grönlund and Grönlund, 2012b; Pettersson, 2013). Slettemark is described to have worked more or less intuitively and in a trance when his art was created (Slettemark et al., 1982; Grönlund and Grönlund, 2012b). He was said to undertake contemporary archaeological excavations, incorporating the finds into his artworks (Slettemark et al., 1982: 32; Husabø, 2009) s. 154). The Norwegian newspaper Dagbladet describes in a report from 1982, how Slettemark swept together the leftovers from the days' work, and laminated it all in plastic (Dagbladet, 1982).

2.1.3 Perception

Slettemark did not make art with a clear opinion on how it should be 'used' or displayed (Slettemark et al., 1982: 5). The sources explain how he opposed to framing of his artwork – also in a wider sense of the word (Grönlund and Grönlund, 2012a). In the art-film ”Videovoodoo” (1981), representing a performative aspect of Slettemark's work, *Time Zero* is assembled and displayed as part of a ’wall’ in the ’jungle of garbage’ (’sopdjungeln’), as it was exhibited in Trondheim and Oslo in 1982 (Pettersson, 2013). In a previous conservation report, Slettemark is also to have suggested the possibility of displaying *Time Zero* with light beaming through the collage from the reverse (1999).

2.1.4 Materials

Slettemark experienced a great sense of freedom through the use of plastic materials, in the sense that norms of how art should look were abolished, and everything was permitted (Slettemark et al., 1982: 5). Even though he used plastics in his artworks, it was neither an ideologic motivation behind his choice of material, nor a desire to explore the possibilities within plastics, but rather because plastics were readily available- and often for free – and because the materials and found plastic objects had clear, bright colours, were malleable and appealed to him (Slettemark et al., 1982: 5). ‘There is an energy in disclaimed material – they have a value proceeding that of garbage’(Denkler, 2001). In *A Retrospective Peep-Show’* Jan Åke Pettersson describes Slettermark’s relationship to plastics: ‘For Kjartan, plastic represented the abolition of norms concerning what a work of art should look like. It moved the boundaries of creativity to realms where nothing was true and everything was permitted.’ (Pettersson, 2012)

2.2 Examination of *Time Zero*

As described in the introduction, *Time Zero* has been examined visually, in different lighting, and chemically by FTIR. Results from the FTIR are presented in Section 6.2, and tabulated in Appendix 3. The FTIR spectrum report is presented in Appendix 2. A visual overview of condition is presented in Appendix 1.

According to the National Museum collection database, *Time Zero* has not been frequently on display. According to previous conservation reports, the artwork is fragile, but no physical treatment is reported. We now know that *Time Zero* was purchased from the exhibition ’JAG SETT’ (‘I have seen’) at Kunstnernes hus in 1982, and has been kept in museum storages for the most part since then. The collage has thus not been exposed to risk handling, indicating other factors to be more prominent influences to the unstable condition. Old readings from the museum storage suggests a winter-RH of 25-35%, and summer-RH of 35-50%. Temperature constant at 20°C. During periods of exhibition, the environmental conditions have been less controlled, both in terms of temperature and relative humidity[2]. As with several of Slettemark's works, *Time Zero* needs special care and handling. This is due to the fact that Slettemark refused to frame his art – in every sense of the word. The large artwork is not mounted on a supporting material, but is now attached to a Plexiglas hanging-system developed in the museum in 1999. *Time Zero* has been stored in a vertical position since it was purchased for the collection. In 2011 a travel frame with a backing support was produced to ease handling as well as facilitate horizontal storage.

Front face *(Image 1): Time Zero* is composed of 25 contact films on the front face. The majority of the surface films are transparent, but a few coloured films are also present. In addition, there are several different tapes on the surface, as well as areas of plastic material without a pressure-sensitive adhesive side. A few smaller areas have PSA completely exposed. The large films are oriented in a vertical position, as if rolled downwards from a off-the-shelf contact film. Smaller pieces of film are adhered unsymmetrically and in a random manner on top of the larger films. The edges of the collage are flimsy and dirty, containing small particles of dust and dirt. The bottom half of the collage has an overall dirty appearance. Some films have small tears, and most films are buckling. The possibility of getting a clearer image of the texts and lettering written on the surface of the films on the front face was explored by examining the surface in UV-light. In addition, a UV examination may have revealed any proteinaceous material present (Appendix 1). Examination of the surface in UV-light did not give any additional information on the condition of the films. A map of the front face films, tapes and UV-image of the front face is given in Appendix 1.

Verso *(Image 2):* The verso is composed of approximately 26 contact films, mainly coloured; yellow, green and blue. Some transparent films are also present. The verso films are not all oriented in the same vertical manner as the front films, suggesting the original format of these films must have been wider, and not from standard off-the-shelf products, but rather from decorative films used on windows and walls, as described by

---

[2] 'Kunst 4. Verk fra samlingen 1950-2007' (2007-2009); 'KjARTan Slettemark. Kunsten å være kunst' (2013/2014).

Grönlund and Grönlund (p.c. 2012b). The original hanging system is still in place on the verso: two cords of polypropylene adhered to the back in between the contact films and secured with yellow masking tape. The masking tape is well adhered, apart for a few loose ends. In these areas of detached masking tape, white residue from the tape is visible on the surface of the contact films. A map of the verso surface films and UV-image of the verso is given in Appendix 1.

2.2.1 *Characterisation of materials*

The materials within Time Zero were further examined and characterised by microscopy and FTIR.

2.2.1.1 Microscopy of Time Zero micro-samples

Some similarities in two of the micro-samples (TZ03 and no TZ04) (Appendix 3) are found in the shapes and sizes of fillers (tiny 'donuts'), and biaxial orientation. One surface film, represented in samples TZ07 and TZ13, appears to be more stable than the others in that it has less prominent adhesive failure, and does not have any adhesive tide lines suggesting the material has not shrunk, unlike the others. This film most likely has an acrylic polymer adhesive, which differs from several of the other films which have a PVA-type pressure-sensitive adhesive. The coloured films from the reverse also have less adhesive tide-lines, and consist of an acrylic type PSA (all confirmed by FTIR at Tate). When viewed in polarising light microscope, tiny, coloured particles are sparsely distributed within the transparent polymer structure. There are no signs of lines or streaks indicating a calendering process, thus suggesting the film represented in sample TZ07 and TZ13 is cast rather than calendered. This production method is said to be more stable to deformation and has a higher tear-resistance (Smith, N.Y.).

2.2.1.2 FTIR of Time Zero micro-samples

The film carriers identified in *Time Zero* are poly(vinyl chloride), one film was identified as degraded cellulose (acetate) with adhesive backing, and one film was poly propylene without any adhesive residue (Ormsby, 2014). Phthalates are identified as the most common plasticiser in the carriers of *Time Zero*. The adhesives were characterised to most likely be butyl acrylates, and PVA with a phthalate component. However, one sample seemed to contain a rubber component.

Image 4. Close-up of adhesive tide-lines. (Photo: Anja Sandtrø/2014)

3 Material properties: plastics and adhesives

3.1 Introduction

Conservators need to ensure safe conservation treatments, and to keep correct and updated records on the objects in a collection. The wide variety of plastics respond just as differently to humidity, light, temperatures and physical impact as other organic materials, thus the knowledge of the specific class of plastic, its manufacture and history is essential (Coxon, 1993, p. 396; Oosten, 1999a, p. 70). Some plastics may even be harmful to other objects and materials in the collection – sometimes called "malignant plastics" (Williams, 2002), while other plastics are susceptible to auto-catalytic degradation and need constant monitoring (Morgan, 1991: 43). This chapter describes some common aspects of plastics, giving a more in-depth presentation of physical and chemical properties, manufacturing processes and degradation patterns of PVC and PSA.

3.2 The properties of plastics

The properties of plastics are described in detail in Ashley-Smith (1992); Brydson (1999); Shashoua (2008a); Horie (2010). However, some key facts are presented below, that may be relevant when identifying and characterising polymers with analytical methods such as FTIR.

Plastics are made up by monomers (single parts), which are repeated to produce polymers (many parts). The way in which monomers are linked together influences the property of the polymer. If the polymers form long chains, they may be categorised as thermoplastics (Ashley-Smith, 1992: 25-44; Barker, 1999: 23-33). These polymers respond to temperature by flowing at certain temperature levels, but remain in a solid state below this specific temperature (Brydson, 1999: 23). If the polymers form a network, they may be categorised as thermoset plastics. Thermosets are branched molecules joined together in a cross-linked three-dimensional structure, and are less affected by heat, solvents or mechanical forces (Ashley-Smith, 1992: 35). A functional group is a combination of atoms within a molecule. Every class of polymers have their specific functional groups present. Each functional group will absorb infrared radiation at the same frequency regardless of the rest of the molecule (Derrick et al., 1999: 11). Crystallinity describes the way in which the polymers arrange themselves. The formation of crystallites happens during manufacture or by physical manipulation and degradation (Shashoua, 2008a: 95). Some polymers may be highly crystalline, while others are dominated by the more random amorphous structure (Ashley-Smith, 1992: 40-41), and some polymers do not have the ability form crystallites at all (Shashoua, 2008a: 95). The grade of crystallinity affects the material strength and interaction with light waves (Shashoua, 2008a: 94-95). In order to modify and tailor plastics for its specific use, additives are introduced in the manufacturing process (Barker, 1999: 27). These additives are organic or inorganic compounds with the purpose of optimising properties such as softness (plasticisers), resistance to light (antioxidants), colour (pigments), bulk (fibrous and non-fibrous fillers), resistance to fire (fire retardants) (Barker, 1999: 40).

3.3 PVC – composition and manufacture

As described in Chapter 2 *Time Zero* is mainly made of window decoration films and films for protecting books found on site, and acquired from stationary shops (Grönlund and Grönlund, 2012a; Pettersson, 2013). Some of the films are transparent, other films are opaque and in various colours. FTIR analysis suggest that the majority of films are made of plasticised poly(vinyl chloride) (PVC) and other vinyls, with an adhesive backing.

Poly(vinyl chloride) was introduced on the market in 1930-1940 (Brydson, 1999: 6). By year 2000 PVC was one of the most used (by tonnage produced) plastics materials in the world together with polyethylene (Brydson, 1999: 6). PVC is made from ethylene, chlorine and oxygen (Shashoua, 2001a: 7), and built of the monomer: $(\text{-CH}_2\text{=CHCl-})_n$ (Brydson, 1999; Shashoua, 2001a: 9). PVC is polymerised by opening the vinyl double bond, creating the more reactive/unstable monomer that is willing to bond with other monomers. PVC is mainly amorphous in structure, i.e. the polymer chains are randomly arranged. However, some smaller (5%), yet very important, areas are crystalline in an organised and rigid structure (Shashoua, 2001a: 10). The presence of chlorine makes PVC highly polar, and also provides fire retardant properties (Shashoua, 2001a: 11).

3.3.1 Additives

In addition to pure PVC, contact film products contain plasticisers, antioxidants, light stabilisers, lubricants and fillers, which all have specific purposes within the plastic film. Plasticisers separate the polymer chains from each other, thus giving the polymer flexibility and softness as well as allowing a reduced processing temperature (Shashoua, 2008a: 59). A Van der Waals interaction takes place between the plasticiser and the polymer (Shashoua, 2001a: 15) and in the areas of crystallinity, no plasticisers are present (Shashoua, 2001a: 15). When a small amount of plasticiser is incorporated into the PVC, the polymer chains tend to rearrange, creating a more crystalline structure, thus creating a more rigid product than unplasticised PVC. Therefore, there is often a lower limit to the amount of plasticiser added to commercial PVC – to avoid this phenomenon called antiplastisation (Shashoua, 2001a: 15). The most common plasticisers are composed of non-volatile solvents with high boiling points, and very high molecular weights (at least 300)(Shashoua, 2008a: 60), such as phthalate esters: DINP (di-isodecyl phthalate), DEHP (di (2-ethylhexyl) phthalate) and DIDP(di-isodecyl phthalate)(Shashoua, 2001a: 14). Rigid PVC, as used in tubing and window frames, contains no or close to no plasticisers. Whereas flexible PVC films, such as the contact films present in *Time Zero*, may contain up to 30 % plasticisers (Shashoua, 1996: 962). The glass transition temperature (Tg) of PVC is 75° – 105°C (Shashoua, 2008a: 252), the Tg reduces as the percentage of plasticiser is increased (Benedek, 2006: 81).
The purpose of fillers may be to modify the polymer properties during processing as well as adding toughness, dimensional and thermal stability, and tensile- and compression strengths (Shashoua, 2008a: 61). The fillers are normally inexpensive materials derived from organic or inorganic materials such as calcium carbonate (Shashoua, 2008a: 61).

Lubricants are present in polymers in order to facilitate the manufacturing by reducing the viscosity of the polymer (internal lubricant), or decreasing adhesion between the metal walls of processing equipment and hot liquid polymer (external lubricant) (Shashoua, 2008a: 66). Lubricants for PVC may be stearic acid and paraffin wax, calcium or lead.

3.3.2 Industrial production of protective films and decorative PVC films

In terms of industrial terminology, the bulk of films in *Time Zero* may be categorised as 'protective films' or 'decorative films'. This class of films is often composed of a carrier (the plastic film), an adhesive – usually a pressure-sensitive adhesive (PSA), and a release liner – usually a silicon-coated paper. The carrier films are commonly coated with a primer to enable better anchoring of the pressure-sensitive adhesive (Benedek and Feldstein, 2009: 8-65). A classic primer may be a butadiene acrylnitrile styrene copolymer, or it may be a cross-linked version of the PSA in the protective film or decorative film (Benedek and Feldstein, 2009: 8-66). According to the literature, the most commonly used carriers for protective- and decorative films have been cellophane, poly(vinyl chloride), polyester, polyethylene, polypropylene and cellulose acetate (Shashoua, 2008a: 77). The films may be cast or calendered, i.e. rolled between large metal rods (Benedek, 1999: 628). High quality films without tension are made by casting the dissolved or dispersed material on a flat surface, which then dries. PVC, cellulose acetate (CA), butyrate (PB) and ethyl cellulose (EC) may all be processed from casting. Once dried, the film is peeled off the support base and rolled. Calendering may be carried out on materials with a broad softening temperature ranges such as PVC, and copolymers of PVC, vinyl acetate (VA), CA, poly ethylene (PE), poly propylene (PP) and PB. The molten plastic is compressed and formed when pushed through cooled rolls (Benedek, 1999: 408).

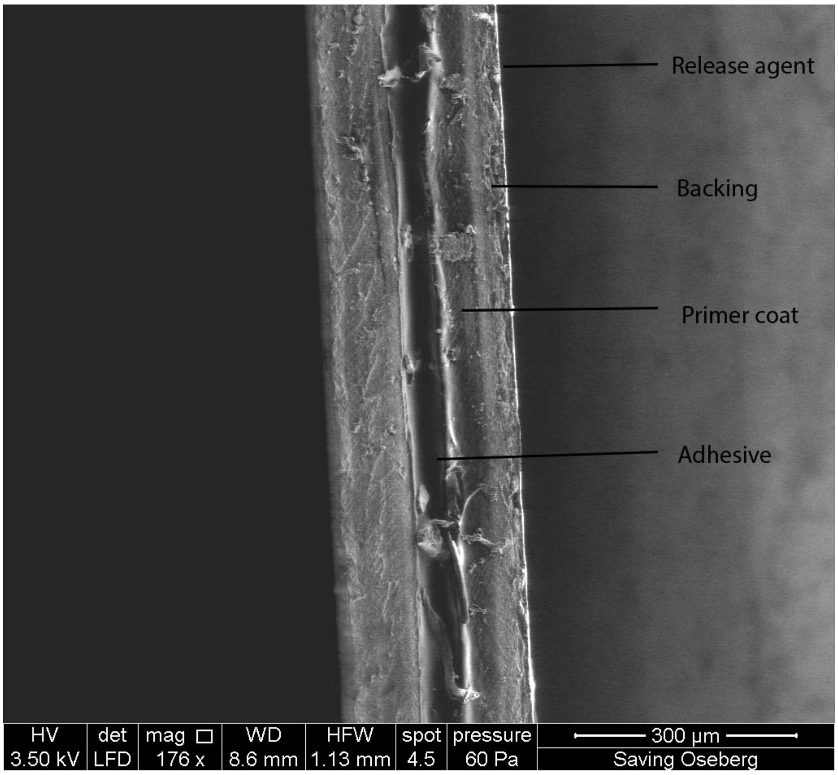


Image 5. SEM image of the layer structure of two pressure-sensitive films joined together

3.4 Characteristics of pressure-sensitive adhesives

One of the common characteristics of pressure-sensitive adhesives (PSA) is that the adhesive keeps its fluid state after bond building (Benedek and Heymans, 1997: 1). Its function is to create immediate adhesion upon application of light pressure. Furthermore, the adhesive should hold its position when shear force is applied (Benedek and Heymans, 1997: 3). In order to create good adhesion, the adhesive's ability to flow into the micro-cavities of the material surface is essential (Benedek, 1999: 82). However, once dispersed and distributed on the surface, the adhesive must remain in this position. Cold flow is characterised by the creep modulus (Benedek, 2004: 127). An ideal PSA should have maximum cold flow during application, and minimum cold flow during removal (as PSA are sometimes produced as temporary and removable products) (Benedek, 2004: 70). However, sometimes PSA has an increase in cold flow, rather than reduction, which may be visible as creeping or oozing around the edge of the carrier material.

In order to be used as a pressure-sensitive adhesive, PVAc needs to be blended with another material. Ethylene vinyl acetate is the most important copolymer product (Benedek, 2004: 182). Poly vinyl ethers (PVE) are also found in PSAs (Benedek, 2004: 182).

Pressure-sensitive adhesives are often composed of a rubbery type elastomer and a liquid or solid resin tackifier, or a mixture of different resins. The addition of fillers and antioxidants are common in these products (Shashoua, 2008a: 127). The adhesive is applied onto the carrier in a solvent solution or by calendar coating. Usually, the film is primed with a very thin coating to improve the bonding between the carrier and the adhesive (Bemmels, 1977: 726). Stabilisers are added to facilitate polymerisation during manufacturing, and to prolong shelf life. These stabilisers are commonly anionic surfactants (Benedek, 2004: 520).

Early, industrially produced products of pressure sensitive adhesive tapes and labels, from the 1920s onwards, often contain rubbers, rosin and hydrocarbon solvents

(Bemmels, 1977: 725). Synthetic viscoelastic polymers were introduced before 1940 (O'Loughlin and Stiber, 1992: 283). Most commonly, plasticisers used in acrylic-based pressure-sensitive adhesives are phosphates, phthalates and sulphonamides (O'Loughlin and Stiber, 1992: 283). Phthalates are identified as the most frequent plasticiser in the PSAs of *Time Zero* (Ormsby, 2014). Plasticisers in PSA will increase tack, but decrease cohesion and the Tg (Benedek, 2004: 477).

The properties of vinyl- and acrylic based pressure-sensitive adhesives are balanced by combining the elastomer with synthetic block polymers and a cross-linked structure (Benedek and Heymans, 1997: 127). Plasticisers are added to make the adhesive flow, and increase tack and peel (Benedek and Heymans, 1997: 142). Cross-linking agents are added to make the adhesive retain its position, and to obtain higher cohesive strength (Benedek and Heymans, 1997: 139). Cross-linking may be induced by using metal complexes, isocyanates, amino resins, polyamide, polyamine epichlorhydrine resins and other compounds (Benedek and Heymans, 1997: 140). Acrylic-based pressure-sensitive adhesives are more resistant to degradation in higher temperatures and during exposure to light and humidity, but are costlier to produce, thus rubber-based tapes are still available (O'Loughlin and Stiber, 1992: 280). Silicon-based pressure-sensitive adhesive products are being introduced to the medical industry in particular. Pressure-sensitive adhesives are very low-Tg polymers in a continuous fluid state, with a low viscosity (Benedek, 2004: 109). Tg or *glass transition temperature*, is the temperature at which the polymer moves from a glassy (rigid) state to rubbery state (Shashoua, 2008a; Horie, 2010: 26). The Tg of vinyl acetate-acrylic PSA is normally in the range of -35 - +5°C, while the Tg of acrylic PSAs ranges from -15 - + 5°C. Pure PVAcs have a high Tg making them hard and brittle in room temperature (Benedek, 2004: 92). In order to lower the Tg, PVAc needs to be mixed with other materials such as butyl acrylate or ethylene (Benedek, 2004: 98). PSAs also have a very low Young’s modulus elastomer in order to wet the surface and provide good contact with only light pressure. An *elastomer* is a long polymer that may be pulled, but retains its original shape and size when released, due to light cross-linking (Horie, 2010: 428). The rate of elasticity may be indicated by *Young’s modulus.* A high Young’s modulus indicates a stiffer elastomer, as opposed to a low Young’s modulus indicating a highly flexible material (Horie, 2010: 28). The tackifier resin must have a higher molecular weight than the base polymer, but a higher Tg than the base polymer (the carrier) (Benedek, 2004: 97). Benedek explains the relation between Tg, molecular weight and elasticity: ‘As the ratio of low molecular weight monomers is increased, the following changes in properties generally occurs: tackiness increases as Tg is lowered; hardness decreases; tensile strength decreases; elongation at break increases.’ (Benedek, 2004: 97).

The pressure-sensitive adhesives present in *Time Zero* are identified as a butyl acrylate polymer, ethyl acrylate, poly vinyl acetate (PVAc) with a phthalate(plasticiser) component, and a styrene-butadiene-containing adhesive (Appendix 13 Ormsby (2014). Some common aspects of degradation processes of PVC (representing the carrier), and also acrylic-based pressure-sensitive adhesives, as observed in *Time Zero*, are described in the following section.

Elastomer material	*rubber*	*acrylic*	*silicone*		
End-use properties	*permanent*	*peelable*	*ultra peelable*	*high-tack*	*freezer*
Elastomer material	*rubber*	*acrylic*	*silicone*		

Table 1. Some common aspects of PSA products.

3.4.1 Degradation patterns in the carrier: plasticised poly(vinyl chloride)

Degradation of plasticised PVC occurs in both the PVC material and in the plasticiser (Shashoua, 2001a: 16). They deteriorate independently. When plasticised PVC (pPVC) degrades, it may produce hydrochloric acid, and releases phthalates, which may initiate or accelerate degradation of other organic materials; it is thus categorised as a ‘malignant plastic’ (Williams, 2002: 177; Shashoua, 2008a).

Plasticisers: The plasticisers are weakly bonded to the PVC-molecules by van der Waals forces, and evaporate from the surface of the plasticized material. Plasticisers have different boiling points, indicating evaporation at different rates (Shashoua, 2008a: 184). A higher boiling point indicates slower evaporation than a plasticiser with a lower boiling point. Heat and light speeds up the rate of degradation in pPVC. Phthalate plasticisers are susceptible to hydrolysis (breaking bonds by gaining water) when exposed to strongly acidic or alkaline environments (1996; Shashoua, 2001a: 19; 2008a: 175). The plasticiser hydrolyses and becomes acidic (Shashoua, 2008a: 186-187) via the presence of oxygen, which speeds up the degradation processes to form phthalic acids.

Literature published on PVC suggests that PVC is prone to shrinkage due to loss of plasticisers (Shashoua, 2008a; Eska, 2011). Because plasticisers are held in position by weak forces, they readily move to the outermost surface layer (Shashoua, 2001a: 22), either by volatilisation, extraction or migration (Shashoua, 2001a: 25). The soft material and movement of plasticisers also cause dirt pick-up and the subsequent movement of dust and dirt from the surface into the bulk material (Horie, 2010: 24). Migrated plasticisers may be evident as an oily exudate on the surface (Richardson et al., 2014: 232).

Even though PVC polymer does not contain chromophores (light absorbing groups), the material does degrade by exposure to light, resulting in discolouration and weakening due to the presence of chromophores in the additives and possibly the presence of auxochromes (Brydson, 1999: 98; Shashoua, 2008a: 167). The PVC degrades by cross-linking and chain scission reactions through loss of chlorine and absorption of light. PVC is particularly vulnerable to heat, and even more so if it is produced by suspension or emulsion as opposed to dry blend (Brydson, 1999: 96). The first stage of deterioration occurs when hydrogen chloride is created, then cross-linking and chain scission reactions follow (Shashoua, 2001a: 17). Once the first chlorine is released from the C-Cl-bond, this creates a 'chain reaction' in the neighbouring chlorine and hydrogen atoms, forming hydrogen chloride. Now the polymer begins to absorb radiation in the ultraviolet region, continuing to other regions as the degradation progresses (Shashoua, 2001a: 18; Horie, 2010: 39). Cross-linking will increase the molecular weight and stiffen the polymers. Chain scission reduces the molecular weight, and increases solubility (Shashoua, 2001a: 17). Polymers that contain carbon-carbon double bonds, such as PVC, will react with ozone. Ozone will cause scission at the polymer backbones, reducing the molecular weight dramatically, again increasing solubility (Shashoua, 2008a: 97).

The plastic films in *Time Zero* are both cast films and calendered films (verified by polarising light microscopy as described in Section 6.1). As the materials ages, internal stress is released. Cast PVC films will have less initial internal stress, thus not undergoing the same rate of physical change as calendered films. The films that have been calendered are more likely to suffer from tears and splits once degradation has reached a certain point (Smith, N.Y.).

3.4.2 *Degradation patterns in pressure-sensitive adhesives (PSA)*

Within the field of conservation, the degradation of pressure-sensitive tapes have been of particular concern in paper conservation, focusing on the effects of degraded pressure-sensitive adhesives on paper, and how to remove the carrier and the adhesive from the paper (Feller and Encke, 1982; O'Loughlin and Stiber, 1992; O'Loughlin, 2001). A study by Feller and Ecke (1982) showed that rubber-based pressure-sensitive adhesives degrade by hydrolysing and becoming more liquid, and then by cross-linking and becoming dry and brittle. Vinyl adhesives commonly degrade by a competition between depolymerisation (chain scission) and cross-linking following deacetylation (forming of acids) (Chelazzi et al., 2014: 319). A similar pattern may be found in acrylic-based adhesives, though less prominent, and without the strong yellowing (Merrily A. Smith, 1984). The advantage of rubber-based PSA is good adhesion and cohesive strength. However, staining and softening often occurs on PVC substrates, they are less resistant to light and elevated temperature, and more prone to cold flow and shear stress (Benedek, 2004: 322). According to Horie, polyvinyl acetates, which may be used as a PSA, have a Tg around room temperature, contributing to dirt pick-up and cold flow over long periods (Horie, 2010: 137).

As in PVC, phthalate esters are commonly used as plasticisers in PSAs. The plasticiser needs to be compatible with the main adhesive polymer to avoid serious migration and loss of plasticiser (Benedek, 2004: 30). Usually 10-20% by weight of adhesive is added, though up to 50% plasticiser may be added. Plasticisers in PSAs may migrate due to fluctuations in temperature and changing the physical characteristics of the adhesive (O'Loughlin and Stiber, 1992: 282). Because acrylic based adhesives often contain a cross-linking monomer, the adhesives become less soluble by time (O'Loughlin and Stiber, 1992: 283). Within a composite, plasticisers may also migrate from flexible PVC film and upon entering a pressure-sensitive adhesive, may cause loss of adhesion due to a lowering of the PSA's cohesive strength (Benedek and Heymans, 1997: 379). It is important to note that in some cases degradation is used as a means to gain specific adhesive properties, such as increased tack, decreased peel resistance and cohesion (Benedek, 2004: 480). The ageing stability and properties may also change if the pH of the adhesive is changed. When adding one adhesive to another, it is therefore necessary to keep the pH within a similar range in order to avoid what Benedek calls 'ionic shock' (Benedek, 2004: 537).

According to Benedek and Heymans (1997: 242) there is a possibility of interactions between the film carrier and the adhesive, causing plasticisers to migrate from the film carrier into the adhesive. Furthermore, monomers, oligomers or surface agents from the adhesive may migrate to the front face material (film carrier), causing stiffening or shrinkage as well as loss of adhesive properties.

4 Methods for testing ageing stability of adhesives

4.1 Introduction

The overall objective of testing adhesives was to make predictions about the products (Bonk et al., 1996: 1). In order to obtain a better understanding of how the selected adhesives may react in an environment similar to that of *Time Zero* it was necessary to systematically evaluate some aspects of the adhesives. Testing directly on the artwork would be both unethical and invalid, thus mock-up samples and accelerated ageing were used as part of the experimental design.

In conservation, when a plastic requires bonding to itself, this often involves the introduction of an additional polymer to the object (Shashoua, 1999: 30). Adhesives may be evaluated for their inherent properties. However, when selecting an adhesive for a specific project, it is necessary to establish the properties of the adhesive in interaction with the specific adherend. Adhesives need to be tested prior to use to prevent the future failure of the adhesive, thus damaging the artwork. The specific need and the criteria for the adhesive must be outlined during preparation of experiments and conservation treatment. The drawback of testing on prepared samples is that only one parameter can be tested at the time, while actual consolidation of an artwork is more complex (Berger and Zeliger, 1984: 13).

There are some key publications dealing with the evaluation of synthetic adhesive materials in the field of conservation (Berger, 1972; Feller and Wilt, 1990; Down et al., 1996; Down, 2009), but fewer when it comes to testing adhesive material on plastics, and plasticised PVC in particular. This chapter covers a literature search related to testing of adhesives and the adhesion process, with a focus on plastics conservation, and stressing the interaction between adhesive and adherend.

The following sections describe several steps including the selection of adhesives to be tested, making a set of criteria for the ideal adhesive, exploration of what makes a good adhesive bond and the evaluation of ageing stability including colour change, strength, flexibility, wettability, surface tension, as well as curing and working properties. At the end of Chapter 4, some specific criteria for the adhesive(s) to be employed on *Time Zero* are listed, as well as a brief discussion of methods chosen for the experiment, as outlined in Chapter 1.4.

4.2 Selected adhesives – general remarks

In his work developing a new adhesive for paintings conservation, Gustav Berger listed three requirements for experimental research: defining the aims of the research; designing tests that will provide information about the mechanical performance (effectiveness) of the adhesive; designing tests that will eliminate the adhesives with hazards to the material (painting) (Berger, 1972: 173). Jane Down at the CCI has published research on adhesive testing since 1984 (Down, 1984). Through eight papers Down et al. examined the properties of up to 52 different adhesives with attention to pH and yellowing of fresh and aged adhesives, as well as tensile strength and the detection of volatiles (1984; 1988; 1995; 1996; 2001; 2006; 2009; 2011; 2015). Down et al. (1984; 1995; 1996; 2009) investigated the adhesives as separated from any material context, i.e. they did not investigate the interaction between adhesive and adherend. The majority of texts discussed in this chapter present studies of adhesives in relation to their application on one or more materials. The early publications aim to identify constituents, pH and setting properties of the adhesives (Down et al., 1996). The latest publications explored pH, colour change and removability (Down, 2011; Down, 2015).

Sale has published a series of studies on adhesive testing on poly methyl methacrylate (PMMA). The literature by Sale first examined adhesive strength and solvent reactions in relation to PMMA (Sale, 1991; Sale, 1995). The second and third studies investigate the ageing properties and colour change of the same sample material (Sale, 1995; Sale, 2011).

Huys and Oosten (2005) and Ward (1999) have studied the adhesion of flexible PVC, focusing on bond strength (peel and creep) and colour change. Winther et al. (2013) carried out research on adhering rigid polystyrene, with an emphasis on working properties, bond strength, colour change and reversibility. Laganá and Oosten (2009; 2011) have undertaken research on adhering poly methyl methacrylate and unsaturated polyester, focusing on stress and refractive index, as well as materials and methods for adhesion and filling. Comiotto and Egger (2009) researched a bonding strategy for PMMA, with an emphasis on mechanical strength and the prevention of stress cracking and crazing during adhesion. Haider and Oosten (Haider and Oosten, 2009b) explored adhering flexible polyethylene by studying photooxidation, wetting properties and bond strength. De Groot et.al (Groot et al., 2011) investigated the degradation and adhesion of polyurethane elastomers by accelerated heat ageing, mechanical testing, measuring refractive index and stress. Siegmantel (Siegmantel, 2011) has investigated the adhesion of silicone rubber, evaluating working properties, bond strength, concluding that silicone adhesives may be the most appropriate to adhere to silicone.

There are also several case studies working through assessing different adhesives, proceeding to treatment proposal and treatment of the damaged object: Bechthold (2007; 2009); Beerkens, Stigter et al. (2007); Beerkens et al. (2011); Lorne, (1999) to mention a few.

4.3 Selecting adhesives for testing

This study will look into adhesives that might be considered suitable for the treatment of *Time Zero*. There are innumerable adhesives to choose from. The following section will look into examples and strategies to limit the number of adhesives to test for a specific treatment purpose. Most studies on adhesive on plastics tests both conservation grade adhesives and commercial adhesives. Finding a selection of adhesives to evaluate may be based on a survey (Feller and Wilt, 1990; Winther et al., 2013), an in-depth study of previously tested materials (Sale, 1991; Ward and Shashoua, 1999; Down, 2009; Haider and Oosten, 2009a; Oosten and Laganà, 2009; Groot et al., 2011; Laganá and van Oosten, 2011); literature search and recommendations by the manufacturer of the plastic material and/or the adhesive (Sale, 1991; Vestergaard and Horie, 1996); or on knowledge of chemical properties in the adhesives and object material alone. For Winther et al. this first method of selection may have been a drawback for the research, as none of the adhesives suited the requirements for adhering polystyrene, i.e. none had a similar refractive index to polystyrene. Chemical incompatibility may be an obstacle when selecting an adhesive. For example Ward and Shashoua (1999: 890) chose to use an adhesive similar to the original material structure, in order to avoid problems with the interaction of different plastics in the conservation of PVC rickshaw components. In Oosten and Laganà (Oosten and Laganà, 2009: 73; 2011) the authors look to glass conservation due to limited studies in the field of adhering transparent unsaturated polyesters. The selection of adhesives was chosen from those typically used in glass conservation, though two of the adhesives are non-reversible despite the fact that one of the aims is reversibility (Oosten and Laganà, 2009: 73).

The object of study in this project contains several films of PVC. The main challenge with bonding PVC are the plasticisers (Skeist, 1977: 657). This is supported by Shashoua (2008a: 217), who explained that, due to migration of oily phthalate plasticisers contaminating the surface, the adhesion of plasticised PVC often fails. According to Skeist, the PVC resin often is compounded with a primary plasticiser, such as a phthalate, and a secondary plasticiser which may be an alkyl aromatic petroleum fraction. The latter may separate from the polymer and 'bloom' or migrate to the surface, resulting in an oily and weak boundary layer. This is why nitrile rubbers and elastomeric adhesives are recommended for adhering PVC, as they partly absorb the oily layer (Skeist, 1977: 657). In the relatively comprehensive project of re-adhering the PVC films of the Panamarenko Aeromedeller OO-PL, the project participants decided to use a rubber-based adhesive, based on the compatibility with similar adhesives, as well as ageing tests and mechanical evaluation (Huys and Oosten, 2005).

4.4 Characteristics of a good adhesive bond

According to Horie (2010: 97), there are three requirements for successful adhesion: good wetting of the surface, optimal setting properties of the adhesive, and minimising stress on the object. Selecting an adhesive requires an appropriate balance between cohesion within the adhesive, and adhesion to the material to be bonded (Skeist, 1977: 729). Shashoua (2008a: 214) describes bonding of solid plastics in terms of mechanical and adsorption theories. In order to obtain sufficient contact between two materials to develop surface force, Shashoua also mentions the importance of good wetting. The adhesive also needs to move into the adherend surface profile and displace any oxygen.

4.5 Requirements for the adhesive bond

Berger and Zeliger stress the need to establish the purpose of the adhesion, and to formulate a set of requirements for an ideal bond (Berger and Zeliger, 1984: 13). Gustav Berger suggests the following 'List of requirements of an adhesive for conservation' (Berger and Zeliger, 1984: 13): *adhesion*; *no continuous chemical interaction*; *no structural interaction*; *compatibility*; *durability*; *applicability*; *reversibility*. However, these may be considered general criteria applicable to most materials for conservation. Comiotto and Egger (2009: 23), Haider and Oosten (2009b: 47), Bechtold (2009: 107) describe criteria for good adhesion of plastics as good wetting properties required by strong surface polarity. The elimination of stress crazing and cracking is essential when creating a bond, as emphasised by Comiotto and Egger (2009). Oosten and Laganá give a more specific set of criteria for creating a proper bond with polyester, also supported by Down, MacDonald et al. (1996). These criteria are: adhesion without dissolving the adherend, a comparable refractive index, appropriate viscosity, suitable working time without creating air bubbles, non-yellowing, reversible, and to be chemically and physically stable (Oosten and Laganà, 2009: 73). Sale 1991 gives similar requirements for adhesives to be used on PMMA (Sale, 1991: 328). Not least, the adhesive should be strong enough to hold the object together, but weaker than the object on which it is applied (Horie, 2010: 106; 111).

4.6 Bond failure

The failure of a bond may be caused by stress in the adhesive or the object during setting, deterioration of the adhesive and/ or object, or movement in the joint (Horie, 2010: 103). The quality of a bond may be assessed by studying the characteristics of the bond-failure during a physical strength test. The three categories of failure are most commonly divided into the following categories: *Cohesive failure in the mass* is when the adhesive material itself fails. *Adhesion failure* is when the join fails at the interface between the object and the adhesive, while *cohesive failure in the substrate* is when part of the object breaks off, and is only attached to the adhesive (Horie, 2010: 103). According to the characteristics of the failed bond, the adhesive may be adjusted accordingly, e.g. a lower Tg, better wettability, more appropriate solvent. Young et al. describes the ideal peak failure load of a gap filler to be just below that of the material to be filled, i.e. the gap filler should have similar stiffness to the material to be filled (Young et al., 2009: 136). According to Horie, failure in the join ideally happens by cohesive failure within the adhesive interface, without affecting the substrate or carrier material in this case (Horie, 2010: 111).

4.7 Evaluating the working properties of an adhesive

Working properties are often part of the criteria when selecting adhesives. Properties such as *toxicity*, *curing time*, *viscosity* etc. play a very important role when it comes to selecting an adhesive for the conservation treatment of a work of art.
Transferring the tests to objects may be the most challenging part of the job, as the surfaces to be joined may contain other factors not included in the tests, and the clamping of the parts (where necessary) may be difficult within the time frame of curing.

The application method may also affect the quality of the bond. Rigid plastics are commonly adhered using similar techniques to those in glass- and ceramics conservation (needle, syringe or fine brush application) (Oosten and Laganà, 2009). Adhering flexible plastics may use similar techniques to paintings- or textile conservation, such as spraying or brushing. Karsten and Kerr also found that the dilution of the adhesive played a significantly role in the quality of the bond (Karsten and Kerr, 2011). Different adhesives may also require different application methods, making the results difficult to compare. Exploring the effects of varying application method is outside the scope of this project due to time-limits.

4.8 Measuring and assessing wettability and surface tension

Another important criteria is that of wettability and surface tension (surface energy). In order to obtain a suitable bond, the adhesive needs to be able to wet the objects' surface completely. A liquid with poor wetting qualities on a surface does not spread properly and is less likely to result in desired adhesion (Horie, 2010: 49). The adhesive should have a surface tension lower than the plastic's surface in order to wet the surface adequately to provide a successful bond (Shashoua, 2008a: 214). Introducing strong solvents or acids to obtain a better contact between adhesive and object surface is usually not an option in conservation as the risk of altering or damaging the object surface is too high. In many cases the introduction of solvents may cause further stress in the object material, inducing degradation rather than slowing down degradation, which is the overall aim for the conservator (Sale, 1988; Shashoua, 2008a, p. 209; Laganá and van Oosten, 2011). Treating the surface with hot air, oxyacetylene or plasma will provide an increase in surface tension (Oosten et al., 2007; Oosten et al., 2008; Shashoua, 2008a: 214; Shashoua, 2008b, p. 18). Using the solubility parameter of the plastic may be a good guide to avoid the most damaging solvents (Oosten et al., 2008; Shashoua, 2008a:215; 2008b; Comiotto and Egger, 2009).

One way of determining the surface tension of an object is by using Tigres test inks brushed onto the surface (Haider and Oosten, 2009b). Shashoua also describes how to put a liquid droplet on the surface and using a USB-microscope to determine the contact angle. If the contact angle of a droplet on a surface is less than 90°, this is considered good wetting, and the precondition for good adhesion is present (Shashoua, 2008a: 214; Shashoua et al., 2009: 57; Horie, 2010: 97-98). Wetting and surface dynamics are thoroughly described by Allen (1984: 6-8).

Unlike some plastics, such as polyethylene, polypropylene, polyesters and polytetrafluorethylene, PVC does not require surface modification prior to adhesion in order to increase the surface tension enough to provide proper bonding (Shashoua, 2008a: 214). This phenomena is investigated by Haider and Oosten (2009b) when searching for a method to re-adhere ripped plastic bags made of polyethylene (PE). The ageing properties of PE were examined using FTIR and DSC before selecting a set of adhesives for further testing. The adhesives were selected based on chemical and physical properties such as similarity in surface tension and application. However, it may also be useful to test the surface tension of the object itself before going for a costly or complicated pre-treatment as an aged plastic surface may have an increased surface tension due to natural ageing (Haider and Oosten, 2009b).

4.9 Measuring and assessing bond strength

Pressure-sensitive adhesives (PSAs) are known to suffer from cold flow. This phenomenon, sometimes characterised as inherent to PSA, is caused by viscoelastic creep in the adhesive layer, in which the PSA flows like a liquid (Zhao, 2014).

To determine whether cold flow as seen in *Time Zero* occurs after the addition of a consolidant to the adhesive layer following artificial ageing, the phenomenon is measured using a mechanical test such as the t-peel test (ASTM, 2015). The implemented test is particularly useful for flexible materials such as plasticised PVC. The strength of the bond is of importance, since it is not desirable to have an adhesive so strong it causes the object material to break off and stick to the adhesive (Horie, 2010). Needless to say, the bond should not be too weak (i.e. lack of cohesion) since this could cause a failure within the adhesive material. There are several ways of evaluating the strength of an adhesive bond, depending on the type of join tested. Most commonly, tests are performed on butt-joints or “overlap” joints using a tension testing machine stretching or pulling several samples prepared with different adhesives, and calculating the point of failure and the amount of shear force required (Bradley, 1984).

Often, it may be useful to perform strength-testing based on ASTM test methods (ASTM D3164 – 03; ASTM D 1876-08) (2011; 2015), or standards in the ISO-system (ISO 9653:1998; ISO 11339:2010) (2013; 2015). Berger and Zelinger (1984) address problems related to the ASTM standard, i.e. the size of the test samples and the speed of peeling. The authors decided to modify the ASTM in their tests. In the selection process of the final test-adhesives, the authors used some preliminary low-tech tests such as rubbing the adhesive between one’s fingers to test consistency and tack, pouring hot melt adhesive on newspaper to see if it stained, and pouring hot melt adhesive into cold water. It is not uncommon to observe that modified standards are used in conservation test methods, as is the case in the studies by Down (2006; 2009; 2015), Sale (1995) and Oosten and Laganà (2009).

Bond failure may be assessed differently in rigid and soft materials. In rigid materials, the fracture is examined and assessed according to where the break is located: did the material break outside the joint? Did the material break in the middle of the joint? Did the material break partially in the joint and partially in the material? In a soft material, the amount of adhesive transfer during peel-strength testing is assessed (Karsten and Kerr, 2011: 10). Flexible materials may be tested using a peel-strength machine according to international standards (ASTM D 1876-08; ISO 11339:2010). However, the speed of the peel will influence the rate of adhesive transfer. Cohesive failure within the adhesive is more likely at slow peel rates (Karsten and Kerr, 2011).

In his 1991-study, Sale investigated the crazing and tensile properties of eleven adhesives as well as the effect of degreasers on PMMA (Sale, 1991). No accelerated ageing was executed. The quality of the failed bond has been studied and described by Winther, Bannerman et al. (2013), Sale (2011), Horie (2010) and Vestergaard & Horie (1996). Attempts to assess any chemical effects on the object material from the adhesive using FTIR have not been conclusive (Vestergaard and Horie, 1996).

There are several ways of testing bond strength. Testing tack and peel will give an indication of bond strength, whereas shear tests will indicate cohesive strength (Benedek, 2004: 699).

4.10 Scanning electron microscopy

The physical quality of the bond may be further assessed using SEM (Vestergaard and Horie, 1996; Karsten and Kerr, 2011; Winther et al., 2013). The scanning electron microscope (SEM) creates an image of the object by scanning the surface with a beam of secondary electrons, creating detailed three-dimensional images up to 100 000 times magnification (Stuart, 2007: 91 - 92). By using SEM to examine the joins, it is possible to observe whether the adhesive has sufficiently wetted the surface resulting in an evenly distributed adhesive and an adequately filled gap. It is also possible to assess whether the adhesive has undergone shrinkage or creep, or if the bond has caused crazing or cracks in the object material. One of the disadvantages of using SEM is that the samples may be somewhat damaged during the preparation and polishing, affecting the final result (Vestergaard and Horie, 1996: 940).

SEM imaging is a destructive method requiring a small sample, prepared for the vacuum chamber of the apparatus. Furthermore, the sample most commonly needs to be coated with carbon or gold. An imbedded sample may be analysed, or the pure sample may be attached to a carbon stub using carbon tape (Stuart, 2007: 94). SEM is occasionally used on plastics, but a low vacuum mode is recommended in order to keep the sample intact during the beam scattering (Shashoua, 2001a: 60). In studies testing adhesives and consolidants for plastics SEM has proved to be useful to visualise the rate of penetration of a consolidant into polyurethane foams (Lavédrine et al., 2012). In combination with

EDS (energy dispersive spectroscopy), the technique may be able to map element distribution, such as the chlorine in PVC compared to oxygen in the phthalates (Shashoua, 2008a: 145 - 146). The instrument was also successfully used in assessing cleaning strategies of plastics (Bollard et al., 2011).

4.11 Accelerated ageing

The ageing stability of the adhesive to be in contact with an object, is commonly listed as a crucial criterion. This normally relates to stability in terms of light exposure, thermal fluctuations, and humidity changes, but also mechanical stress and strain through use (Feller, 1994: 1). Stability may be defined as: *the resistance to change in terms of physical or chemical properties* (Feller and Wilt, 1990: 37). However, physical and chemical changes are most commonly measured in relation to each other, and not to the material the adhesive is applied on (Feller and Wilt, 1990: 37). The interpretation of the results from accelerated ageing is not done in a straightforward manner. This is, amongst other factors, due to the differences in ageing behaviour in a material when exposed to one degrading factor compared to a sum of degrading factors (Brydson, 1999: 99).

To determine the ageing stability of an adhesive, accelerated ageing tests are frequently used, as seen in van Oosten and Fundenau et al. (2007); Haider and van Oosten (2009b); van Oosten and Laganá (2009); Laganá and van Oosten (2011); Howells, Burnsock et al. (1984); Huys and van Oosten (2005); de Groot, Laganà et al. (2011) and Winther, Bannermann et al. (2013). Accelerated ageing tests are dealt with in depth by Feller (1994) in *Accelerated Ageing. Photochemical and Thermal Aspects*. Accelerated ageing is, broadly speaking, about exposing samples to elevated temperatures or light levels to speed up the degradation process.

4.11.1 Ageing studies

Both Down (1984; 1996; 2001; 2009; 2011; 2015) and Sale (1995; 2011) rely heavily on ageing studies in their experiments. They revisit their studies at different intervals to detect any changes during natural ageing. In the study on epoxy-resins for glass conservation Down (2001) abandons the use of thermal ageing, due to inconsistencies with thermochemical accelerated ageing as compared to natural dark ageing. It was hypothesised that the catalyst evaporated at the higher temperatures, and was thus not available to accelerate the yellowing reaction, as happened in the dark aged samples (Down, 2001: 40). Also, Blitz and Grattan describe problems with applying the Arrhenius equation to predict the longevity of a material. The differences in results were particularly notable when materials were aged at elevated temperatures up to 200°C. It was advised to reduce the temperatures and prolong the time of exposure in order to obtain more reliable results (Blitz and Grattan, 1996). Sale also mentions the dilemma of predicting the longevity of a material. In his experiments he clearly states that the results may be compared but are not conclusive in terms of natural ageing rates (Sale, 1995: 17).

4.11.2 Limitations in ageing studies

Down and Howells et al. found that there were extensive differences between the rates of natural ageing, compared to accelerated ageing, and subsequently abandoned the Arrhenius equation to calculate the rate of degradation (Down, 1984; Howells et al., 1984; 2001). In Down's early studies on the ageing and stability of epoxy resins, it was discovered that the artificially aged samples compared to naturally aged samples, did not yellow at the same rate. Rather, the naturally aged samples aged 31 times faster than that predicted by the Arrhenius equation from accelerated ageing (Down, 1984: 18). Down concluded that accelerated ageing is not reliable to predict the rate of yellowing. Future tests would focus on ageing at room temperature under high light levels and in the dark (Down, 1984: 18). Nonetheless, artificial ageing is still widely used. However, it is more often used in order to compare results rather than to predict the rate of degradation. Reliable accelerated ageing studies are still in demand. The effect of heat and light in combination may be quite dramatic, whereas individually their effect on a polymer may be negligible (Brydson, 1999: 99).

4.12 FTIR as a method to characterise materials and assessing ageing

Previously in this study, Fourier transform infrared spectroscopy (FTIR), was employed for the identification of carriers and adhesives in *Time Zero*. As the instrumental method has been used as a tool to evaluate degradation properties in the test-material, a more thorough description is given below.

FTIR has been widely used in studying polymers for conservation (Derrick et al., 1999; Oosten, 1999a: 72; Learner, 2004; Shashoua, 2008a). The technique uses a *spectrometer* and the results are presented in a *spectrum*, equal to a “fingerprint” of the material (Oosten, 1999b: 159). FTIR is used to identify the main organic component in a polymer, degradation products on a material surface, and polymer bond changes as well as to monitor loss of plasticiser (Oosten, 1999a: 72; Nielsen, 2008; Nord and Tonner, 2008: 55-62; Waentig, 2008: 162). Information on degradation of certain synthetic polymers may be obtained when this technique is used prior to, and after accelerated ageing (Haider and Oosten, 2011: 44).

4.12.1 Instrument

FTIR is a method of scattering infrared beams on a sample, normally in the mid-infrared region from 4000 - 500 cm^{-1}, exciting the molecules to move in specific ways at specific wavelengths, identifying the various motions and wavelengths at the dipole moment. The instrument compares wavelengths that are scattered on the sample with the wavelengths that are transmitted through the sample or reflected off the sample, calculating the absorbance within the sample. The absorbance is visualised as bands in the *spectrum*. (Derrick et al., 1999; Mills and White, 1999: 20-21; Oosten, 1999a: 74; Stuart, 2007; Shashoua, 2008a). The intensity of the absorption or transmittance is represented in the vertical axis, while the frequency range (wavenumber in cm^{-1}) is represented in the horizontal axis in the spectrum (Derrick et al., 1999: 12; Learner, 2004: 81).

4.12.2 Sample preparation

The sample size required for FTIR is at the size of a full stop or $1mm^3$ (Oosten, 1999a: 73). The benchtop attenuated reflectance (ATR) accessory requires no preparation, except flattening of the sample (Oosten, 1999a: 74). The sample is simply placed in an ATR accessory (Keneghan, 2012: 45). In standard FTIR, the sample is grinded with potassium bromide for example, and pressed under pressure into a disc (Oosten, 1999a: 74) or squashed onto a diamond cell (Learner, 2004). Various methods of sample preparation may eliminate some of the components in the plastic sample (Shashoua, 2008a: 136). If the cross section of a sample needs to be studied, the sample is first embedded in a resin and then sectioned into thin slices and polished, which can be put in the micro-ATR-accessory (Oosten, 2012: 99).

4.12.3 Spectra reference libraries

The spectrum of an unknown sample is compared to a reference spectrum of a known plastic or plasticiser, or to study tables to find IR absorption energies that correlate to specific chemical bonds (Oosten, 1999a: 74; Shashoua, 2008a: 136). When starting to analyse synthetic polymers with FTIR, the user needs to build up a proper library from samples of known sources (Learner, 2004: 35). It is also possible to use commercial or online databases such as from the Infrared and Raman user group (www.irug.org).

4.12.4 Characterisation

The characterisation of plastics is the additional information about the polymers behaviour including quantitative analysis of molecular weight distribution, polymer size, physical properties etc. (Stringari and Pratt, 1991: 411-440; Learner, 2004; Oosten and Learner, 2012: 31). The presence of plasticisers may also be confirmed or disproved using FTIR (Winther, 2008; Ploeger et al., 2009: 195-199).

When a polymer is being identified using FTIR, it is at the level of identifying the class of the polymer (Oosten and Learner, 2012: 31). The mid-infrared spectrum (4000 – 500 cm^{-1}) is often divided into the functional group region (4000 – 1300 cm^{-1}) and the fingerprint region (1300 – 500 cm^{1}) when the spectrum is interpreted (Learner, 2004: 34). In the functional group region of the spectrum, the presence or absence of specific functional groups may indicate the class of polymer analysed (Derrick et al., 1999: 93, 94). Derrick, Stulik and Landry recommend dividing the spectrum into several regions in order to gain a more systematic approach to the interpretation (Derrick et al., 1999: 93-94). A strong bond between atoms causes a higher wavenumber when absorption occurs. Lower atom mass causes reduced wavenumber (Shashoua, 2008a: 134). Co-polymers contain two or more different types of monomers in one chain. Polymer blends are quite common to come across, and the infrared spectrum of a sample combines spectra of all components (Stringari and Pratt, 1991: 420), and makes them complicated to distinguish. The interaction between the two components may be seen in the shifts in wavenumber and band broadening. When interpreting an IR spectrum it may be useful to pay attention to the following parameters: frequency, shape and intensity of the absorption band (Derrick et al., 1999: 83).

4.12.5 Degradation

Degradation processes in plastics may be complex to study using FTIR, as degradation processes vary according to the polymer composition and environment. Upon ageing specific functional groups may show an increase or decrease in absorption. The result of the ratio is called the *relative absorption* (Oosten, 2011: 63). Most commonly degradation of plastics is identified as chain scission or cross-linking of the molecular bonds, and the loss of atoms or gain of atoms (e.g. by hydrolysis). There may be some difficulties in using FTIR to evaluate degradation of plastics after a conservation treatment, as the material used for consolidation may obscure the absorption of some functional groups (Oosten, 2011: 63). Degradation may also give false results as described in Price et al. (2007: 84) when a severely degraded sculpture was positively analysed as regenerated cellulose. However, knowledge about the production of the sheets opposed the findings. The specific thickness of the sheets was not in manufacture. The knowledge about the chemical degradation of cellulose nitrate supported the suspicion that the results from FTIR were false. The final identification was performed using Py-GC-MS, confirming degraded cellulose acetate rather than regenerated cellulose. Py-GC-MS has also been used to identify the degradation processes (discolouration, tackiness and crystallisation) in PVC (Shashoua et al., 2002: 69-79). Studies have been done using FTIR specifically to evaluate photo-oxidation processes (Oosten and Aten, 1996; Oosten et al., 2007; Haider and Oosten, 2009a), and also degradation of plastics in relation to darkness, humidity and temperature (Oosten, 2002; Colombini and Valegas, 2009; Toniolo et al., 2009).

FTIR has been used to identify degradation products on the surface of plastics (Balcar et al., 2012: 295), and also as a complementary technique in the surveys of plastic collections in museums, either on all objects or on selected items (Nord and Tonner, 2008; Bacci et al., 2012: 139-149; Keneghan et al., 2012: 109-137). In Learner (2004), FTIR was successfully used to identify and distinguish between different types of acrylic resins, alkyd resins, nitrocellulose, organic pigments and some extenders (Learner, 2004: 81-116).

FTIR may also be coupled with a light microscope (FTIR imaging), so that the morphology of a homogenous or layered structure may be mapped and studied in conjunction with its chemical composition (Stringari and Pratt, 1991: 418; Derrick et al., 1999: 76). FTIR imaging is used to study the degradation and oxidation of multi-layered samples. In this way the degradation and oxidation profiles may be visualised and the condition of the object may be established. However samples should preferably be embedded in a resin prior to analysis (Oosten, 2012: 99).

4.12.6 Limitations of FTIR

Additives (like fillers, colorants or stabilisers) of less than 2 – 3 % cannot be detected through FTIR (Oosten, 2006: 45; Nord and Tonner, 2008: 56; Lavédrine et al., 2012: 105). Mixed plastics, such as laminates, may be difficult to identify as one component feature may be obscured by another component feature (Oosten, 1999a: 32; Nord and Tonner, 2008: 56; Oosten and Learner, 2012: 32). As FTIR relies on comparison with a known material to identify or characterise the sample, it is essential to have a good reference library in order to produce a valid interpretation (Oosten, 1999a: 71). A successful reading of a sample should have a match of at least 80-90% to the reference database to be considered a positive match (Nord and Tonner, 2008: 56). Thus, in order to positively identify additives and plasticisers, they need to be present in higher concentration than 3% (Oosten and Learner, 2012). FTIR also has the advantage of being a non-destructive method, i.e. the samples may be kept and also re-analysed. Recent developments in the technique make it possible to do analysis directly onto an object using portable systems.

FTIR does not require advanced skills to run, and basic information may be interpreted by the aid of reference library. However, the knowledge about the history of plastics and manufacturing processes, as well as the chemical and physical degradation patterns of the different plastics is essential in order to interpret chemical changes and degradation in a material. A successful interpretation is always dependent on the experience of the interpreter.

4.12.7 Other instrumental techniques for assessing ageing stability of adhesives

Recent research (Oosten and Learner, 2012: 34) presents promising results with other instrumental techniques that may overlap with FTIR and (Py)GC-MS, such as Raman spectroscopy, near infrared spectroscopy (NIR), UV-Vis spectroscopy, chemiluminesence (CL), differential scanning calorimetry and solid phase micro extraction-gas chromatography-mass spectrometery (SPME-GCMS). Despite this, the POPART project concludes that, for identification purposes, FTIR is still the most widely used technique (Oosten, 2012: 31) due to accessibility, cost and time per analysis and growing sophistication in the interpretation of results.

4.13 Measuring and assessing colour stability of adhesive

4.13.1 Colorimetry

Evaluation of colour change (before and after ageing) may be performed using colorimetric methods (CIELab1976). Colorimetry is mathematically expressed in a three dimensional space/ coordinates. Sale (1995; 2011), Feller and Wilt (1990, p. 41), Howells et al. (1984, p. 38), Kaukovalta (2002) p. 111 Colombini and Valageas (2009), and Winther, Bannerman et al. (2013) all use the CIE Lab scale to measure colour change in the samples. Down et al (1996; 2009) uses a different equation. However in her latest papers (2011) the spectrophotometer is used to measure the rate of yellowing in the samples. In Comiotto and Egger (2009) and van Oosten an Laganà (2009), the yellowing of the adhesives was not considered, thus stressing the importance of similar refractive indexes. Sale focuses on delta b (yellowness-blueness difference), though the study shows the samples also change colour to tints of red, green and brown, suggesting additional comparison of results of delta a (redness-greenness difference) to D (colour difference). The Blue Wool Standard (BWS) (ISO R105) was used to control and make sure all samples had the same exposure of light. However, Sale also points out that the BWS may react differently to different light sources, thus not being reliable proof (Sale, 1995; 2011).

4.13.2 Colour change by other methods

While the use of a spectrometer and the CIE Lab scale may visualise the rate of yellowing in a material, other analytical techniques such as FTIR, SEM and DSC may give evidence of what chemical or physical reactions cause yellowing, as suggested in van Oosten and Laganà (2009: 77). Oosten and Aten (1996), Shashoua et al. (2002: 69) , Oosten and Haider (1996: 972) and De Groot et.al. (2009b: 42; 2011) compare FTIR spectra before and after ageing to determine crystallinity and change in FTIR absorbance, thus resulting in colour change. This method requires a deeper knowledge about the degradation chemistry and physics of the specific material examined. Colour change is more easily measured on “open samples”, such as in the studies of Sale (1995; 2011) and Winther (2013), as opposed to laminate samples.

4.14 Measuring pH of adhesive

In the studies by Down et. al., the group has focused a great deal on the pH of the adhesives as they age, since the pH may accelerate the degradation of an object (Down, 1984; 2009; 2011; 2015). Measuring pH is rarely mentioned in literature on adhesive testing on plastics. However, the method may be applicable as some polymers are very sensitive to changes in pH, which could for example cause cross-linking (2009; 2011; 2015). The result of a drop or rise in pH during ageing gives information about the ageing properties, and may be relevant to test since it is preferable to have an adhesive that remains within the neutral range as it ages (Down, 1984: 19). In this project, the rate of change in pH may give an indication of the rate of degradation (the more acidic, the more progressed the degradation) (Ward and Shashoua, 1999: 892). Furthermore, it may be interesting to test pH when two adhesives are aged together, in order to possibly detect any major shifts in pH compared to the samples containing PSA alone. In previous studies, an acceptable range of pH of adhesives for use on museum objects was determined to be between 5.5 and 8 (Down, 2015: 36). For synthetic polymers, the pH will vary according to the material; acrylic dispersions are normally delivered at pH 5-6; vinyl acetates at pH 4-5; natural rubbers and neoprene are neutral (Benedek, 2004: 537). However, it is not mentioned what pH is acceptable when a polymer has already aged and thus, possibly, undergone a change in pH. By adjusting the pH towards more alkaline values, it may positively affect the storage life of fresh adhesives (Benedek, 2004: 537 - 538).

Down et.al., used a cold water extraction method (modified ASTM D1583-61) to measure pH in most studies (1984; 1996; 2009; 2011; 2015). Another method as described by Strlic et al. (2004) is surface pH measurement by placing a droplet of distilled water on the surface and measuring the pH in the droplet. The method proved to display systematically lower pH readings than a standard method such as ASTM D778-97 (Strlic et al., 2004). This method also requires the presence of free hydrogen ions, presumably from additives rather than the main polymer, in order to measure the pH from the adhesive, rather than from the water itself.

4.15 Measuring re-treatability

Only a few articles investigate the removability of an adhesive (Down, 1984; Howells et al., 1984; Down, 2001; Comiotto and Egger, 2009; Down, 2011; Laganá and van Oosten, 2011; Winther et al., 2013). Down describes two methods of testing and measuring removability: a swell-test which is detected by microscopic means, and a solution-test by rolling a swab on the surface (Down, 1984, p. 20). The swelling-technique is further described in Down (1999). The author also stresses the need for scientific research to determine the degree to which conservation materials or treatments are reversible, soluble or removable (Down, 1999, p. 111). In the 2011-article, testing of mechanical removal is also described when evaluating self-adhesive tapes (Down, 2011).

4.16 Conclusions

The different stages of evaluation of an adhesive for conservation may include making a selection of adhesives based on a survey, literature search or recommendations from the manufacturer. Further, a set of criteria for the adhesive and required adhesion should be outlined to fit the specific project. Bond strength may be measured mechanically according to various international test standards such as ISO or ASTM. The quality of the bond may then be assessed visually or by more advanced analytical techniques such as FTIR or SEM. The ageing stability of an adhesive may be investigated by running the samples through a process of accelerated ageing or natural ageing. The samples then need to be evaluated and compared in terms of colour change, molecular weight, change in viscosity or change in solubility. The samples may also be examined in terms of change in pH. By assessing the adhesive wettability and the material surface tension, it gives an indication as to whether the adhesive is suitable for the specific adherend and the specific project.

4.17 Methods related to *Time Zero*

Because *Time Zero* has several transparent films, the visual ageing properties are highly relevant, and are valued above that of a very strong bond. Acrylic adhesives prove to be relatively stable when it comes to yellowing and come in different glass transition temperatures, making them suitable for application on flexible materials. Based on a literature review, 8 adhesives were selected for this study. The adhesives are presented in Chapter 5.

4.17.1 Requirements to Time Zero bond

The bond in *Time Zero* needs to be strong enough to hold the plastic films and other materials together without causing strain to the individual materials or the object as a whole. As cold flow is a problem in *Time Zero*, the bond should be able to terminate or restrict adhesive flow once set.

The ideal adhesive for *Time Zero* needs to fill the following requirements:

- appropriate surface tension and adhesive flow
- resistance to creep (cold flow)
- appropriate bonding properties to both original adhesive and original material
- good adhesive strength
- retain flexibility after curing
- remain transparent
- refractive index similar to original material
- no harm to original materials in the artwork
- not add too much weight to the artwork
- re-treatable
- good resistance to ageing

This list rules out most solvent-based adhesives, high-viscosity adhesives, adhesives prone to yellowing or photo-oxidation, adhesives with a very high Tg and adhesives emitting acids, solvents or heat during curing. The adhesive should be slightly weaker than the plastic film, and have a Tg above room temperature (Horie, 2010: 106). Acrylic adhesives may seem appropriate to test, as they are said to be more stable when it comes to ageing and they also come in different ranges of Tg and pH. The risk of further damage to the original films is very high, due to brittleness, as well as the displacement of films and loss of the original folds and creases if the collage films are to be separated (Lorne, 1999: 873). It was decided to try to avoid the opening of the original films to remove the original degraded pressure-sensitive adhesives.

4.17.2 Wettability and curing

In order to obtain an appropriate balance between cohesion within the adhesive, and adhesion to the material to be bonded, adhesives with a lower viscosity have been prioritised in this study; these adhesives should conform easily into the surface profile, displacing any oxygen (Skeist, 1977: 729). Furthermore, the adhesive needs to cure without the emission of harmful gases or volatile products that may become entrapped between the carrier films. It was also decided to test only conservation-grade adhesives, in order to create a platform for further comparison, as well as reducing the variables when it comes to material composition and use.

4.17.3 Ageing regime

Extreme temperature conditions in accelerated ageing may exceed the Tg of the PSA, and also possibly cause the PVC the samples to melt or slip apart too early in the process to give adequate results. Light ageing and natural dark ageing therefore seem more appropriate for this study. It is also important to study how the adhesives react to different lighting conditions, as many foils are transparent, exposing the adhesives to museum lighting for the duration of an exhibition period, (and darkness during periods of storage.)

4.17.4 Studying degradation

Based on the fact that FTIR is frequently employed to study degradation of materials, as well as being readily available, the project has taken the opportunity to explore this tool in the context of accelerated ageing of plastics. Several of the films in *Time Zero* are transparent. It is therefore extremely relevant to measure whether the adhesive layer will change in colour upon ageing. Yellowing of the adhesive would be visually disturbing and could alter the original expression of the artwork. Furthermore, yellowing may indicate degradation in progress, which may be used to understand how the material reacts as it ages.

4.17.5 Studying harmful degradation products

As mentioned in chapter 3, phthalate plasticisers are susceptible to hydrolysis when exposed to strongly acidic or alkaline environments. If alkalis are present, this may lead to saponification of acidic products, via salts formed from hydrolysis (Shashoua, 2001a: 19). When plasticisers migrate to the adhesive side of the films rather than to the surface, these plasticisers then hydrolyse to form phthalic acids (Shashoua, 2008a: 186-187). These acids will, under normal circumstances evaporate quickly. However, in this particular environment, capsuled in between non-porous plastic films, the likelihood of the acids to remain within the adhesive layer for longer may be considerably higher. Furthermore, dust and dirt from the environment, as well as paper and other organic material in *Time Zero*, may have an influence on the pH in proximity to the plastics. Because the plastic films themselves do not contain any free hydrogen ions, any change in pH may be interpreted as influences from surrounding materials such as paper, additives in PSA and dust.

4.17.6 Ensuring flexibility

Tg may, in general terms, indicate the softness of a polymer[3]. In order to enable further handling of *Time Zero* without the risk of mechanical damage, the adhesive to be used on the collage needs to remain flexible. Tg also indicates the movability and flexibility of a polymer chain (Benedek, 2004: 92). When a material is below its Tg it will be hard and brittle, and may break. However, by selecting adhesives with a variety of Tgs, it might be possible to detect an interaction between the adhesives, resulting in reduced or increased flexibility after ageing.

---

[3] Tg is more thoroughly explained in Chapter 3.4.

5 Experimental design

Based on the findings described in Chapter 2.2, an experimental set-up was modified to explore *if* and *how* the carrier and the pressure-sensitive adhesive affect each other during ageing, and to evaluate whether the addition of a consolidant acts as a stabilising agent to the composite material(s).

In order to simulate some of the mechanics in *Time Zero*, a series of mock-up samples were prepared, coated with adhesive, aged and tested. Different analytical techniques were employed to elucidate different aspects of ageing in the composite of materials, focusing on the adhesive side in particular.

The experiments were completed in the following stages:

- Preparation of mock-up samples from commercially available films, applied with a conservation-grade consolidant, aged in museum condition lighting, and naturally in a dark environment
- FTIR characterisation before and after ageing
- Measurement of colour before and after ageing
- Measurement of pH before and after ageing
- Mechanical testing and evaluation after ageing

5.1 Mock-up films

The mock-up films were commercially available rolls of film, of similar material to some of the films in *Time Zero.* Film #3 was a white 0,13mm polyvinyl chloride film with a phthalate component, with a solvent free acrylic-based pressure-sensitive adhesive (*d-c-fix® "Designfolie"*). Attempts to get hold of PVC film with a vinyl-based PSA did not succeed. The materials were confirmed by FTIR analysis. The same apparatus and settings as employed for the characterisation of the *Time Zero* original samples were used for the analysis of the mock-up samples[4]. A total amount of 77 samples were prepared; 37 open samples, 40 closed samples.

---

[4] Described in Chapter 1.4.5.

	Name	Chemical properties	Manufacturer	pH	Tg	Solid parts	Solution	Note	#open samples	#closed samples
I	Acronal D 500	nBA/VAC/VC, acrylic acid ester copolymer	Kremer pigmente	3,5 – 4,7	-13 ˚C	50%	Dispersion	1	5	5
II	Primal WS24	nBMA (nbutyl methacrylate)	Kremer pigmente	7 – 8	46 ˚C	33 – 35%	Dispersion	1	5	5
III	Dispersion K360	Aqueous emulsion of a thermoplastic acrylic polymer BA/MMA (butyl acrylate/methyl methacrylate)	Kremer pigemnte	2 – 3,5	-31 ˚C	59 – 61%	Emulsion	1	5	5
IV	Lascaux medium for conslidation	Aqueous dispersion of acrylic copolymers based on acrylate ester, styrene and methacrylic ester	Lascaux Colours and Restauro	8 – 9	4 ˚C	25%	Dispersion	2	5	5
V	Mowilith DMC2	Aqueous dispersion of a copolymer based on vinyl acetate and maleic acid di-n-butyl ester. 35% dibutylmaleate with a cellulose ether stabiliser	Lascaux Colours and Restauro	4 – 5	11 ˚C	25%	Dispersion		2	5
VI	Aquazol 200	Poly (2-ethyl-2-oxazoline)	Polymer Chemistry Inivation Inc.	—	69 – 71 ˚C	100%	Solution		5	5
VII	Plexigum PQ611	Isobutyl methacrylate solution of an acrylic polymer.	Kremer pigmente	—	32 ˚C	100%	Solution	3, 4	5	5
VII	Paraloid B67	Isobutyl methacrylate	Kremer pigmente	—	50 ˚C	100%	Solution			
VIII	PSA only	Butyl acrylate	Konrad Hornschuch AG	—	—	—	—		5	5

Note: 1) Kremer pigmente information sheet; 2) Lascaux MSDS; 3) conservation-wiki.com; 4) 1:1 in 30% Shellsol TD

Table 2. Test adhesives and sample overview

5.2 Preparing the mock-up samples

All samples were cut from rolls of commercially available contact films, to equal size. One set of open samples and one set of closed samples were prepared as follows:

I. Open samples: Carrier film (*d-c-fix® "Designfolie"*). – pressure-sensitive adhesive – conservation grade adhesive
II. Closed samples: Carrier film (*d-c-fix® "Designfolie"*). – pressure-sensitive adhesive – conservation grade adhesive – pressure-sensitive adhesive – carrier film (see Fig. xx)

There was a set of five mock-ups of each film of each adhesive (Table 2). All mock-up series were labelled with film number and adhesive code. The test adhesive was applied with a pipette on to the PSA-side of the mock-up sample, distributed with a glass slide and left to dry (open samples). An elevation of release liner was applied on the long sides of each film, in order to create 0.1mm space for the adhesive to be distributed. The closed samples were immediately covered with an additional test-film. All closed samples were prepared at the National Museum Conservation Department in Oslo, whereas the open samples were prepared at Tate Conservation Department. The open samples were prepared using an adjustable film applicator.

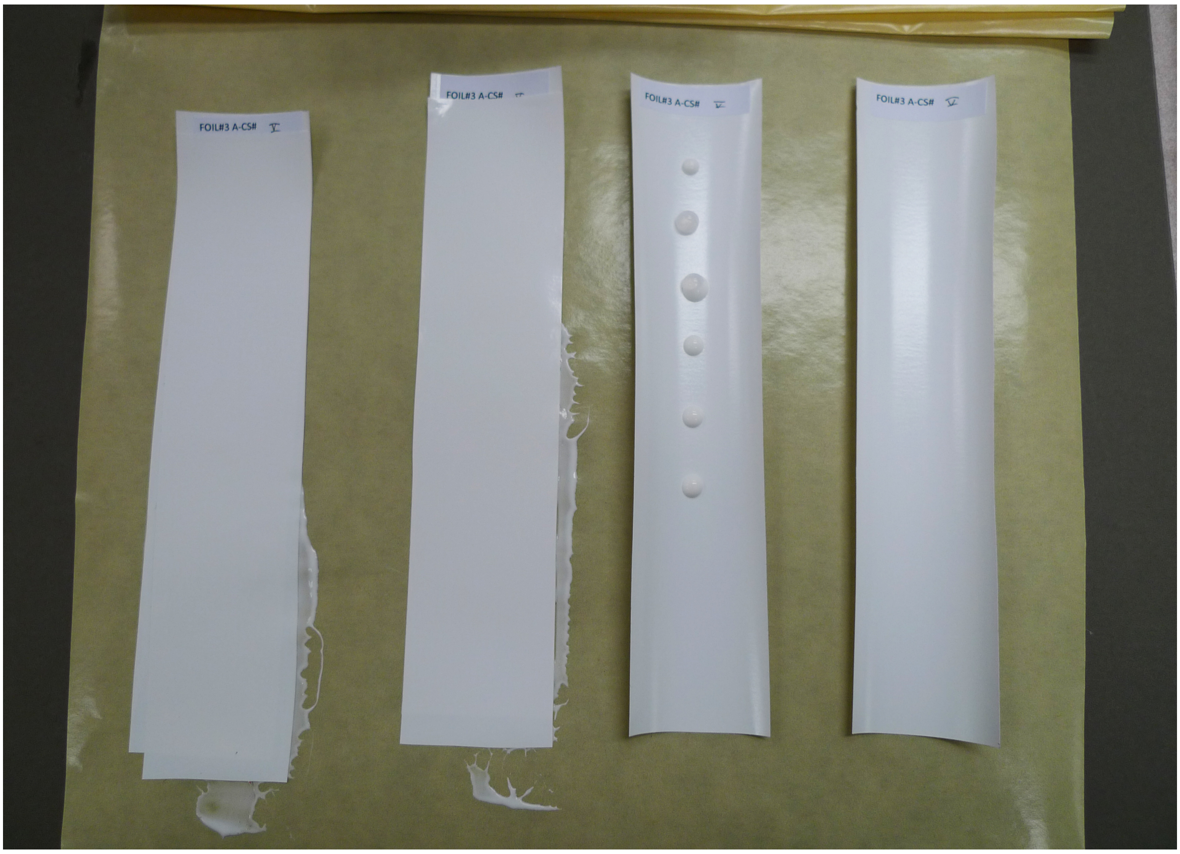


Image 6. Closed sample: adhesive was applied by pipette onto the test-material before the second film was applied on top, and the sandwich was pushed together by dragging a microscope slide across the sample applying firm force. (Photo: Anja Sandtrø/2014)

5.3 The test adhesives

Eight adhesives were tested, two of which were combined in a mixture. In addition, one set of samples was prepared without the addition of an adhesive, only the presence of the PSA from the manufacturing. Three aqueous acrylic dispersions, two vinyl acetate copolymers, one PEOX, and one mixture of two acrylics, all of which are conservation-grade adhesives, were selected for the study (Table 2). The chosen adhesives represent a variety in glass transition temperature (Tg) and pH. Adhesive selection was based on literature reviews.

5.4 Contact angle measurement

Water (25 µL) was applied by syringe onto the cured open mock-up samples, and a simple, low-cost Veho VMS-004 Discovery Deluxe USB microscope (x 10) was used to capture the droplets on the surface. Contact angles were determined by analysing photographs with the Micro Capture software DinoLite supplied with the USB microscope. The procedure was performed at the National Museum Conservation Department in Oslo, Norway.

5.5 Ageing regime

One half of the samples were placed on metal wire shelves in the Tate environmental ageing chamber, Sanyo MLR 351 (Image 7). To mimic a museum environment, UV-free lighting was preferred. Temperature and relative humidity was set to 21°C and 55%RH respectively. Accelerated light ageing using UV-filtered Phillips daylight tubes was estimated to the equivalent of 77 years. [5] 16 closed samples and 15 open samples were light aged and the equivalent 16 closed samples and 15 open samples were naturally aged in the dark. Eight open samples and eight closed samples were kept as a reference, wrapped in aluminium foil and kept in environmentally controlled storage at the National Museum in Oslo (45%RH +/- 5, 20°C).

Accelerated light ageing (ALA)	**Natural ageing in the dark (NDA)**	**Reference (R)**
Tate-light chamber 21°C 55% RH 90 – 120 days 17 000 Lux UV-free	Tate conservation lab drawers Temperature 16 - 21°C 35 – 50% RH 90-120 days	National museum storage Wrapped individually in aluminium foil 21°C 35-55% RH 90 – 120 days

Table 3. Ageing regime

---

[5] *Average of 9000 Lux – across samples. 100 Lux for 8 hours per day is average display. If samples left in 103 days for 24 hours/day. This is equal to 2472 hours at 9000 Lux =22248000 lux hours. Assuming reciprocity and an exposure of 100 lux for 8 hours per day = 800 lux hours per day. 22248000/800 = 27810 days. 27810 days = 927 months at 30 days per month = 77.25 years equivalent*

Image 7. Tate environmental ageing chamber, Sanyo MLR 351. (Photo: Anja Sandtrø/2014)

5.6 Colour change

The measurements focus on the ΔE* (single value based on the calculations of the difference between the L*, a* and b* value of a measured sample) and Δb* (yellow – blue) values. Commonly, ΔE* values at 1 or 2 are considered colour changes perceptible to the eye, and a ΔE above 5 is considered a substantial colour change (Down, 2011: 4). The transparent films were measured over a white ceramic tile. The purpose was to measure the relative variation of colour between the eight adhesives, and to detect any changes in chromophores with ageing. Colour changes were measured using the CIE-Lab*(1965) system with a Minolta CM-2600d Spectrophotometer on the adhesive side of the open samples before and after ageing. The wave length range was 400 – 800nm. Measurements were performed at the Tate Conservation Department.

Image 8 Minolta CM-2600d Spectrophotometer used for measuring colour change in the samples before and after ageing. (Photo: Anja Sandtrø/2014)

5.7 Change in pH of the adhesives

Changes in pH were measured on a selection of eight open films using a WTW pH3210 surface pH-meter calibrated prior to measurements, before and after ageing of the open samples. The procedure followed instructions from the WTW pH3210-manual, and was executed at the National Museum Conservation Department.

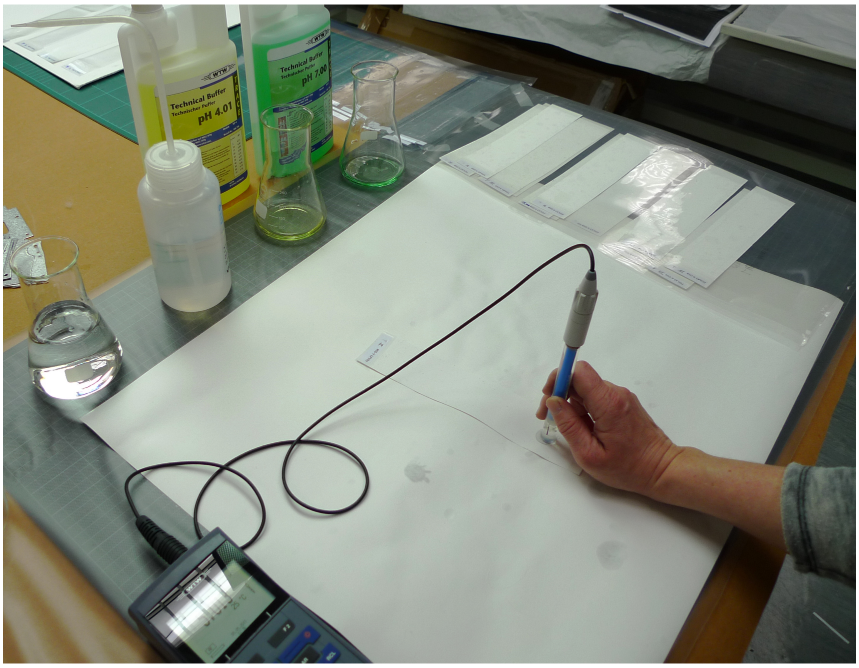


Image 9 Surface pH measurements of the samples were performed using WTW pH3210. (Photo: Anja Sandtrø/2014)

5.8 Bond strength – T-peel test

The bond strength of all closed samples were tested by using an adapted version of the ASTM D 1876 T-peel test. Any differences in force to pull comparing aged samples to reference was noted to get an indication on whether the bond had become stronger or weaker during ageing. All the samples were trimmed to the exact same size (225mm x 25mm). The samples were pulled apart by fixing one end in a vice and attaching a baggage spring weight to the other end and measuring the force (N) required to pull the films apart. The amount of force was noted, as well as the type of failure: adhesive failure, cohesive failure in the adhesive or cohesive failure in the adherend (PVC carrier), as described by Horie (2010).

A spring weight was hooked to the wall with an s-hook. A clamp was hooked into the spring scale. Another clamp was hooked to a tape-measure fixed to the table. The closed sample was slightly opened at one end, allowing it to be fixed between the jaws of the clamps. One part of the plastic sample was clamped to the windable tape measure - 20mm from the edge. The other part of the sample was clamped to the spring weight. The tape measure was wound out 1 meter. A camera was fixed in position to film the scale of the weight during pulling. The assembly was pulled tight, and the tape measure was carefully wound in, until the two plastic films were pulled apart. The filmed action was re-played and the maximum Newton is noted. The ambient temperature and humidity was 19 - 22°C / 30 +/-5 % RH. These conditions may affect the results of the strength-test.

Image 10 T-peel set up. Woundable tape measurer fixed to a table, pulling the laminate sample apart. A spring weight attached to the other end of the sample is filmed using a standard digital camera. (Photo: Anja Sandtrø/2015)

5.9 Visual examination of bond failure

Bond failure was examined in terms of adhesive failure, cohesive failure or film failure, as well as degree of adhesive pull-off. The adhesive surface was further examined and documented using a Veho VMS-004 Discovery Deluxe USB microscope (x 10).

5.10 Scanning Electron Microscopy

A selection of four films[6] were examined using SEM at the Saving Oseberg lab in Oslo, to look at the adhesive side of the pulled-off samples to look for drying patterns, creep or flow of the adhesive. From the cut-offs of the samples, some samples were examined as a cross-section sandwich, to look for voids or flow in the adhered areas. The instrument was a FEI QUANTA 450 with xT microscope Control software. The adhesive side was examined in high vacuum mode, with no surface preparation and pressure at 1.94e-2Pa, 1 kV. Samples were cut to triangles of approximately 3x3x3mm and fixed in the apparatus with carbon tape. The cross section samples were examined in low vacuum mode with no surface preparation and power and pressure varying from 3.50 – 5.00kV, and 60Pa. The samples were cut into rectangles of approximately 3x6mm, and fixed in a

---

[6] Lascaux MFC, light aged and unaged; Primal WS24, light aged and unaged; PSA, unaged.

small clamp before being placed inside the SEM chamber. The EDX-detector was not functioning at the time of analysis, and could not be employed to map element distribution.

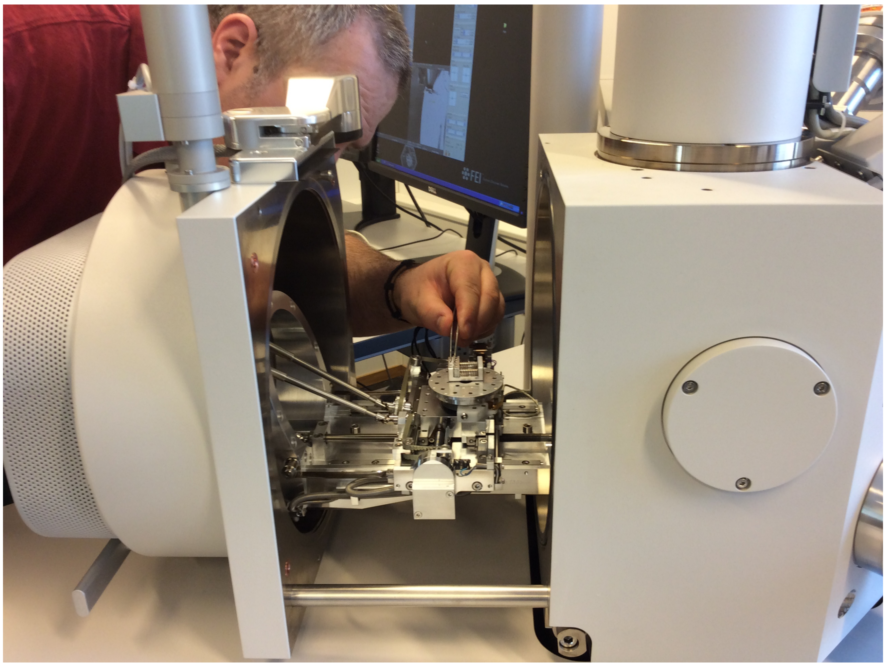


Image 11 The sample is placed into the vacuum chamber of the SEM at the Saving Oseberg lab. (Photo: Anja Sandtrø/2015)

5.11 FTIR

The adhesive side of the 37 open mock-up samples were characterised using Fourier Transform Infrared Spectroscopy (FTIR) prior to and after ageing. The purpose was to detect any shift in the carbonyl and hydroxyl indices, or the disappearance of any functional groups (p.c. Shashoua, 2014), indicating degradation and oxidation. The following indices were of particular interest:

- carbon-hydrogen stretching at 3100 – 2850 cm^{-1}; Hydrocarbons
- carbon – oxygen double bond at 1730 – 1740 cm^{-1}; Carboxylate carbonyl
- 1620 – 1560 cm^{-1}; presence of phthalate.
- carbon-carbon double bond at 1670 cm^{-1};
- the shift in carbon – hydrogen vibration at 1430 to 1455 cm^{-1} may be the result of loss of chlorine or an increase in the CH_3 concentration;
- removal of band at 690 cm^{-1} C-Cl stretching vibration equals the removal of chlorine atoms.

6 Results

6.1 Scanning Electron Microscopy of mock-ups

SEM was successfully employed on a selection of four samples after the t-peel test. The following was of particular interest: the appearance of the adhesive in the joint; contact between the adhesive layers, and between the adhesive layer and the PVC carrier; distortion, voids and bubbles in the adhesive layer.

Images obtained from the SEM showed even and coherent adhesive layers. The contact between PVC carrier and adhesive was likewise consistent. No bubbles, voids or distortion were visible in the adhesive layer. In several samples, the middle part (adhesive layer) of the sample had a sloping/ concave shape, indicating that the adhesive had shrunk, and had a high modulus, rather than flowing outside edges. The adhesive side of the Lascaux MFC-sample show areas of ripples in the adhesive surface, which may also relate to a high modulus compared to the PSA alone.

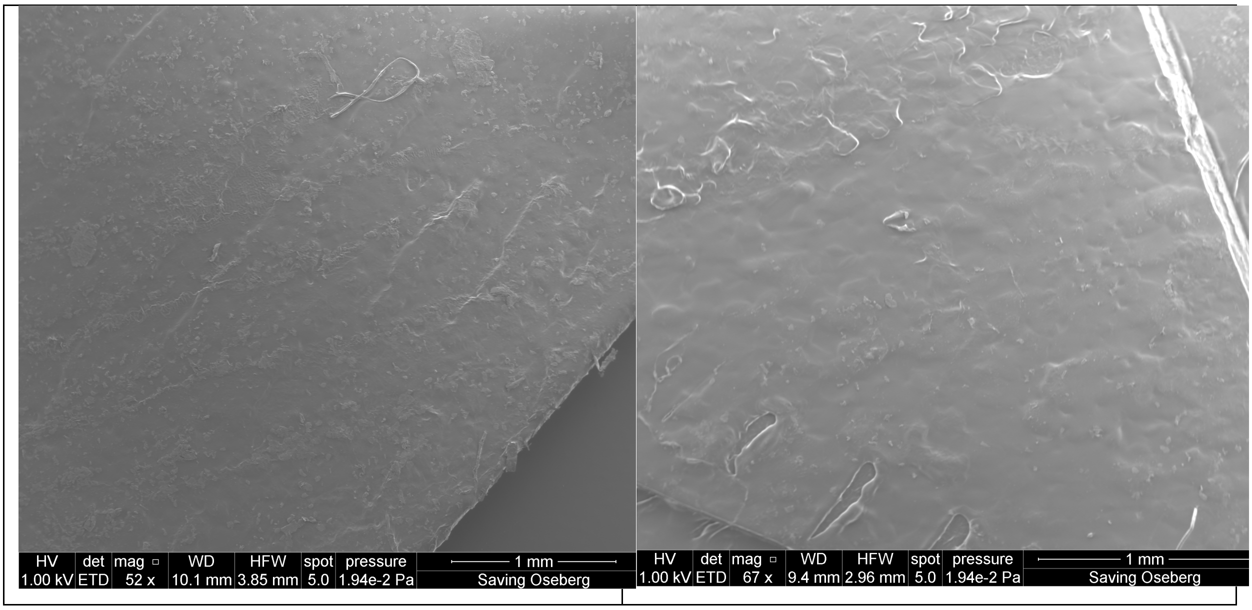


Image 12 SEM image of Lascaux MFC and PSA.

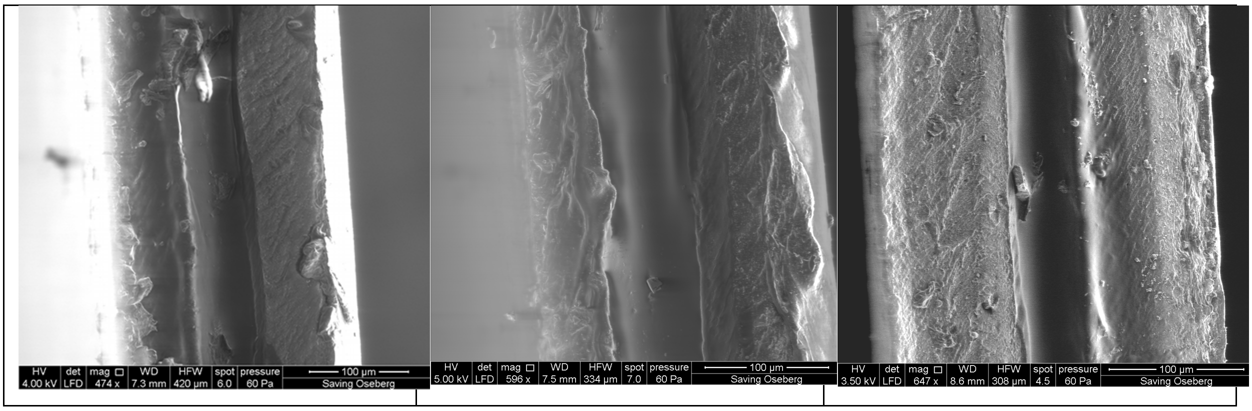


Image 13 Closed samples of Lascaux MFC light aged; Primal MS24 light aged; PSA light aged.

6.2 Bond strength of mock-ups

A summary of the overall results is given in Appendix 12.

6.2.1 T-peel test after ageing

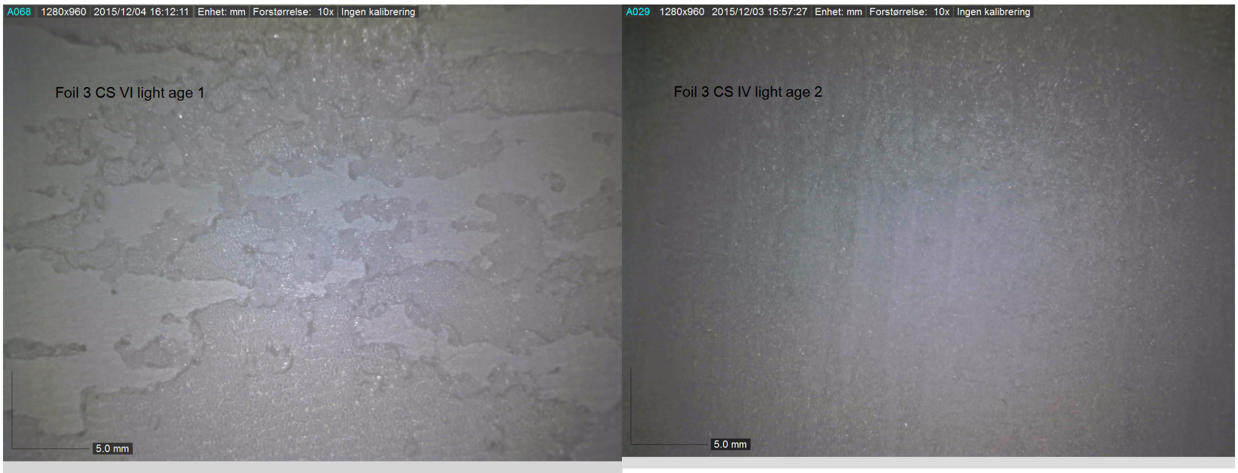
To compare bond strength, all closed samples were pulled apart in a simplified t-peel test adjusted from the ASTM D 1876. The simplification meant that the speed of the pull varied slightly for each sample, thus not giving the opportunity to calculate exact performance. However, each pull lasted between 12 - 28 seconds. According to the ASTM-standard, the speed should be at 254 mm/ min (the length of the sample should be 241mm), confirming that the test performed at reasonable speed, as samples were 220mm. The spring weight was tested in advance, although the majority of the actual test material required a higher force than was within the scale of the weight (20N). When testing the set-up on fresh mock-ups, 20 N was sufficient; indicating that cross-linking may have occurred to the aged mock-ups during ageing. There were, however, slight differences in types of failure.

Primal WS24 and Dispersion K360 mostly failed at no more than 20 N. Lascaux Medium for Consolidation required a pull above 20N, and also displayed both adhesive and cohesive failure with strong pull-off of adhesive in both samples aged in the dark and samples aged in the light. More adhesive pull-off was evident at the beginning of each pull, as the speed was somewhat slower at the start of the pull. Most samples had an even pull and only cohesive failure, however two of the Mowilith DMC2 samples also had adhesive failure and strong pull-off of adhesive. All samples with Aquazol 200 required a force above 20N. Several samples also showed pull-off of adhesive, with no difference in samples aged in the dark and samples aged in light. The samples with the addition of Paraloid B67/Plexigum PQ611 also required a pulling force above 20 N, and displayed both cohesive and adhesive failure. The samples displayed more adhesive tack to the touch after pull than the rest of the samples.

- There was no obvious relation between adhesive failure and ageing conditions (light/ dark).
- No samples had failure in the carrier nor failure in bond, film and adhesive (Horie, 2010, p. 103).

Dispersion K360. Aged in the dark.

Pressure-sensitive adhesive only. Light aged.



Aquazol 200 light aged displaying adhesive pull-off

Lascaux MFC light aged displaying adhesive pull-off

Table 4. Adhesive side of closed samples after t-peel test. Different degrees of adhesive pull-off is evident. (All photos: Anja Sandtrø/2015)

6.3 Contact angle of mock-ups

The contact angle was measured on the adhesive side, only prior to ageing. It became apparent that the contact angle image had to be taken immediately after placing the droplet on the surface, as some droplets spread out fairly quickly. Therefore, the images are taken immediately after placing the droplet. The aim was to get a relative indication of surface wetting properties of the cured adhesives. Results from the contact angle measurements are given in Appendix 10.

The contact angle of PSA alone was 57°, well below the 90° angle indication of limited wetting properties. All samples displayed a contact angle below 90°, suggesting good wetting properties of all tested adhesives in conjunction with PSA.

- Lascaux MFC, Acronal D500 and Aquazol 200 had the lowest contact angle, i.e. the best wetting properties.
- Plexigum PQ611/ Paraloid B67 and Dispersion K360 had the highest contact angle.

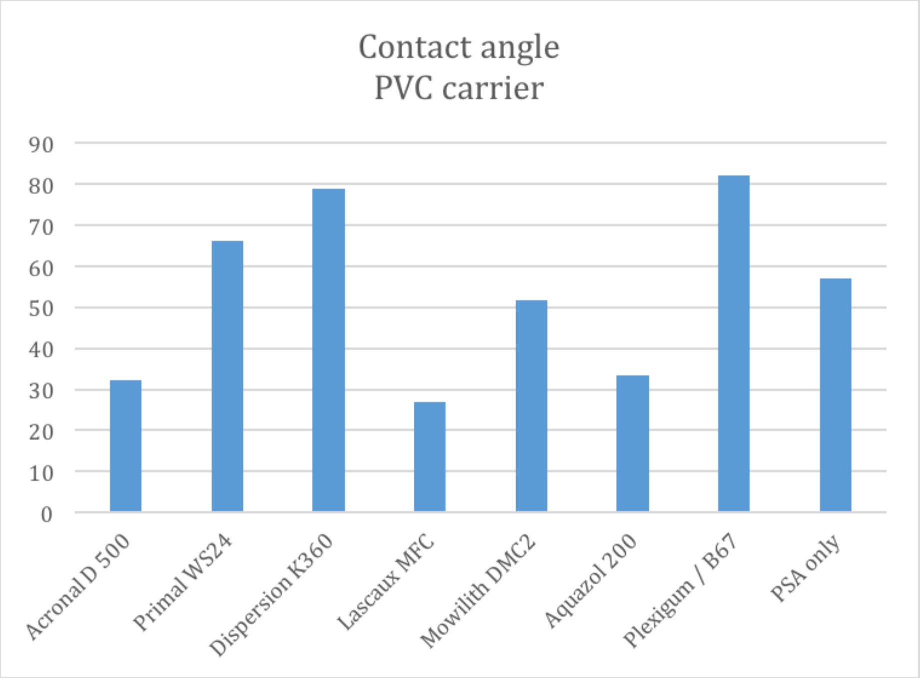


Table 5. Contact angle measurements.

6.4 Colour measurements of mock-ups

Colour measurements were successfully performed prior to and after ageing. However, several of the samples aged in the dark displayed some dust build-up on the surface. The samples aged in the light-chamber had tiny crystals on the surface from the ageing process. These crystals were carefully brushed off using a goat's hair Japanese brush. Unfortunately, the measurements from samples with Mowilith DMC2 were lacking or insufficient to be compared and are therefore not mentioned in the results. Results from the colour measurements are presented in Appendix 8.

There is a significant difference in colour before and after ageing. Samples aged in the light displayed the greatest difference in ΔE*. Samples aged in the dark caused less overall difference than light ageing. The samples undergoing natural ageing in the dark had a difference of 3 points in ΔE* from the greatest change to the least change in colour.

- PlexigumPQ611/Paraloid B67 had the least change and Acronal D500 had the most significant change.
- Primal WS24 had the least change in ΔE* of the samples aged in the light, though still a significant difference (19.0).
- Lascaux MFC and PSA seemed to be influenced the greatest in light environments. However, the difference from the least change to the greatest change from light ageing is minor (1.0).

When studying Δb* separately, the samples aged naturally in the dark had more yellowing than samples aged in the light. None of the samples had a Δb* above 5 (Primal WS24 at 3.9), and all samples had a difference of less than 3, thus being within the acceptable range of change as described in section 5.6.

- Acronal D500 had the greatest change towards yellowing.

When studying ΔL* separately, the change in L* value varied quite considerably after light aging in particular. This indicates that the samples became lighter upon light ageing, rather than significant changes in the blue—yellow scale and the green—red scale. Because the carrier side is opaque white, this change is not visible to the eye.

- Primal had the greatest change in ΔL* from both light ageing and ageing in the dark, whereas PSA had the least change, though still significant.

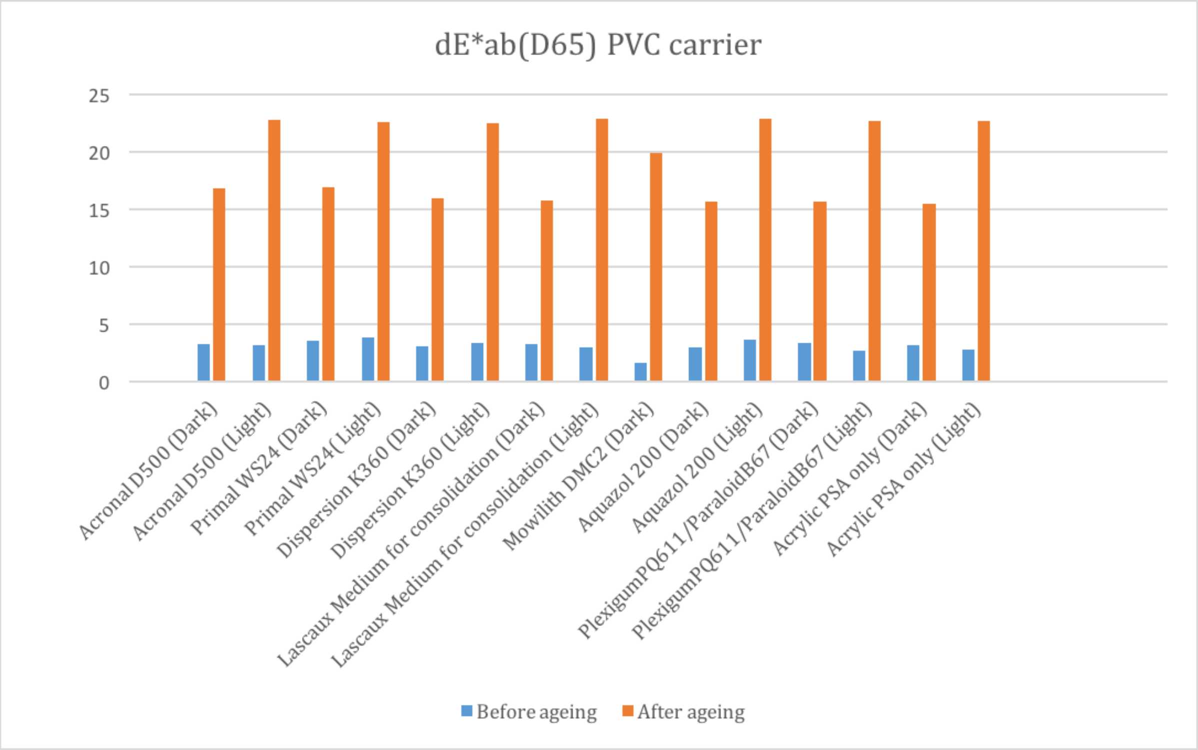


Table 6. Colour change (dE) measured on adhesive side of mock-up samples before and after ageing.*

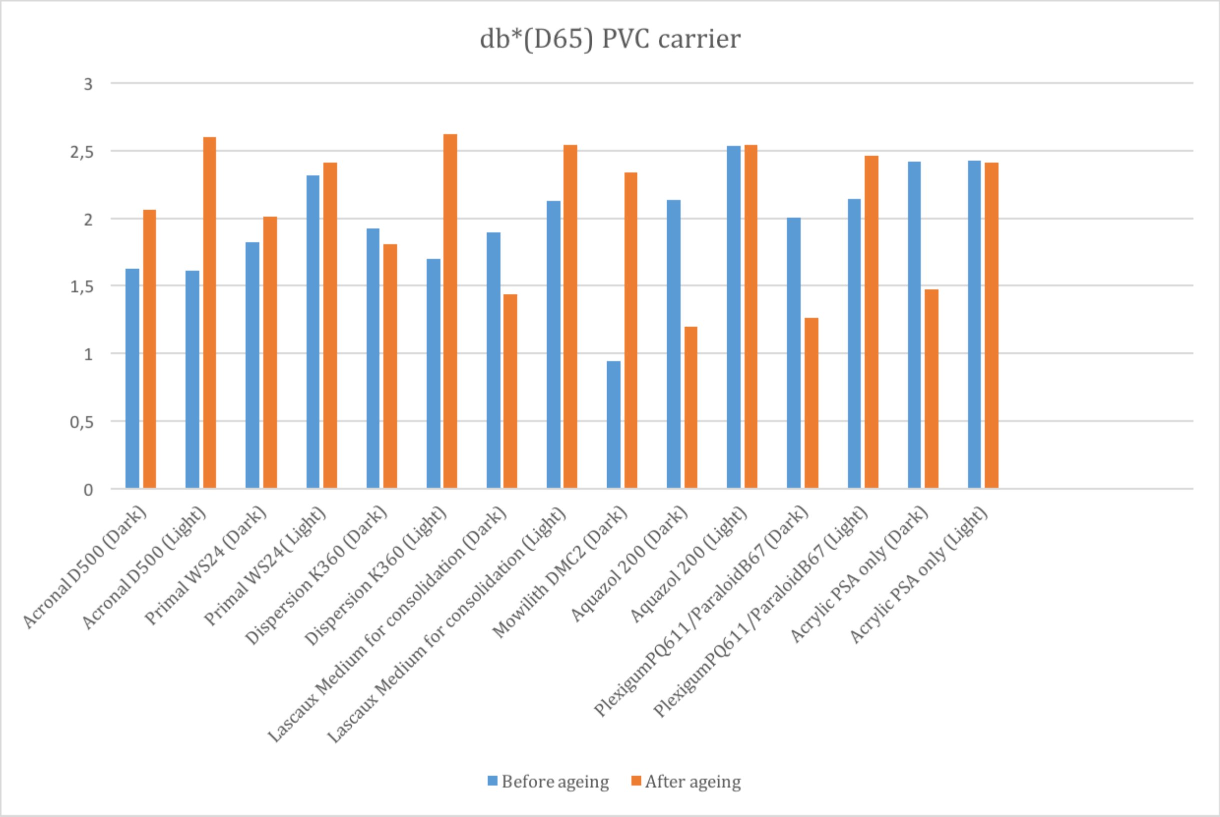


Table 7. Yellowing (db) measured on adhesive side of mock-up samples before and after ageing.*

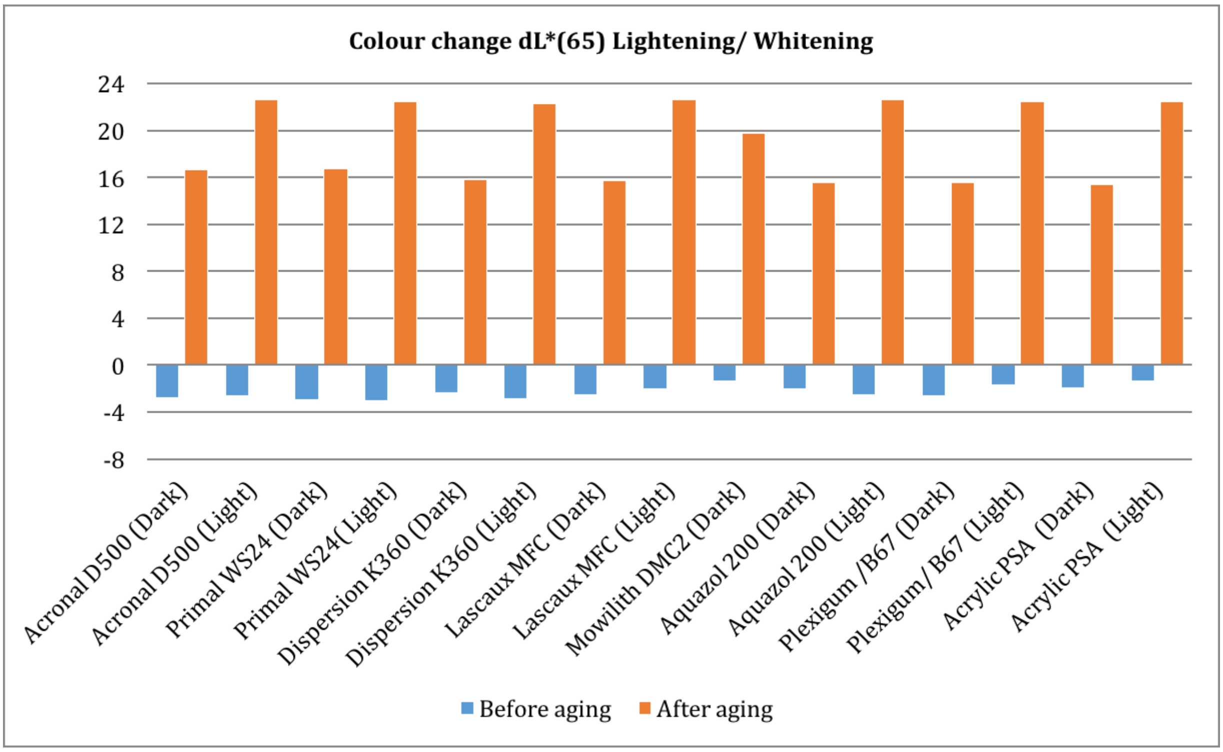


Table 8. Lightening/ whitening (dL) measured on adhesive side of mock-up samples before and after ageing.*

6.5 pH measurements of mock-ups

All samples aged by light were measured before and after ageing to observe any changes in surface pH. However, when measuring the same sample twice, the results were very inconsistent, thus the reliability of the results may be questioned. The results are to be considered relative to each other, rather than actual pH readings on their own. Results from the pH measurements are presented in Appendix 11.

- There seem to be a minor change in pH after ageing in all samples.
- Plexigum PQ611/Paraloid B67 showed a pH closest to neutral prior to ageing.
- All samples became slightly more acidic (except one measurement of Primal WS24).
- Plexigum PQ611/ParaloidB67 and PSA alone underwent the greatest shift in pH, towards a more acidic nature after ageing, followed by PSA only and Dispersion K360 had the greatest shift in pH after ageing.
- Primal WS24, Aquazol 200 and Lascaux MFC had the least change in pH after ageing, showing a minor shift towards a more acidic value.

- Lascaux MFC and Mowilith DMC2 remained in the same acidic region of pH after ageing, thus somewhat more acidic than Aquazol 200.

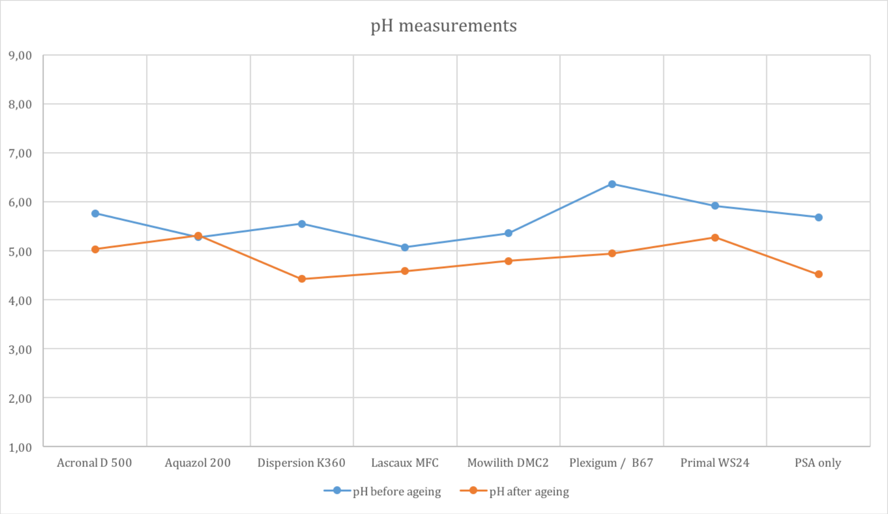


Table 9. Surface pH measurements before and after ageing.

6.6 FTIR of mock-ups

All aged open samples were scanned and characterised by the aid of FTIR (ATR) before and after ageing. Minor differences were visible when studied carefully and results are summarised in Appendix 4.

- Samples with Acronal D500 and PSA had the least changes in absorption bands after ageing. Only slight changes in the C-O region (1260-1050 cm^{-}1) was detectable.
- Samples with Lascaux MFC, Aquazol 200 and Plexigum/B67 had detectable changes in all band regions studied, apart from in the phthtalate region (1620 – 1560 cm^{-}1) in which no change was detected in the Lascaux MFC-samples.
- Possibly appearance of phthalates in samples with Primal WS24, Mowilith DMC2 and Plexigum/B67.

None of the spectra gained from FTIR displayed strong shifts, broadening or splitting in the carbonyl group or other relevant bands. Only a change in absorbance intensity in the carbonyl region in particular was readily visible.

6.7 Tack and visual examination of mock-ups

The samples were examined visually, and by touching and rubbing a finger on the surface. The samples with Aquazol 200 have some web-like raised lines in the open samples, indicating pulling during curing. The appearance of these thin lines in the adhesive film was also evident when bending the sample. Dispersion K360 has high tack in open samples, with visible yellowing as well. Primal WS24 has slight tack. Acronal D500 and Plexigum PQ611/Paraloid B67 have slightly more tack than Primal WS24 in the open samples after light ageing. However, in an area of slightly thicker adhesive, the Primal cracked in very thin, straight lines when the film was bent. PSA alone also retained tack after ageing. The other adhesive samples cured more or less completely, being dry to the touch.

Adhesive type		Acronal D500	Primal WS24	Dispersion K360	Lascaux MFC	Mowilith DMC2	Aquazol 200	Plexigum PQ611/ ParaloidB 67	Acrylic PSA only
Tg *		-13° C	46° C	- 31° C	4° C	11° C	69°—71° C	32° C / 50° C	
Bond strength (Newton)	Dark	20N	20N	20N	20N	20N	20N	20N	20N
	Light	20N	20N	20N	20N	20N	20N	20N	20N
Bond failure - cohesive	Dark	Y	Y	Y	Y	Y	Y	Y	Y
	Light	Y	Y	Y	Y	Y	Y	Y	Y
Bond failure - adhesive	Dark				Y		Y	Y	
	Light				Y		Y	Y	
Colour (ΔE) before ageing	Dark	3,31	3,52	3,13	3,26	1,66	3,00	3,37	3,16
	Light	3,19	3,85	3,42	3,00	0	3,66	2,75	2,83
Colour (ΔE) after ageing	Dark	16,79	16,90	15,90	15,80	19,91	15,64	15,62	15,47
	Light	22,77	22,58	22,48	22,84		22,84	22,63	22,65
Yellowing (Δb) after ageing	Dark	1,61	1,83	1,93	1,90	0,94	2,14	2,01	2,42
	Light	1,62	2,32	1,70	2,13		2,54	2,14	2,43
Yellowing (Δb) after ageing	Dark	2,07	2,01	1,81	1,44	2,34	1,20	1,26	1,47
	Light	2,60	2,42	2,63	2,55		2,55	2,46	2,41
pH change	Before ageing	5,77	5,28	5,55	5,07	5,36	6,36	5,92	5,69
	After ageing	5,03	5,31	4,42	4,59	4,79	4,94	5,27	4,52
Contact angle		32,3°	66,2°	78,8°	26,8°	51,7°	33,3°	82,3°	57°
Polymer		1	2	3	4	5	6	7	8

Polymers:

1. nBA/VAC/VC, acrylic acid ester copolymer
2. nBMA (nbutyl methacrylate)
3. Aqueous emulsion of a thermoplastic acrylic polymer BA/MMA (butyl acrylate/methyl methacrylate)
4. Aqueous dispersion of acrylic copolymers based on acrylate ester, styrene and methacrylic ester
5. Aqueous dispersion of a copolymer based on vinyl acetate and maleic acid di-n-butyl ester. 35% dibutylmaleate with a celluloce ether stabiliser
6. Poly (2-ethyl-2-oxazoline)
7. Isobutyl methacrylate solution of an acrylic polymer / Isobutyl methacrylate
8. Butyl acrylate

Table 9. Overall results.

6.8 Summary results PP film mock-ups

6.8.1 Bond strength (Appendix 13)

- All samples of poly propylene (PP) film carrier displayed less adhesive strength than the PVC carrier films.
- After light ageing, PSA, displayed the strongest bond, and Aquazol 200 had the weakest bond. The former being a butyl acrylate, and the latter is a poly (2-ethyl-oxazoline).
- After natural ageing in the dark Lascaux MFC and Mowilith DMC 2 had strongest bonds, and are acrylic copolymer and vinyl acetate, accordingly.
- Acronal D500, Aquazol 200 and PSA had the lowest force to pull samples apart after ageing in the dark. Acronal D500 is an acrylic acid ester copolymer.
- In general, ageing in the dark required less force to pull than samples aged in light.

6.8.2 Colour change (Appendix 9)

- After light ageing, Lascaux MFC had the most significant change in colour (dE*(65)), and Dispersion K360 had the least change in colour.
- Plexigum PQ611/Paraloid B67 had the most significant colour change from natural ageing in the dark, and Acronal D500 had the least change in colour.
- Overall, natural ageing in the dark caused less colour change (dE*) than ageing in light. However, as with the PVC-samples, all PP samples displayed very high dL*-values after ageing. All dL* values are significantly higher after light ageing compared to natural ageing in the dark.

6.8.3 FTIR (Appendix 5 and 7)

- The most prominent changes from ageing are seen in samples prepared with Acronal D500 (nBA/VAC/VC), Primal WS24 (nBMA) and Plexigum PQ611/ Paraloid B67 (BMA/MA). Changes in the carbonyl-region (C=O) is particularly noticeable in these samples.
- Acronal D500, Lascaux Medium of consolidation and Plexigum PQ611/ Paraloid B67 also had a decrease in absorbance in the hydroxyl region (C-H) after ageing.
- All samples had minor changes in the ‘fingerprint’ region after ageing.

6.9 Summary of results

From assessing the mock-up samples prior to and after ageing, results indicate changes in physical and chemical structure. Results from the t-peel test of the PVC-samples do not display a particular relation between bond failure and ageing conditions. Several samples had different degrees of adhesive pull-off, apart from Acronal D500 (Tg -13), Dispersion K360 (Tg – 31). There are no major differences between results from aged samples compared to reference samples except less adhesive pull-off on two reference samples. A significant colour change in the aged samples is particularly evident in the dL*-values (whitening or lightening). Surface pH measurements indicate a slight shift in pH towards a more acidic region after ageing. The assessment of the samples using FTIR show least change in Acronal D500 and PSA, while samples prepared with Mowilith MC2, Aquazol 200 and Plexigum /B67 possibly indicate a change in the phthalate region. The samples show changes from both ageing in the dark and light ageing, though visible in different band regions of the spectrum. The two adhesives with the highest Tg suffered from very fine cracks when bent after ageing.

All values in the test series are to be considered relative to each other, rather than exact values for each material.

7 Discussion

In the following, several research questions will be re-visited: What are the driving forces behind degradation and loss of adhesion? What is the effect of introducing a new adhesive into the laminate of a PVC carrier and pressure-sensitive adhesive? Will the addition of a second adhesive reduce cold flow in the pressure-sensitive adhesive? Finally, the acceptable values for use on the study object *Time Zero* are discussed at the end of this chapter.

7.1 What are the driving forces behind the degradation process to cause loss of adhesion?

The following section will focus on findings that may indicate mechanisms of degradation in the pressure-sensitive adhesive layer in particular. Findings indicating cross-linking, chain scission, hydrolysis or oxidation are of particular interest when looking at processes of degradation.

The adhesive tide lines surrounding most of the PVC surface films in *Time Zero* point to *firstly*: hydrolysis of the adhesive layer due to dirt pick-up and degradation of additives such as plasticisers. *Secondly*: shrinkage, deformation and creep of the films. Shrinkage is caused by loss of material (plasticisers, chlorine). *Thirdly*, plasticisers lost from the PVC carrier may have migrated indo the adhesive layer, creating more space between the molecular chains i.e. movability of the adhesive polymer.

Results from the t-peel test show that bonds require a higher force to be pulled apart after both light ageing and ageing in the dark. One of the degradation mechanisms causing stronger bonding, is cross-linking. When a material cross-links, the solubility decreases, making the adhesive layer more difficult to remove by means of solvents. Several of the aged test-materials displayed adhesive failure at the interface of adhesive and carrier after the addition of a conservation grade adhesive and light ageing involving accelerated lux hours. Adhesive failure causing pull-off of adhesive from one carrier side may indicate strong cross-linking. However, the intention in this study was to investigate the possibility of gaining adhesion rather than making weak bonds. In this respect, cross-linking may be favourable. On the other hand, removability of the adhesive in the future may be more difficult if cross-linking occurs. At this stage, though, it is not known whether cross-linking in the tested material will continue, creating an even more rigid and dense material.

Another possibility is that plasticisers have migrated out of the adhesive layer towards the carrier side of the samples due to increased cross-linking, causing less adhesion between carrier and adhesive. FTIR spectra from three of the mock-ups may indicate such a movement of plasticisers. However, neither of the samples seem to have become very rigid or hard, which could indicate crystallisation.

In opposition to cross-linking, chain scission breaks polymer bonds, decreases average molecular weight and weakens the structure. The mechanical tests did not indicate any chain scission was taking place as cohesion in all samples proved to be fairly strong. Even when the samples were pulled apart by strong force, the film carrier did not fail. This finding supports the assumption that no chain scission has taken place in the carrier or the adhesive layer, under these ageing conditions.

Results from colour measurements suggest that the acrylic PSA alone may be very sensitive to light, but not by yellowing. Lightening or whitening of the adhesive seems to be a greater challenge when exposed to light ageing. This implies the result will also affect all the tested adhesives applied on top of the PSA. It is, however, difficult to give an explanation for what causes the lightening, and whether this is a result of degradation or not, and needs to be further explored. Yellowing may indicate cross-linking of a material or through Norrish reactions[7]; it is most evident in the samples aged in the dark, supporting the finds by Howells et al. (1984); Sale (2011); Down (2015). Looking at *Time Zero*, these results suggest that the yellowing within the laminates may just as well be caused by dark storage. Yellowing in *Time Zero* is most evident in the upper part of the face side, and less prominent in other areas. The lightening and yellowing do not seem to have a significant correlation to adhesive failure. However, as already stated, the t-peel test is not completely representative, due to the upper force limits of the scale (20N).

---

[7] Photochemical reactions involving the carbonyl groups.

Acids present on the adhesive surface may indicate the presence of degradation products such as phthalic acids. All test material displayed a shift towards acidity, except dilute Plexigum PQ611/ Paraloid B67, indicating the presence of degradation products from the ageing process. The sample of pressure-sensitive adhesive alone displayed a significant shift from the neutral to the acidic region after ageing, also confirming degradation to some degree. However, as pH measurements are very difficult to compare, it may be difficult to explain an increase in acidity after ageing simply through degradation (Ashley-Smith, 1992). That said, polymers do not normally contain free hydrogen ions (Shashoua, 2014); thus, the shift in pH is most likely to evolve from degradation products from additives such as plasticisers or stabilisers, or from external contaminants (dust and dirt) accumulated on the surface, which are also present within "garbage collages" like *Time Zero* . These contaminants are likely to contain H+ ions, which readily react with water to form acids (i.e. hydrolysis). pH measurements are useful to distinguish the most acidic adhesive surfaces from the least acidic surfaces, and also to document the pH of the base material and the proposed conservation material in order to avoid ionic shock during a conservation treatment. The change in pH is not fully explained in the studies by Down et.al., other than as an indication of degradation. It is reported, however, that the acrylic adhesives are more neutral as a group than the PVAC adhesives (Down, 2015: 38). It may seem legitimate to study the change of pH within a synthetic adhesive more in normally depth, in order to understand the cause of change in pH. However, the ASTM-procedure used by Down et.al. may be more applicable than the surface pH measurement method. If acidic products are formed during ageing, do they remain within the material matrix, do they evaporate, or do they immediately form new chemical bonds? Furthermore, the effect of applying an adhesive with a different pH to the already degraded material substrate, as well as the use of buffers on polymers, needs to be further explored; however, in this case, such as study was outside the scope of this project.

Spectra from FTIR can indicate if changes after ageing occur on a molecular level. The sample consisting of PVC carrier and acrylic PSA alone may represent the 'untreated' material, and is the most likely to mimic reactions within the films in *Time Zero*. Only minor changes are detectable from the spectra, and are most prominent in the spectra from natural ageing in the dark than from accelerated light ageing. These findings support the fact that colour change occurs more prominently from ageing in the dark. PSA and Acronal D500 (which is sometimes used as a component in pressure sensitive products) displayed the least changes in spectrum bands, indicating good chemical stability when stored in the dark, and Acronal D500 is slightly more sensitive to light conditions than PSA when exposed to high values of light, and stable temperature and relative humidity[8]. As already mentioned, accelerated ageing is often not considered reliable enough to calculate and predict the longevity of a conservation material or a conservation treatment. There are too many factors that may influence the initiation and rate of degradation (Brydson, 1999: 99). However, the method may be used to compare products and conservation methods relative to each other, to elucidate some of the factors that may play a more significant role in degradation processes, as well as factors that may reduce or inhibit degradation. Studying the test material by natural ageing in sunlight or in the dark, may give more reliable results as to longevity of the materials and methods. This would, however, be very time consuming, and could carry the risk that the conservation products are discontinued by the end of the study. Looking at *Time Zero*, storage environments have fluctuated annually (approximately 25-35% in the winter/ 35-45% RH in the summer). In order to understand the degradation processes within the artwork, environmental conditions may be further explored.

Images from the scanning electron microscope do not display any voids, cracks or droplets, which would indicate degradation of the adhesive layer. However, some rippling of the adhesive in adhesive side of the Lascaux MFC is visible. The ageing procedure in this study has not been able to create embrittlement in the PVC carrier, as seen in the original *Time Zero* material. Furthermore, neither deformation nor loss of adhesion are detectable in the study material, though they are both prominent in the original artwork.

As described in chapter 3, pressure-sensitive adhesives degrade by hydrolysis (gaining water), becoming more liquid, and then by cross-linking and becoming dry and brittle. In this project, an acrylic PSA has been the object of study. Acrylic pressure-sensitive adhesives have, in previous studies, proved to be more stable to degradation than

---

[8] A greater difference is visible in the PP film mock-ups.

rubber-based PSA and vinyl-type PSA. Preliminary research on the carriers and adhesives in *Time Zero* supports the assumption that the more stable areas are those in which acrylic PSA is present, as opposed to the more unstable PVAc PSA. Plasticisers present in the PSA may migrate to the carrier material, or plasticisers from the carrier material may migrate into the adhesive layer. When plasticisers contact oxygen, or heat in particular, they start to degrade, forming phthalic acids. Measuring dimensional changes have been outside the scope of this project. No test samples suffered failure in the PVC carrier, nor did any of the samples display cold flow, suggesting light ageing is not the single main initiator of mechanical degradation of pPVC and acrylic PSA. Lastly, the glass transition temperature of the PSA may originally have been very low, remaining in a liquid-like state in room temperature even today, 34 years after it was made (Horie, 2010, p. 46).

According to Horie (2010: 37), deterioration is any change in the polymer that makes it unfit for use in its context. This experiment has not been able to reveal the degradation processes causing loss of adhesion. In order to find evidence of plasticisers migrating from the carrier side to the adhesive layer during ageing, further investigation is needed. However, some findings confirmed that degradation does occur, taking place during ageing in the dark in particular.

7.2 What is the effect on the bond when introducing a new adhesive to the degraded material?

This research question cannot be fully answered due to the following: the testing was not performed on the original, degraded material, as this would be highly inappropriate. Furthermore, the test-material was not pre-aged, thus not reacting as degraded material prior to the application of test-adhesives. However, some aspects of how the materials interact may be understood when comparing the adhesive requirements listed in Chapter 4 to the results from the experiments. These are discussed below; specifically, prerequisites for good adhesion, and necessary conditions for use in the conservation of *Time Zero*.

7.2.1 The adhesive needs the appropriate surface tension and adhesive flow

In order to ensure complete distribution of adhesive between the two layers of PVC films and PSA, good wetting is essential for the treatment result. Adhesives tested in this project were all medium to low viscosity-adhesives. The surface tension of the adhesives applied to the test material were all within the acceptable range of good wetting (less than 90°). Due to the method of application, all adhesives were well distributed on the surface, not being repelled by the PSA-surface, but resting sound once applied. Thin layer application and even distribution was essential to avoid adhesive build-up, and also to obtain a consolidating effect of the PSA, rather than mere adhesion between two separate layers of adhesive. In theory, the low-viscosity adhesives with a low contact angle will be the most suitable adhesives for bonding *Time Zero*, as they would flow more easily in between the film layers, displacing oxygen, and ensuring the fundamentals of a good bond. However, in the experiment, all adhesives required some level of mechanical manipulation to be evenly distributed. The droplets placed on the surface did not flow in all directions at once, though the contact angle measurements concur with the flow-rate of the adhesives when applied. However, the contact angle of the adhesive droplet on the PSA-surface may give more accurate results when it comes to properties of flow and viscosity. It may be concluded that any method of application will require some level of mechanical manipulation (e.g. pressure) of the pure adhesives to get the appropriate distribution.

7.2.2 The adhesive needs resistance to creep

As *Time Zero* is self-supportive, i.e. not fixed to a secondary support, the films in the artwork are under constant strain when hanging vertically. It is therefore essential that any adhesive applied to the art-work will resist creep, thereby preventing movement or delamination of the films. Under normal circumstances, Horie recommends to use adhesives with a Tg above 40°C in order to avoid creep (Horie, 2010: 115). However, due to the flexible nature of the PVC carrier, a lower Tg-adhesive would be appropriate for *Time Zero*. The resistance to creep is not fully understood from the test results, as creep-tests were not performed. According to Benedek (2004, p. 305), creep will be reduced by plasticisers of high molecular weight, and less plasticiser. This phenomenon may be further explored in relation to the interaction of adhesives, migration of plasticisers and possible paths of manipulating the adhesive layer. To better understand creep-resistance, both the molecular weight of the adhesive and its affinity to plasticisers need to be analysed. Shashoua explains that too little plasticiser in PVC may result in a rigid material, with a higher tensile strength, but poorer impact resistance and elongation than even unplasticised PVC (antiplastisation) (Shashoua, 2001a, p. 15). The t-peel test gives some indication of creep properties in the adhesive layer. However, a shear test may give more accurate values, as the samples are adhered by lap-bond, and pulled apart by force, or statically by applying weights (as in *The international standard EN 1943 Self Adhesive Tapes – Measurement of Static Shear Adhesion*). However, none of the test material indicated creep from the mechanical test. Furthermore, the SEM-images confirms that the adhesive layer had not spread to the outside edge of the carrier, but rather pulled slightly back. It is important to note that the addition of a second adhesive to the test material did not cause buckling or deformation of the films as caused by too strong modulus in the adhesive. The adhesive needs to be able to remain bonded despite the presence of plasticisers, and the possible movement of plasticisers towards or into the added adhesive. This aspect needs to be further explored.

7.2.3 The adhesive needs appropriate bonding properties to both original adhesive and original material

Because the test-adhesives were not applied directly to the original material, the adhesives properties can only be confirmed when all appropriate tests are done, and the first treatment test is executed on *Time Zero*. As described in Chapter 4, a good bond is recognised by a balance between cohesion within the adhesive, and adhesion to the material to be bonded. The images obtained from SEM confirms good bonding properties in the adhesives, as the adhesive layers are coherent - it is not possible to distinguish the PSA from the additional adhesive, and there are no voids, cracks or air-bubbles in the adhesive layer, nor between adhesive layer and carrier material, which would indicate weaknesses in the bond. Horie describes setting properties as a criterion for good adhesion(Horie, 2010: 100). This aspect was not explored in this study. The samples were pressed in a vice during ageing, forcing all samples flat during curing. If the samples had been cured in open air, the setting properties may have been studied in more detail to observe deformation or whether the adhesive caused the carrier material to relax. The original PSAs are also in contact with other materials such as degraded paper, photography and various plastics. A more comprehensive literature review alongside further tests on these materials may ensure compatibility. Furthermore, the adhesives need to be tested on already degraded material to better understand the reactions and interactions between fresh conservation adhesive and degraded PSA and PVC.

7.2.4 The adhesive needs good adhesive strength

The mechanical tests confirm good adhesive strength in all materials. There is, however, a stronger adhesion between PSA and test-adhesive than between adhesive layer and carrier material in the majority of test-material. It may be suggested that the PSA and the additional adhesive seems to bond well, creating good cohesion. Thus, the adhesive pull-off in several samples indicates that there might be the possibility of failure between adhesive and carrier in the future. Whether this failure is within the acceptable limits for *Time Zero* may be evaluated in conjunction with the other results and threats to the longevity of the artwork. Alternatively, a join should ideally fail in the adhesive layer, rather than at the adhesive—carrier interface, or within the carrier and adhesive, favouring the adhesives without adhesive failure: Acronal D500, Dispersion K360 and Primal WS24.

Adhesive failure may be explained by the cross-linking of the adhesive layer and a simultaneous migration of secondary plasticisers to the intermediate layer between PVC carrier and adhesive layer (Skeist, 1977: 657), causing strong pull-off of adhesive from the carrier. This is supported by the fact that adhesive pull-off occurred most prominently in the samples in which traces of phthalates were visible. The rate of cross-linking may be confirmed by Differential Scanning Calorimetry (DSC).

The dispersions Acronal D500 (nBA/VAC/VC), Primal WS24 (nBMA) and Dispersion K360 ((BA/MMA) had the least adhesive failure and pull-off. Is this due to the absorption of plasticisers by the adhesives? Or because of a lesser rate of cross-linking within the adhesive? A more diverse t-peel test may further clarify these topics, since less cross-linked adhesives would make a weaker bond and less force would be necessary in the t-peel test. These three adhesives were also amongst the most yellowed during natural ageing in the dark. There seem to be no relation between adhesive failure and lightening (luminance). In the studies by Howells et.al. (1984), even the samples with greatest yellowing after ageing, did not display any apparent mechanical change when tested in a tensile machine.

The tensile strength of a polymer decreases as the temperature rises above Tg (Benedek, 2004: 90). The Tg of acrylic PSA used in this project is unknown; however, Benedek (2004: 91 - 92) gives a Tg of –15°C to +5°C to be a normal range for PSA.

7.2.5 The adhesive needs to retain flexibility after curing

If flexibility is lost in *Time Zero*, it is more likely to suffer mechanical damages such as splitting and tearing during handling. The combined size of the artwork and lack of a secondary support directs stress directly to the films and other materials in the collage; thus some flexibility would somewhat reduce the stress. The experimental design did not contain any specific tests for evaluating flexibility. Nevertheless, the visual examinations of the open samples gave some indications of how the test material reacts in terms of flexibility after ageing. When examined flat, most samples seemed to have an even and slightly tacky surface, though a few were dry to the touch. When the 'dry' samples were bent at a steep angle, thin lines appeared in the adhesive layer as a result of cracking. Two of the samples in which this occurred consisted of high-Tg adhesives (as explained in the previous chapter). All carriers were flexible and without change. All samples had remained soft and flexible to the touch after ageing. This phenomenon was not studied, as it was expected that the differences in flexibility would be too minor to detect. Aquazol samples were the only samples where cockling and buckling of the edges of the films could be observed. This cockling may be due to shrinkage of the adhesive during curing. If the consolidant applied to *Time Zero* has a too high Young's modulus — and at the same time shrinks during curing — it may cause tension on the surrounding material, i.e. the PVC carrier, causing permanent damage (Horie 2010, p. 29). Or if the PSA and the consolidant have a higher Tg than the PVC, this also may cause stress to the PVC carrier if temperatures are fluctuating.

The glass transition temperature is an indication of the softness of a polymer (Horie, 2010: 22) and is set at the temperature at which the polymer changes from a glassy (hard) state, to a liquid one (Horie, 2010: 23). For instance, the Tg of Lascaux Medium for Consolidation is 4°C, and if used on a material to be stored below this temperature, the LMC is hard and brittle. Once the consolidant is warmed to room temperature, it will appear more flexible. Cross-linked adhesives (such as epoxies) will not flow above Tg, but will become rubbery.

The hypothesis of this experiment was that plasticisers migrate into adhesives and make the adhesives prone to cold-flow. It was therefore expected in this experiment that the adhesives with a very high Tg, such as butyl acrylates Primal WS24, PlexigumPQ611/ Paraloid B67 and Aquazol 200 (poly (2-ethyl2-oxazoline), would become too brittle to resist t-peel. However, all films performed well in the t-peel test. The hypothesis was therefore not supported for adhesives with very high Tg. In these adhesives cold-flow does not occur. Instead, in PlexigumPQ611/Paraloid B67 — as well as a denser Primal WS24 sample — craquelure appeared on the adhesive side when the sample films were bent.

It was outside the scope of this project to map the curing mechanisms of each of the test-adhesives. However, if these adhesives crystallise upon curing and ageing, they are less likely to be able to include plasticisers. If the PSA and the additional adhesive mixes well, it is expected that the Tg will be lowered in the adhesive layer due to the movement of plasticisers into the new adhesive (Horie, 2010: 24, 35). This is an area to be further explored. The adhesives with a very low Tg, such as Acronal D500 and Dispersion K360 would be expected to be too soft to withstand t-peel. However, even these samples displayed strong bonds in the test, thus implying that cross-linking may have happened. It is probable that all test adhesives have undergone a shift in Tg once applied on top of the PSA, and aged. The measurement of Tg before and after ageing should be further studied using differential scanning calorimetry (DSC) as suggested by Down (1984: 19) and Feller and Wilt (1990: 47).

7.2.6 The adhesive needs to retain transparency

The majority of surface films in *Time Zero* are transparent. Any loss of transparency due to adhesive application will obscure the visibility of the materials underneath the surface films, and completely alter the visual impression of the collage. Because the tests were performed on opaque, white films, the transparency could not be measured. Testing on transparent PVC is required to test if the materials fulfil this requirement.

However, results from the colour measurements give strong indication of a lightening effect in all samples, which may manifest itself as cloudiness in the adhesive layer. Overall, in this study, natural ageing in the dark caused less colour change (ΔE*) than light ageing. Compared to other studies, heat seemed to give a more significant influence on colour change than light ageing (Howells et al., 1984). In the studies by Howells (1984), Sale (2011)and Down (2015) samples were bleached by light ageing *after* thermal ageing. There is a similar tendency in this study, in that an increase in yellowing occurred more frequently and to a greater extent in the samples aged naturally in the dark. When comparing the samples by PVA and PSA alone, the results were very inconsistent. Lightening (ΔL*) occurred to a great extent, yet occurred little to medium from natural ageing in the dark, and little to most when aged in light. Yellowing (Δb*) is likewise, very inconsistent in the PSA samples. PVC does not contain chromophores (light absorbing groups) (Shashoua, 2008a: 167). The rather considerable change in L* value after ageing, and light ageing in particular, indicates that the samples have become more cloudy white than before ageing. The most significant changes towards more cloudiness were found within the light aged samples. Changes in the blue—yellow scale and the green—red scale were less significant. Because the carrier side is opaque white, this change is not visible to the eye. Commonly, ΔE values at 1 or 2 are considered colour changes perceptible to the eye, and a ΔE above 5 is considered a substantial colour change (Down, 2011: 4). In this study, all samples had a colour change exceeding ΔE 5. The main reason for this is the significant change in *L. Even though it may be difficult to explain the actual values from the colour measurements, the main purpose has been to measure the relative variation of colour between the eight adhesives, and to detect any changes in chromophores. Further studies may discover specific connections between cloudiness and degradation of synthetic adhesives, as suggested by (Whitmore et al., 1996)

7.2.7 The adhesive should have a similar refractive index to the original material

Several of the films in *Time Zero* are transparent. In order to remain transparent and ‘invisible’, the dried adhesives need to have a refractive index similar to that of the original material (Shashoua, 2008a, p. 101). Even though refractive indices may be collected from literature, they may be slightly different on this material due to the PSA layer. Because the test-films were opaque white, the refractive index was not measured.

To get reliable results, the test-adhesives should be applied on transparent carrier material. Although very relevant in a screening process of adhesives to test further for suitability, measuring the refractive index is somewhat outside the scope of this project, as it is not immediately related to bonding properties.

7.2.8 The adhesive should do no harm to original materials in the artwork

This statement is linked to the fact that some adhesives have chemical properties, or require solvents for application, which may possibly harm the material to be bonded. Furthermore, some adhesives produce degradation by-products, such as acids, that may be harmful to the original material. Apart from Plexigum PQ611/Paraloid B67, the adhesives in this experiment are solvent-free. However, they do add an aqueous component to the material.

The measurement of pH is relevant, as highly acidic or alkaline environments may lead to hydrolysis of some products within the adhesive layer of carrier material (Shashoua, 2008a: 175). Furthermore, polymers that readily react with water by hydrolysis, will be very sensitive to changes in pH (Horie, 2010: 55). Hydrolysis of a material may proceed to cross-linking, and the formation of acids.

Consistent with other ageing studies on ageing properties of adhesives (Howells et al., 1984; Down, 2015), the adhesive layer in all samples had a slight shift towards acidity. Down et.al. also found that light ageing tended to make the adhesives more acidic than samples aged in the dark (Down, 2015: 36). All samples to be aged by light were measured before and after ageing to observe any changes in surface pH. However, the results vary within each test adhesive, showing the margins of measuring pH are quite slim. One of the challenges of measuring pH on a dry surface is that measurements only have validity when water is present (Ashley-Smith, 1992: 101). In Science for Conservators 2, the surface measurement of pH is stated to only confirm the presence of acid. However, the concentration and actual pH result is not obtainable from this kind of measuring. This is why the pH results in this study are presented as relative results only to be compared within this study, and not as actual pH readings on their own. The adhesives with the least change in pH were Primal WS24, Aquazol 200 and Lascaux MFC. The adhesive closest to neutral after ageing was Plexigum PQ611/Paraloid B67. As

Mowilith DMC2 contains a phthalate plaisticiser, it is expected to form phthalic acids when degraded (Shashoua, 2008a). However, measurements were not conclusive.
It is recommended to use adhesives closest to neutral for treating objects, and material that does not change pH over time. An acceptable change in pH according to Down is 5.5 to 8 (1996: 27; 2009: 92). What needs to be further investigated is: what is the acceptable change in pH for PSA. Also, because the test material in this study consisted of pressure-sensitive adhesive and additional adhesive only, without 'contaminants' such as paper and hair that are present in *Time Zero*, it is not known how the adhesive layer reacts in an acidic environment. It can only be assumed that the degraded organic material within the laminate will initiate or accelerate hydrolysis of the adhesive, causing cross-linking or chain scission.

7.2.9 Any adhesive should not add too much weight to the artwork

A further consideration, is that any adhesive should not add too much weight to the artwork. Because the films in *Time Zero* are not fixed to a secondary support, and are holding their own weight, the new added adhesive cannot add thickness or be a heavy material. Even if the material may be somewhat light, the total amount of surface to be covered and therefore the total amount of added material, may cause strain on the art-work. This is particularly important when the carrier films move into further decay with the potential of tearing. However, weight measurements have been outside the scope of this project, and may be further considered when the method of application, as well as extent of treatment, has been decided.

7.2.10 The adhesive should have good resistance to ageing

It is important for the conservator to have some assurance as to the longevity of the material applied on the artwork. Even if the adhesive has good wetting properties, the right refractive index and good strength and flexibility, it may still be less favourable if it proves to undergo changes in these properties within a few years. The statement contains several aspects, both *visual change*, possible changes in *mechanical properties*, and also *chemical changes* that might affect the surrounding material, as well as the adhesives themselves.

Identifying adhesives that are resistant to ageing is not simple. Studies in accelerated ageing are not conclusive, as explained above. In addition, literature confirms that the degradation of polymers most likely occurs as the result of several factors working simultaneously, such as light, temperature and RH. Predicting changes through ageing is therefore difficult. As discussed above, all samples exhibited visual changes (lightening as well as yellowing), while some samples also underwent mechanical changes (becoming brittle). Chemical changes are more challenging to identify.

The results from FTIR may give some indication of chemical changes during ageing, and whether these are minor changes, or significant changes, possibly making them unfit for the adhesion of *Time Zero*. It is important to bear in mind that some changes in the absorbance spectra may be due to the interaction of the two adhesives on the carrier surface, and some bands may obscure other bands.

Changes in pH have been discussed above. This study has not provided conclusive results on whether ionic salts or acids are formed upon ageing, and whether they affect the PVC carrier and adhesive layer negatively. We know that if acids form upon ageing in the light these are not sufficient to degrade the adhesive to the extent of losing adhesive properties, or visibly change colour. However, we do not know the pH within *Time Zero*, which may be far more acidic than fresh plastic films due to the amount of organic material within the laminate. Very acidic environments may affect the bond in a far more serious manner than in the experiments in this study, e.g. plasticisers may form phthalic acids in acidic environment (Shashoua, 2008a: 186). If phthalic acids are present, they would be visible as small, white crystals on the surface. No such crystals have been observed on the test samples as yet. Phthalic acids may also lead to disfigurement (due to loss of material), but will not accelerate degradation processes in PVC (Shashoua, 2008a: 186).

In the samples there were no obvious shifts in the absorbance peaks of the carboxylic acid carbonyl groups in the 1740 cm^{-1} region, but only a change in intensity. Some shoulders appear or disappear, although a trained eye is needed to interpret the information. *If* there was a shift in the carbonyl absorption band towards a higher frequency, this may be interpreted as a sign of miscibility (Lindstöm, 2004: 31). When studied in detail, more information about other aspects such as change in intensity of the plasticisers, may be detected. Degradation is mainly determined by looking at the shift of peaks towards a higher or lower absorbance. As with Sale's studies (2011) on adhesives for polymethyl methacrylates, the application of FTIR did not give any conclusive results on the degradation in the aged material. Instead, visual inspection and colour measurements provided more useful information. FTIR proved to be less useful for studying ageing properties in synthetic adhesives, in particular when the layer of interest is composed of several materials. FTIR imaging of the cross section may give some information about the movement of material (Stringari and Pratt, 1991: 418; Derrick et al., 1999: 76). A more advanced technique of studying ageing differences in the various materials is through extraction calculation of analytical results by employing principal component analysis (Mitchell et al., 2013). However, this is outside the scope of this study.

7.2.11 The adhesive should be re-treatable

As mentioned in the introduction, removability is outside the scope of this project. The possibility of re-treatment should however be considered when planning a conservation treatment of an object. The main topics of re-treatability are outlined in the section 8.4 'Further studies'.

By introducing different conservation grade adhesives to the pressures sensitive adhesive films, this study aimed to reveal any desired or undesired reactions in the adhesive blend, possibly giving an indication to whether a treatment of an additional adhesive will re-stabilise the adhesive layer or not. As already mentioned, this study builds upon the hypothesis that the materials in the samples all interact. By applying a conservation grade adhesive to fresh PVC carrier and acrylic PSA, the mixture may well have altered the ageing properties of the PSA altogether. If the test adhesive had been applied to already aged PSA, the results may have been very different. As the sample material is white rather than transparent compatibility, with regard to visual properties was only examined to a certain extent. Some adhesives become slightly milky upon curing, while others remain perfectly clear.

7.2.12 In conclusion, the addition of new adhesive has few adverse effects

From this study, it may be concluded that the addition of a conservation-grade adhesive to a pressure-sensitive adhesive creates a good bond. No major reactions with negative effects to the material take place when exposed to light in museum environments. There is no indication of further loss of adhesion. Only samples with adhesives of high Tg and a bulkier adhesive layer display cracking and loss of flexibility. Colour change was not visible apart from in the Dispersion K360. However, some aspects need to be further explored, and will be dealt with in the chapter 'Further studies'.

The original PSA contains cross-linking agents in order to obtain cohesive strength and keep it in its original position. However, once pulled apart, all samples fail cohesively. The overall assessment from the t-peel test indicates that the addition of a second adhesive to the PSA side has not caused loss of strength in the bond. Indeed, when examining some of the samples in the scanning electron microscope, the opposite seems to be the case. All cross-sections show a consistent adhesive layer, with a slightly concave orientation in the middle part of the laminate. This phenomenon (concave and dense impression of the adhesive layer of the closed samples) may suggest that the samples are in the stage of cross-linking rather than hydrolysis, as described in chapter 3 (Feller and Wilt, 1990). Because the samples were not examined and evaluated at several intervals during ageing, as suggested by Feller (1994: 32), it is not possible to conclude if the adhesive has been in the hydrolysing state prior to cross-linking. Interestingly, it is not possible to isolate the PSA from the additional adhesive by visually examining the samples and SEM images. It may be of interest to further study the interaction of the two adhesives upon curing and ageing.

7.3 Can the addition of a second adhesive reduce cold flow?

As previously presented, literature suggests that cold flow occurs due to migration of plasticisers. The samples in this study did not display obvious signs of cold flow, including even those consisting of PVC carrier and PSA alone. This may be due to the fact that acrylic PSA is less prone to cold flow than PVAc PSA. Also, other environmental conditions may be more important in terms of inducing cold flow. The analytical techniques have not been suitable to map the movement of plasticisers within the laminates. Therefore, it has not been possible to confirm or disprove the statement that plasticisers from the carrier migrate into the adhesive layer causing cold flow.

7.4 Are the results acceptable if applied on *Time Zero*?

According to Horie, (2010: 37) deterioration is any change in the polymer that makes it unfit for use in its context. The data collected from the experiments are interpreted and presented in tables and graphically, however, the ethical considerations when it comes to interpretation of the results should not be underestimated. The values from the experiments are to be considered relative to each other, but how does one decide what is an acceptable value? Will the material itself and the object as a whole be valued differently? When measuring colour change in a material, what is acceptable colour change, and how does this value relate to the artwork as a whole?

7.4.1 Who decides the acceptable values and treatment?

Traditional conservation principles are based on respect for the original material, documentation, applying reversible treatment methods and materials, and minimal intervention, all enshrined in several ethical guidelines and charters (ICOMOS, 1964; E.C.C.O., 2002; ICOM, 2013). In relation to modern and contemporary art made with modern materials, and in unconventional combinations, these guidelines, according to Szmelter, may be constrictive when deciding on a treatment method (Szmelter, 2012: 101). In contemporary conservation theory there has been an attempt to widen the boundaries of conservation, without affecting the materials and meaning of the art object. It is not the material *alone* that will dictate the treatment. Rather, the meaning and content of the artwork itself plays an equal part. If an artist uses garbage in his or her artwork, cleaning actions need to be thoroughly evaluated, as clean, fresh materials may go against the intention of using garbage, even though dirt is known to accelerate degradation of certain materials.

Research into the immaterial aspects of art should not be underestimated. There may be a parallel to the philosophy on ‘meaning’ in art, to the ’copernican revolution’ (Bonsanti, 1997 cited in Muñoz Viñas (2005: 27 - 29), in which the objects need to be directed from human knowledge, whereas earlier it had been the rule that humans needed to adjust to the objects of knowledge. In other words, the object is not treated by the idea that it owns one truth, and that this truth is preserved through the conservation treatment (Svendsen, 2013).

The field of conservation has been widened to value ideas and interpretations, in addition to already implemented values such as aesthetics, artistic- and historic value and authenticity (Szmelter, 2012: 15). Such a holistic approach also invites further discussion on decisions, and gives the opportunity for people other than conservators and art historians to have an opinion about what is to be preserved and how. Muñoz Viñas calls this ’a democratic decision process’ (Muñoz Viñas, 2005: 31). The idea is that everyone with a meaningful relationship to the object are invited to participate in the negotiations around a treatment. Even if it is not possible in practice, it encourages a more relaxed approach to standards than traditional conservation.

Last, is the principle of sustainable treatment (Muñoz Viñas, 2005: 31). This principle has an open approach to the principles of minimal intervention, respect of original materials and reversibility. The choice of treatment should not limit the future ’use’ of the object. Contemporary theory of conservation may value aspects of subjectivity and flexibility in the treatment of contemporary art, but it also puts an alternative responsibility on the conservator to document not only the artwork itself, but also its context and cultural values (Schädler-Saub, 2010: 69).

It seems important that the ethical framework does not lead to indecision regarding what treatment the artwork needs. Neither should it cause limited ‘use’ and display of the artwork to the public.

7.4.2 Limitations to ageing studies

Even though ageing studies are frequently applied to understand ageing properties of conservation-material, there are several uncertain factors making these studies hard to trust completely. Firstly, the conservation material is often tested alone, and not on the exact same composition or material to be treated, thus making it difficult to properly test all the factors. Secondly, several studies stress the limitation when only one or two ageing factors are incorporated into the study, such as heat and/ or light, rather than a combination of heat, light, humidity and pollutants. On the other hand, it will be extremely difficult to pinpoint the specific factors that induce or accelerate degradation in the tested material in a study with multiple environmental factors. Thirdly, the method of application is of great importance to the final result of treatment (Karsten and Kerr, 2011).

7.4.3 Preliminary conclusion on ethical considerations

Preliminary studies suggest that there might be an option to re-adhere the films in *Time Zero*, while retaining flexibility and transparency if the artwork is kept in stable museum conditions.

However, several factors need to be further investigated before making a final decision on whether to choose a passive or invasive treatment. The addition of a 'consolidant' will not be possible to remove. If it turns out that the adhesive layer becomes opaque over time, or if the adhesion eventually fails again, it is important to consider the next possible steps, such as re-treatment. The loss of adhesion may possibly be a 'safer' option than choosing a conservation material that might turn opaque or yellow with time, as this will alter the visual impression to a greater extent than loss of adhesion. Loss of adhesion may be re-treated by the same method, but opacity or yellowing may be very difficult or even impossible to eliminate. If selecting an adhesive with good bonding properties, but that may cross-link during ageing, the re-treatment may prove more difficult, as cross-linked material is less likely to bond with another material.

7.5 Decisions

The treatment of *Time Zero* should not be dictated by scientific investigations alone. If the results from this study point towards the application of a second adhesive to secure the films from falling off, other values are just as relevant to consider. Every case of treating an artwork needs to be individually evaluated and negotiated in terms of visual significance, original material, and whether function and display should be prioritised. In addition to discussing values, significance and optimum methods, financial and technical limitations and health and safety needs to be considered. The final decisions will always be a compromise and a concurrent reflection upon the relevant factors (Art, 1999).

It is not an option to assign *Time Zero* to a life in storage, i.e. on a flat bed in a dark room in cool and stable RH conditions, and without access to the public. Although the collage would have a long life with that treatment, the art is deprived from the all essential communication with a viewer, an audience – the public.

8 Conclusions

The garbage-collage *Time Zero* by Kjartan Slettemark displays signs of degradation that require stabilisation and remedial treatment within a short time. Due to invisible degradation processes in plastics suddenly coming to revelation, and with few means of treatment, possible paths of conservation need to be explored. In this study, the focus has been on some of the most challenging materials in museum collections, namely plasticised poly(vinyl chloride) and pressure-sensitive adhesives. Through experiments, causes of loss of adhesion of the PVC films, the possibility of stopping cold flow and re-gaining adhesion has been studied.

The study has elucidated some aspects of the research questions:

- What are the driving forces behind the degradation process that causes loss of adhesion?
- Can the addition of a consolidant stop or slow down further cold flow?
- What is the effect of introducing a new adhesive to the degraded material?

8.1 The selected adhesives may all be relevant for the purpose of conservation of *Time Zero*

The adhesives performed fairly consistently and similarly in all the tests. There was no severe yellowing, nor severe failures in the mechanical test. This gives good prospects for the adhesives commonly used in conservation, and supports the selection of adhesives that best exploits working properties and viscosity.

There does not seem to be any immediate damaging interaction between PVC carrier and acrylic PSA, or between acrylic PSA and the additional consolidant, apart from when adhesives with a high Tg were added to the PSA, causing cracking in the adhesive layer. That said, simple visual evaluation methods are insufficient to determine the quality of the laminate bond. Advanced analytical techniques are needed to reveal signs of degradation. Once degradation is visible to the eye, the process may already be long developed, and the material at a critical stage of degradation (Richardson et al., 2014: 231).

According to literature from previous studies, PVAc or vinyl-based pressure-sensitive adhesives are less stable, and prone to cold flow and hydrolysis, causing dirt pick-up and loss of tack. It is therefore relevant to study the interaction of degraded PVAc in relation to a second adhesive. The areas consisting of PVAc PSA in *Time Zero* display extensive cold flow. A better understanding of whether, and possibly how, an acrylic conservation adhesive may arrest or reduce cold flow, and potentially regain stability within the bond may be highly beneficial for the decision of treatment for *Time Zero* and similar objects.

8.2 The effect of ageing on the adhesives in this study

There are different ways of setting up accelerated ageing programs. Due to access to the particular equipment, the emphasis was on lengthy exposure to UV-free light, while temperature and relative humidity remained controlled within standard museum recommendations, in this study. Whereas the samples naturally aged in the dark had no environmental control. Ageing at elevated temperatures seemed less appropriate for this material due to the low Tg of the pressure-sensitive adhesives, and the associated risk of melting and oozing of the adhesive. Natural ageing in light and dark environments may be the best way to study ageing properties of the joined materials. Even if no large finds were revealed in this study, it does not mean degradation does not occur in PVC and PSA by exposure to light. It may only be concluded that the design of the experiment did not detect any changes that may lead to a conclusion on ageing properties of a specific blend of materials.

In the end, Tg and the molecular weight of the adhesive should be thoroughly evaluated before selecting the consolidant to prevent further cold flow of the PSA, as well as optical ageing properties such as colour change and refractive index. However, ageing studies have shown that acrylic adhesives are generally more stable than vinyl- and rubber-based adhesives.

8.3 Movement and ageing of plasticisers

This study confirms that adhesives with a glass transition temperature above room temperature should be avoided for the treatment of plasticized PVC and acrylic-based pressure-sensitive adhesive, unless used in very low dosages without adhesive build-up, as the adhesive layer will remain too brittle. It is of importance to have a balance between the amounts of adhesive to the amount of adherend to obtain the most efficient bond. A Tg similar to that of the PVC carrier should be the aim when selecting the appropriate adhesive. The Tg of the carrier needs to be established prior to treatment. Similarly, the Tg of the combined PSA and additional adhesive should be measured after ageing to get an impression of change in Tg when used together, even if applied in separate layers. A t-peel test is still useful to evaluate bond strength. However, very low Tg will most likely result in further cold flow in the adhesive layer, and insufficient cohesion. Lack of adhesion may also be caused by hydrolysis. Measuring Tg will not confirm if hydrolysis takes place. This degradation mechanism needs to be studied using other techniques. FTIR alone is not capable of detecting and determining ageing properties in the adhesive layer. If it is of interest to study degradation through the formation of acids, surface measurements of pH are not the most precise tool to employ, as other factors such as dust and pollution from the air may contaminate the surface. Colorimetric methods are useful to detect changes in colour from ageing, and also to indicate any chemical change within the material, although the finds need to be supported by knowledge of molecular degradation in all materials present in order to understand how the colour change occurs. Colour change may also occur in additives within the adhesive, rather than in the main adhesive component. The degradation mechanism in the additive — such as a plasticiser or stabiliser — may lead to a different degradation path than if present in the main adhesive component. When visual properties are of importance, measuring the refractive index of the carrier and the adhesive blend may be equally important. Compared to the original films in *Time Zero*, the test films have remained flexible after ageing, whereas the films in *Time Zero* are more brittle. The study has not been able to induce the process causing embrittlement in the carrier. Furthermore, the mechanics of embrittlement have not been investigated in relation to degradation processes in the PSA. It is not known whether the embrittelment of the PVC carrier affects the loss of adhesion in the PSA or vice versa, or if the mechanisms operate independently.

The investigation of consolidating contact adhesive films has not given any clear answers to the hypothesis that migration of plasticisers from the plastic films into the adhesive layer is causing creep and deformation of plastic films, and cold flow of the adhesive. Despite studying selected materials and processes of ageing within *Time Zero,* paired with tests and assessments of mock-up material of a similar composition, it is not possible to conclude that the movement of plasticisers alone are the cause of creep and deformation of the film carrier, nor cold flow of the adhesive. Other phenomena such as hydrolysis (of PSA), loss of material (chlorine, plasticisers), cross-linking and chain scission (of PVC), may play an equal part in the degradation process.

For the conservator it is important to have some reassurance that the material to be used for remedial treatment will remain somewhat unchanged upon ageing. The need to know if the selected adhesive will have the desired effect, in the case of *Time Zero* strengthening and stabilising the bond without causing unwanted effects such as yellowing or buckling, or disposal of harmful products within the material, is relevant. The methods used in this study has not been able to reveal how the plasticisers move within the plastic structure. Methods that are able to identify the specific plasticisers present in both PVC carrier and PSA, as well as quantifying gain or loss of plasticisers, may give a more reliable result. Because different plasticisers have different molecular weights and different boiling points, it is possible to differentiate them by using analytical techniques such as DSC and PyGCMS. When it comes to mapping the movement of plasticisers within the material, this proves more difficult, as both PVC and PSA contain plasticisers.

The prevention of hydrolysis, excessive cross-linking and acid formation may lie in the studies of how to obtain the most appropriate conditions for storage, handling and display. However, finding the means to deal with the phenomena when already in progress needs further exploration. This study has been an attempt to elucidate some aspects of the latter.

8.5 Further studies

Degradation processes in poly(vinyl acetate), acrylic adhesives adhesives have been well explained and understood through research and publications. However, the interaction between materials needs to be further explored. The processes of how PVC and acrylic pressure-sensitive adhesives influence each other in terms of degradation processes and also bonding quality are less understood, as is the interaction between PVC and polyvinyl acetate PSA.

The pre-ageing of the model material may be necessary in order to better mimic the conservation treatment of adding a fresh adhesive to a degraded pressure-sensitive adhesive and poly(vinyl chloride). Furthermore, the presence of plasticisers in both carrier and PSA requires a better understanding of the material in relation to acidic and alkali environments. Ageing methods including acidic-vapour, as explained in Carr et al. (2003), may be an interesting approach to establish the acceptable range of pH for pPVC and acrylic PSA.

The question about removability or re-treatability may be further explored in the future. The adhesive layer in *Time Zero* is integrated in the art-work in such a manner that it may be difficult to remove without affecting the collage as a whole.

Interaction of materials and change during degradation may have more focus on glass transition temperature (Tg) by measuring the material at even intervals. The significant lightening of the test samples after ageing are not well explained in literature in terms of degradation or chemical change, and needs further attention. Finally, other adhesives, as well as alternative methods of application, need to be studied in more detail to guide decisions on appropriate means by which to preserve *Time Zero* and objects of a similar nature or composition.

Literature

The Beilstein test: Screening Organic and Polymeric Materials for the Presence of Chlorine, with Examples of Products Tested. *CCI Notes* [Online], 17. [Accessed 22.10.2014].

Allen, K. W. 1984. Adhesion and Adheisves - Some Fundamentals. *In:* Brommelle, N. S., Pye, E. M., Smith, P. & Thomson, G. (eds.) *Adhesives and Consloidants.* Paris: The International Institute of Conservation of Historic and Artistic Works.

Art, F. F. T. C. O. M. 1999. The Decicion-making Model for the Conservation and Restoration of Modern and Contemporary Art. Available: http://www.incca.nl/files/pdf/resources/sbmk_icn_decision-making_model.pdf.

Ashley-Smith, J. (ed.) 1992. *Adhesives and Coatings,* London: Routledge.

Astm 2011. ASTM D3164 - 03. *Standard Test Method for Strength Properties of Adhesively Bonded Plastic Lap-Shear Sandwich Joints in Shear by Tension Loading.* West Conshohocken, PA: ASTM International.

Astm 2015. ASTM D 1876-08 *Standard Test Method for Peel Resistance of Adhesives (T-peel Test).* West Conshohocken, PA: ASTM International.

Bacci, M., Cucci, C., Oosten, T. V., Shashoua, Y. & Rychly, J. 2012. Surveying plastic artefacts in museums. *In:* Lavéndrine, B., Fournier, A. & Martin, G. (eds.) *Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiqes et scientifiqes.

Balcar, N., Barabant, G., Bollard, C., Kuperholc, S., Keneghan, B., Laganà, A., Oosten, T. V., Segel, K. & Shashoua, Y. 2012. Application of experimental findings to case histories. *In:* Lavéndrine, B., Fournier, A. & Martin, G. (eds.) *Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiqes et scientifiqes.

Barker, M. 1999. Defining Plastics. *In:* Quaye, A. & Williamson, C. (eds.) *Plastics. Collecting and Conserving.* Edinburgh: NMS Publishing Limited.

Bechthold, T. 2007. Houston - we have a problem: when flying saucers become brittle. *In:* Keneghan, B. & Egan, L. (eds.) *Plastics. Looking at the future and Learning from the Past.* London: Archetype Publications Ltd.

Bechthold, T. 2009. Stiletto. Double sided problems with a self-adhering, flexible PVC-film. *In:* Bechthold, T. (ed.) *Future Talks 009. The Conservation of Modern Materials in Applied Arts and Design.* Munich: Die Neue Sammlung The International Design Museum.

Beerkens, L., Stigter, S., Oosten, T. V. & Keulen, H. V. Go with the flow: conservation of a floating sculpture from 1961 made from glass fibre reinforced polyester resin. *In:* Keneghan, B. & Egan, L., eds. PLASTICS. Loking at the Future and Learning from the Past, 2007 London. Archetype Publications Limited, 45-51.

Beerkens, L., Supply, S. & Bechthold, T. 2013. Matti Suuronnen's Futuro House Prototype. *In:* Bechthold, T., ed. Future Talks 011, 2011 Munich. Munich: Die Neue Sammung The International Design Museum, 128 - 137.

Bemmels, C. V. 1977. Pressure-Sensitive Tapes and Labels. *In:* Skeist, I. (ed.) *Handbook of Adheisves.* 2nd ed. New York: Van Nostrand Reinhold Company Inc.

Benedek, I. 1999. *Development and Manufacture of Pressure-Sensitive Products,* New York, Marcel Dekker, Inc.

Benedek, I. 2004. *Pressure Sensitive Adhesives and Applications,* New York, Marcel Dekker, Inc.

Benedek, I. 2006. *Developments in the Pressure-sensitive Products,* Boca Raton, Florida, Taylor & Francis Group.

Benedek, I. & Feldstein, M., M. 2009. *Technology of pressure-sensitive adhesives and products,* Florida, Taylor and Francis Group.

Benedek, I. & Heymans, L. J. 1997. *Pressure-Sensitive Adhesives Technology,* New York, Marcel Dekker, Inc.

Berger, G. 1972. Testing adhesives for the consolidation of paintings. *Studies in Conservation,* Volume 17**,** pp 173-194.

Berger, G. & Zeliger, H. I. 1984. The Procedure of Developing an Adhesive for Paintings: The Importance of Valid Tests. *In:* Brommelle, N. S., Pye, E. M., Smith, P. & Thomson, G. (eds.) *Adhesives and Consolidants.* Paris: IIC.

Blitz, M. & Grattan, D. W. 1996. The ageing of Parylene: difficulties with the Arrhenius approach. *In:* Bridgeland, J. (ed.) *ICOM Committee for Conservation 11th triennial meeting, Edinburgh, 1 -6 September 1996 Preprints.* James & James.

Bollard, C., Kuperholc, S., Balcar, N. & Barabant, G. 2011. Effects of cleaning gel systems on plastics. A preliminary study on plasticized poly(vinyl chloride). *In:* Bechthold, T. (ed.) *Future Talks 01. Technology and Conservation of Modern Materials in Design.* Munich: Die Neue Sammlung The International Design Museum.

Bonk, R., Osternhof, J. F., Pettenger, B. L. & Ambrosio, A. M. 1996. Methods for evaluating adhesive systems and adhesion. *Technical Report ARAED-TR-95025.* New Jersey: U.S. Army Armament research, Development and Engenieering Center.

Bradley, S. 1984. Strength testing of Adhesives and Consolidants for Conservation Purposes. *In:* Brommelle, N. S., Pye, E. M., Smith, P. & Thomson, G. (eds.) *Adhesives and Consolidants.* Paris: IIC.

Brydson, J. 1999. *Plastics Materials,* Oxford, Buterworth-Heinemann.

Carr, D. J., Young, C. R. T., Phenix, A. & Hibberd, R. D. 2003. Development of a Physical Model of a Typical Nineteenth-Century English Canvas Painting. *Studies in Conservation***,** 145 - 154.

Chelazzi, D., Chevaier, A., Pizzorusso, G. & Giorgi, R. 2014. Characterization and degradation of poly(vinyl acetate)-based adhesives for canvas paintings. *Polymer degradation and stability***,** 314 - 320.

Colombini, A. & Valegas, C. 2009. Characterization and Degradation of Fluorescent Colours in Works of Art: Pleliminary Studies. *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Sammlung, The International Design Museum Munich.

Comiotto, A. & Egger, M. 2009. Naum Gabo's sculpture 'Construction in Space: Crystal' (1937): Evaluating a suitable bonding strategy for stress loaded poly (methyl methacrylate). *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Sammlung. The International Design Museum.

Coxon, H. C. 1993. Practical Pitfalls in the Identification of Plastics. *In:* Grattan, D. W. (ed.) *Saving the Twentieth Century: The Conservation of Modern Materials.* Ottawa, Canada: Canadian Conservation Institute.

Dagbladet 1982. Kjartan kommer. *Dagbladet.* Oslo.

Denkler, M. 2001. Don Quijote. *In:* Denkler, M. (ed.) *Egenart.* Stockholm: Silander & Fromholtz Förlags AB.

Department, C. 1999. MS2789/88 Condition report. Museet for samtidskunst.

Derrick, M. R., Stulik, D. & Landry, J. M. 1999. *Infrared spectroscopy in conservation science* Los Angeles, USA, Getty Conservation Institute.

Down, J. 1984. Adhesive testing at the Canadian Conservation institure, past and future.

Adhesives and consolidants. London: IIC.

Down, J. 1995. Adhesive projects at the Canadian Conservation Institute. *In:* Wright, M. M. & Townsend, J. H. (eds.) *Resins: ancient and modern.* Edinburgh: Scottish Society for Conservation and Restoration.

Down, J. 1999. Swelling as an indicator of removability. *In:* Oddy, W. A. & Carroll, S. (eds.) *Occasional paper (British Museum).* London: British Museum.

Down, J. Update on the CCI Adhesive Tape and Heat-Set Tissues Project. CCI Symposium. Adhesives and Consolidants for Conservation: Research and Applications, 2011 Ottawa, Canada.

Down, J. 2015. Evaluation of selected poly(vinyl acetate) and acrylic adhesives. *Studies in Conservation,* 60**,** 33 - 54.

Down, J., Macdonald, M. A., Tétrault, J. & Williams, R. S. 1996. Adhesive Testing at the Canadian Conservation Institute - An Evaluation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives. *Studies in Conservation,* 41**,** 19 - 44.

Down, J. & Williams, R. S. A report on the evaluation of selected poly(vinyl acetate) and acrylic adhesives for use in paper conservation. *In:* Burgess, H. D., ed. Conservation of historic and artistic works on paper: proceedings of a conference, Ottawa, Canada, October 3 to 7, 1988, 1994 1988 Ottawa, Canada. Ottawa: Canadian Conservation Institute, pp. 163-180.

Down, J. L. 2001. "Review of CCI research on epoxy resin adhesives for glass conservation" *Reviews in conservation***,** 39-46

Down, J. L. 2009. "Poly(vinyl acetate) and acrylic adhesives: a research update" *In:* Ambers, J., Higgitt, C., Harrison, L. & Saunders, D. (eds.) *Holding it all together : ancient and modern approaches to joining, repair and consolidation* London, United Kingdom: Archetype Publications in association with the British Museum

Down, J. L., Williams, R. S., Tse, S. & Guild, S. 2006. "The CCI tapes and heat-set tissues project: description and status report". *Papierrestaurierung* 7**,** 13-17

E.C.C.O. 2002. E.C.C.O. Professional Guidelines. Available: http://www.ecco-eu.org/about-e.c.c.o./professional-guidelines.html.

Eska, M. 2011. Self-Adhesive Plastic Labels. *In:* Bechthold, T. (ed.) *Future Talks 011. Technology and Conservation of Modern Materials in Design.* Munich: Die Neue Sammlung. The International Design Museum.

Feller, R. I. 1994. *Accelerated Ageing. Photochemical and Thermal Aspects,* The Getty Conservation Institute, United States of America, The J. Paul Getty Trust.

Feller, R. L. & Encke, D. B. 1982. Stages in deterioration: the examples of rubber cement and transparent mending tape. *Studies in Conservation,* Volume 27**,** 19-23.

Feller, R. L. & Wilt, M. H. 1990. *Evaluation of cellulose ethers for conservation* Research in conservation, 3, The Getty Conservation Institute.

Groot, S. D., Laganà, A., Oosten, T. V., Keulen, H. V. & Palmeira, M. 2011. The Wear and Tear of Polyurethane Elastomers. Investigation into Properties, Degradation and Treatments. *In:* Bechthold, T. (ed.) *Future Talks 011. Technology and Conservation of Modern Materials in Design.* Munich: Die Neue Sammlung. The International Design Museum.

Grönlund, K. & Grönlund, M. 06.11.2012 2012a. *RE: Samtale om materialbruk.*

Grönlund, K. & Grönlund, M. 05.11.2012 2012b. *RE: Samtale om Time Zero.*

Haider, K. & Oosten, T. V. 2009a. Plastic bags - Research into Polyethylene Bags of the Series "Bicycles" by Andreas Slominski. *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Sammlung, The international Design Museum Munich.

Haider, K. & Oosten, T. V. 2009b. Plastic Bags - Research into polyethylene bags of the series "Bicycles" by andreas Slominsky. *In:* Bechthold, T. (ed.) *Future Talks 009: The Conservation of Modern Materials in applied Arts and Design. October 22/23 2009* Munich: Die Neue Sammlung The International Design Museum.

Horie, C. V. 2010. *Materials for Conservation: Organic consolidants, adhesives and coatings,* Oxford, Butterworth-Heinemann.

Horie, C. V. 2011. Does What We Want Exist? *CCI Symposium ICC. Adhesives and Consolidants for Conservation: Research and Applications.* Ottawa, Canada.

Howells, R., Burnstock, A., Hedley, G. & Hackney, S. 1984. Polymer dispersions artificially aged. *In:* Brommelle, N. S., Pye, E. M., Smith, P. & Thomson, G. (eds.) *Adhesives and Consolidants,.* Paris: IIC.

Husabø, I. A. 2009. *Kjartan Slettemark : kunsten å falle,* Skald AS.

Huys, F. & Oosten, T. V. 2005. The 'Aeromodeller OO-PL'; the conservation of a PVC balloon. *14th ICOM-CC Triennial Meeting.* The Hague. 12-16 September 2005: ICOM committee for Conservation.

Högkvist, S. 2013. Av Kunst er du kommet, til Kunst skal du bli. *In:* Högkvist, S., Sauge, B. & Yvenes, M. (eds.) *KjARTan Slettemark. Kunsten å være kunst/ KjARTan Slettemark. The Art of being Art.* Oslo: Nasjonalmuseet for kunst, arkitektur og design.

Icom. 2013. ICOM Code of Ethics for Museums. Available: http://icom.museum/fileadmin/user_upload/pdf/Codes/code_ethics2013_eng.pdf.

Icomos 1964. The Venice charter - International Charter for the Conservation and Restoration of Monuments and Sites.

Iso 2013. ISO 9653:1998. *Adhesives — Test method for shear impact strength of adhesive bonds.* ISO.

Iso 2015. ISO 11339:2010. *Adhesives -- T-peel test for flexible-to-flexible bonded assemblies.* ISO.

Karsten, I. & Kerr, N. Peel Strength of Silk and Nylon Textiles Adhered ti Sheer Support Fabricks. Adhesives and Consolidants for Conservation: REsearch and Applications, 2011 Ottawa, Canada. Canadian Conservation Institute, 1 - 20.

Kaukovalta, M. 2002. A Study of Synthetic Polymer Gessoes and their Behaviour in Artificial Ageing Tests. *In:* Oosten, T. V., Shashoua, Y. & Waentig, F. (eds.) *Plastics in Art. History, Technology, Preservation.* Munich: Siegls Fachbuch Handlung.

Keneghan, B. 2012. Fourier-transform infrared spectroscopy (FTIR). *In:* Lavéndrine, B., Fournier, A. & Martin, G. (eds.) *The Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiqes et scientifiqes.

Keneghan, B., Oosten, T. V., Laganà, A., Wagenaar, M., Barabant, G., Balcar, N., Bluzat, H., Bollard, C., Fayein, J., Kuperholc, S., Ramel, S. & Lattuati-Derieux, A. 2012. In what condition are my artefacts? Case studies. *In:* Lavédrine, B., Fournier, A. & Martin, G. (eds.) *Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiques et scientifiques.

Laganá, A. & Van Oosten, T. B. 2011. Back to transparency, back to life: research into the restoration of broken transparent unsaturated polyester and poly(methyl methacrylate) works of art. *In:* Conservation, I. C. F. & Bridgland, J. (eds.) *ICOM-CC 16th triennial conference.* Lisbon: Critério--Produção Grafica, Lda.

Lavédrine, B., Fournier, A. & Martin, G. (eds.) 2012. *Preservation of plastic artefacts in museum collections,* Paris: Comité des travaux historiques et scientifiques.

Lavéndrine, B., Fournier, A. & Martin, G. (eds.) 2012. *Preservation of plastic artefacts in museum collections,* Paris : Comité des travaux historiques et scientifiques.

Learner, T. J. 2004. *Analysis of Modern Paints,* Los Angeles, The Getty Conservation Institute.

Lindstöm, A. 2004. *Environmentally Friendly Plasticizers for PVC – Improved Material Properties and Long-Term Performance through Plasticizer Design.* PhD, Kungliga Tekniska Högskolan.

Lorne, A. 1999. The poly(methyl methacrylate) objects in the collection of The Netherlands Institute of Cultural Heritage. *ICOM-CC 12th Triennial Meeting.* Lyon: James & James (Science Publisher) Ltd.

Merrily A. Smith, N. M. M. J., Susan L. Page, & Marian Peck Dirda 1984. "Pressure-Sensitive Tape and Techniques for its Removal From Paper". *JAIC,* Volume 23**,** pp. 101 to 113.

Mills, J. S. & White, R. 1999. *The organic chemistry of museum objects,* Oxford, Butterworth-Heinemann.

Mitchell, G., France, F., Nordon, A., Tang, P. L. & Gibson, L. T. 2013. Assessment of historical polymers using attenuated total reflectance-Fourier transform infra-red spectroscopy with principal component analysis. *Heritage Science,* 1**,** 1 - 10.

Morgan, J. 1993. A Joint Project on the Conservation of Plastics by the Conservation Unit and the Plastics Historical Society. *In:* Grattan, D. W., ed. Saving the Twentieth Century: The Conservation of Modern Materials, 1991 Ottawa, Canada. Ottawa: Canadian Conservation Institute, 43 - 49.

Muñoz Viñas, S. 2005. *Contemporary Theory of Conservation,* Amsterdam, Elsevier Butterworth Heinemann.

Nasjonalgalleriet 1982. Årsrapport Nasjonalgalleriet. Oslo: Nasjonalgalleriet.

Nielsen, C. J. 2008. KJM-MENA 4010 IR/Raman Module. University of Oslo.

Nord, A. G. & Tonner, K. (eds.) 2008. *PLAST Morgondagens kulturobjekt,* Stockholm: Riksantikvarieämbetet.

O'loughlin, E. 2001. Pressure sensitive tapes an our cultural heritage. *Sharing Global Pressure Sensitive Tape Innovations.* Orlando, USA.

O'loughlin, E. & Stiber, L. S. 1992. A closer look at pressure-sensitive adhesive tapes: update on conservation strategies. *In:* Fairbrass, S. (ed.). Manchester: The Institute of Paper Conservation.

Oosten, T. V. 1999a. Analytical methods. *In:* Quaye, A. & Williamson, C. (eds.) *Plastics. Collecting and Conserving.* Edinburgh: NMS Publishing Ltd.

Oosten, T. V. 1999b. Here Today, Gone Tomorrow? Problems with Plastic in Contemporary Art. *In:* Hummelen, I. & Sillé, D. (eds.) *Modern Art: Who Cares?* Amsterdam: The Foundation for the Conservation of Modern Art and the Netherlands Institute for Cultural Heritage.

Oosten, T. V. 2002. Crystals and Crazes: Degradation in Plastics Due to Microclimates. *In:* Oosten, T. V., Shashoua, Y. & Waentig, F. (eds.) *Plastics in Art. History, Technology, Preservation.* Cologne: Siegls fachbuch handlung.

Oosten, T. V. 2006. Working with Plastics. Syllabus. Amsterdam: Netherlands Institute for Cultural Heritage (ICN).

Oosten, T. V. 2011. *PUR-facts. Conservation of Polyurethane Foam in Art and Design,* Amsterdam, Amsterdam University Press.

Oosten, T. V. 2012. FTIR imaging. *In:* Lavéndrine, B., Fournier, A. & Martin, G. (eds.) *The Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiqes et scientifiqes.

Oosten, T. V. & Aten, A. 1996. Life Long Guaranteed: The Effect of Accelerated Ageing on Tupperware Objects Made of Polyethylene. ICOM-CC 11th Triennial Meeting Edinburgh 1-6 September 1996 1996 Edinburgh. 971 - 977.

Oosten, T. V., Fundeanu, I., Bollard, C., Castro, C. D. & Laganà, A. 2008. Lights out! The conservation of polypropylene wall tapestries. *In:* Keneghan, B. & Egan, L., eds. Platics: Looking at the Future and Learning from the Past, 2007 London. Archetype Pubications Ltd, 97 - 105.

Oosten, T. V., Keulen, H. V., Kuperholc, S., Bollard, C. & Laganà, A. Between make-up and make over: protective layers on modern and contemporary art plastic objects. *In:* Bridgland, J., ed. ICOM-CC, 2008 2008 New Delhi. ICOM Committee for Conservation, Paris, France, 505-514.

Oosten, T. V. & Laganà, A. 2009. Mending Broken Pieces. Research into Methods and Materials for Adhering Broken Unsaturated Polyester. *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Sammlung. The International Design Museum Munich.

Oosten, T. V. & Learner, T. 2012. Identification and characterisation of plastic artefacts. Introduction. *In:* Lavéndrine, B., Fournier, A. & Martin, G. (eds.) *Preservation of Plastic Artefacts in Museum Collections.* Paris: Comité des travaux historiques et scientifiques.

Ormsby, B. 2014. Slettemark. Time Zero (TZ). FTIR analysis report: transmission and ATR. Tate.

Pettersson, J. Å. 2012. *A Retrospective Peep-Show by Jan- Åke Pettersson* [Online]. Kjartan Slettemark/NoMad of ART. Available: http://www.kjartan.se/hemex.htm.

Pettersson, J. Å. 2013. *RE: Personal communication 20.02.2013.*

Ploeger, R., Verteramo, R. & Chiantore, O. 2009. "Figura n. 37" by Antonio Bueno: A Plastic Conservation Case Study from the Modern Art Gallery (GAM) if Turin, Italy. *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Samlung, The International Design Museum Munich.

Popart. 2012. *POPART Damage Atlas* [Online]. Available: http://popart-highlights.mnhn.fr/wp-content/uploads/3_Collection_survey/5_Damage_atlas/Damage_atlas.pdf [Accessed 05.06.2013 2013].

Price, B. A., Malenka, S., Sutherland, K., Lins, A. & Carlson, J. H. 2007. Naum Gabo's Construction in Space: Two Cones: history and materials. *In:* Keneghan, B. & Egan, L. (eds.) *Plastics: Looking at the Future and Learning from the Past.* London: Archetype Publications Ltd.

Quye, A. & Keneghan, B. 1999. Degredation. *In:* Quye, A. & Williamson, C. (eds.) *Plastics: Collecting and Conserving.* Edinburgh: NMS Publishing Limited.

Richardson, E., Giachet, M. T., Schilling, M. & Learner, T. 2014. Assessing the physical stability of archival cellulose acetate films by monitoring plasticizer loss. *Polymer Degradation and Stability*, 231 - 236.

Sale, D. 1988. The Effect of Solvents on Four Flastics Found in Museum Collections: A Treatment Dilemma. *Modern Organic Materials.* Edinburgh: The Scottish Society for Conservation and Restoration.

Sale, D. An Evaluation of Eleven Adhesives for Repairing Poly(methyl methacrylate) Objects and Sculpture. *In:* Grattan, D. W., ed. Saving the Twentieth Century: The Conservation of Modern Materials, 1991 Ottawa, Canada. Canadian Conservation Institute, 325 - 339.

Sale, D. 1995. Evaluating adheisves for repairing poly(methyl methacrylate) objects and sculpture: changes in tensile strength and colou after accelerated ageing. *In:* Wright, M. M. & Townsend, J. H. (eds.) *Resins: Ancient and Modern.* Aberdeen: Scottish Society for Conservation and Restoration.

Sale, D. ￼￼Yellowing and Appearance of Conservation Adhesives for Poly (methyl methacrylate): A Reappraisal of 20-year-old Samples and Test Methods. CCI Symposium. Adhesives and Consolidants for Conservation: Resarch and Application, 2011 Ottawa, Canada.

Schädler-Saub, U. 2010. Conservation of modern and conteporary art: what remains of Cesare Brandi's Teoria del restauro? *In:* Schädler-Saub, U. & Wyer, A. (eds.) *Theory and Practice in the Conservation of Modern and Contemporary Art: Reflections on the Roots and Perspectives.* London: Archetype Publications Ltd.

Shashoua, Y. 1996. A Passive Approach to the Conservation of Polyvinyl Chloride. *11th triennial meeting of the ICOM Committee for Conservation.* Edinburgh: International Council of Museums.

Shashoua, Y. 1999. Back to Plastics. *In:* Oddy, A. & Caroll, S. (eds.) *Reversibility - Does it Exist?* London: The British Museum.

Shashoua, Y. 2001a. *Inhibiting the deterioration of plasticised poly (vinyl chloride) - a museum perspective.* Ph.D., The technical University of Denmark.

Shashoua, Y. 2008a. *Conservation of plastics : materials science, degradation and preservation,* Amsterdam, Elsevier.

Shashoua, Y. 2008b. Conservation of plastics: is it possible today? *In:* Keneghan, B. & Egan, L. (eds.) *Plastics: looking at the future and learning from the past: papers from the conference held at the Victoria and Albert Museum, London: 23-25 May 2007.* London United Kingdom: Archetype Publications Ltd.

Shashoua, Y. 22.09.2014 2014. *RE: PVC and pH.*

Shashoua, Y., Petersen, A. L. & Rapoport, E. 2009. The price of pristine PMMA. *In:* Bechthold, T. (ed.) *Future Talks 009. The Conservation of Modern Materials in Applied Arts and Design.* Munich: Die Neue Sammlung The International Design Museum.

Shashoua, Y., Schnell, U. & Young, L. 2002. Deterioration of Plasticised PVC Components in Apollo Spacessuits. *In:* Oosten, T. V., Shashoua, Y. & Waentig, F. (eds.) *Plastics in Art. History, Technology, Preservation.* Cologne: Siegls Fachbuch Handlung.

Shashoua, Y. R. 2001b. *Inhibiting the deterioration of plastized poly (vinyl chloride) : a museum perspective,* København, National Museum of Denmark.

Siegmantel, M. 2011. Adhesives for silicone rubber. *In:* Bechthold, T. (ed.) *Future Talks 011. Technology and Conservation of Modern Materials in Design.* Munich: Die Neue Sammlung. The International Design Museum.

Skeist, I. (ed.) 1977. *Handbook of Adhesives,* New York: Van Nostrand Reinhold Company Inc.

Slettemark, K.-., Pettersson, J. Å. & Munter, H. 1982. *Kjartan Slettemark : "Titta jag sett" / [Trondhjems kunstforening, Kunstnernes hus, Oslo, 17 maj-4 juli 1982 ; Concept och urval: Jan Åke Pettersson],* Trondheim, Galleriet.

Slöör, S. 2009. Å vere sin eigen kunst. *In:* Husabø, I. A. (ed.) *Kjartan Slettemark: kunsten å falle.* Skald AS.

Smith, J. M. N.Y. *Polarized light microscope examinations of oriented polymer films* [Online]. Missouri, USA. Available: https://www.pstc.org/files/public/smith-06.pdf [Accessed 04.04.2016 2016].

Stringari, C. & Pratt, E. The Identification and Characterization of Acrylic Emulsion Paint. *In:* Grattan, D. W., ed. Saving the Twentieth Century: The Conservation of Modern Materials, 1991 Ottawa, Canada. Canadian Conservation Institute, 411 - 440.

Strlic, M., Kolar, J., Drnovsek, T., Selih, V. S., Susic, R. & Philar, B. 2004. What is the pH of alkaline paper? *e-PS,* 1**,** 35-47.

Stuart, B. 2007. *Analytical Techniques in Materials Conservation,* West Sussex, England, John Wiley & Sons Ltd.

Svendsen, L. F. H. 2013. *Kopernikansk vending* [Online]. Available: http://snl.no/kopernikansk_vending/filosofi.

Szmelter, I. (ed.) 2012. *Innovative Approaches ro the Complex Care if Contemporary Art,* Warsaw, London: Academy of Fine Arts in Warsaw and Archetype Publications Ltd.

Toniolo, L., Bellavitis Dell'aqua, A., Annicchiarico, S., Comelli, D., Galleani, G., Levi, M., Nevin, A. & Toja, F. 2009. Caring for Design Objects: Daily Practice and Advanced Analytical Tools. *In:* Bechthold, T. (ed.) *Future Talks 009.* Munich: Die Neue Sammlung, The International Design Museum Munich.

Vestergaard, I. K. L. & Horie, C. V. 1996. A Comparison of Interaction of Five Adheisves with Mastodon Tooth Adherends. *ICOM-CC 11th Triennial Meeting.* Edinburgh: ICOM Committee for Conservation.

Waentig, F. 2008. *Plastics in art : a study from the conservation point of view,* Petersberg, Michael Imhof Verl.

Ward, C. & Shashoua, Y. 1999. Interventive Conservation Treatments for Plastics and Rubber Artefacts in The British Museum. *ICOM-CC 12th Triennial Meeting.* Lyon: James & James (Science Publishers) Ltd.

Whitmore, P., Colaluca, V. G. & Farell, E. 1996. A note on the origin of turbidity in films on an artits' acrylic paint medium. *Studies in Conservation,* 41**,** 50 - 255.

Williams, R. S. 2002. Care of Plastics - Malignant Plastics. *WAAC Newsletter,* 24.

Winther, T. 2008. Analys av "Modell till den lille generalen". *Meddelelser om konservering***,** 3-19.

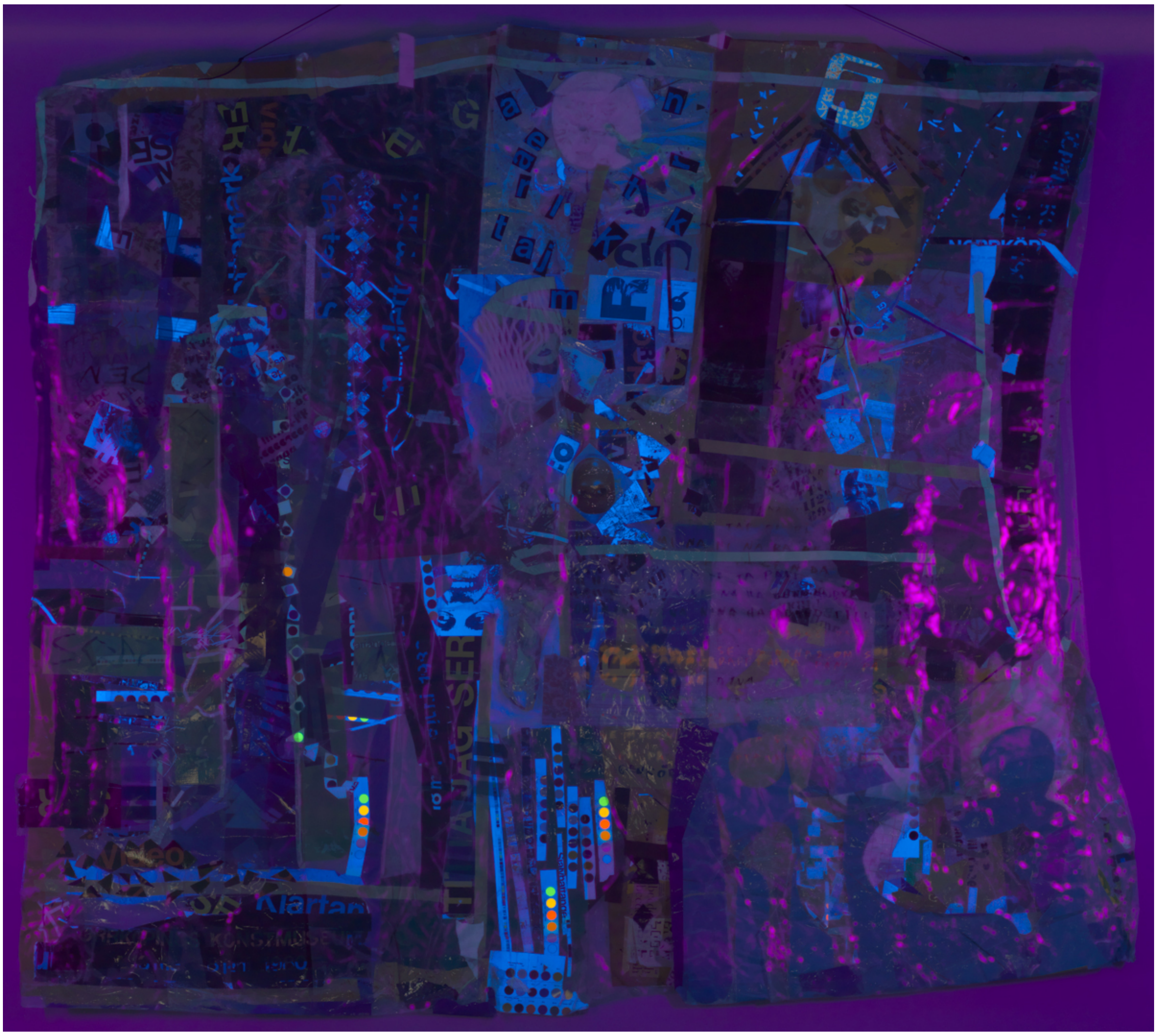
Winther, T., Bannerman, J., Skogstad, H., Johansson, M. K. G., Jacobson, K. & Samuelsson, J. 2013. Adhesives for adhering polystyrene plastic and their long-term effect. *Studies in Conservation/ MORE Open Choice***,** 1 - 14.

Young, C., New, B. & Marchant, R. Experimental Evaluation of Adhesive Gap Filler Combinations for Joining Panel Paintings. *In:* Phenix, A. & Chui, S. A., eds. Facing the Challenges of Panel Paintings Conservation: Trends, Treatments, and Training: Proceedings from the Symposium Facing the Challenges of Panel Paintings Conservation: Trends, Treatments, and Training, 2011 2009 Los Angeles. The Getty Conservation Institute, pp. 125-139.

Zhao, Y. 2014. *Quantitative Detection of Cold Flow in Transdermal Drug Delivery System.* Master of Science, University of Maryland, Baltimore.

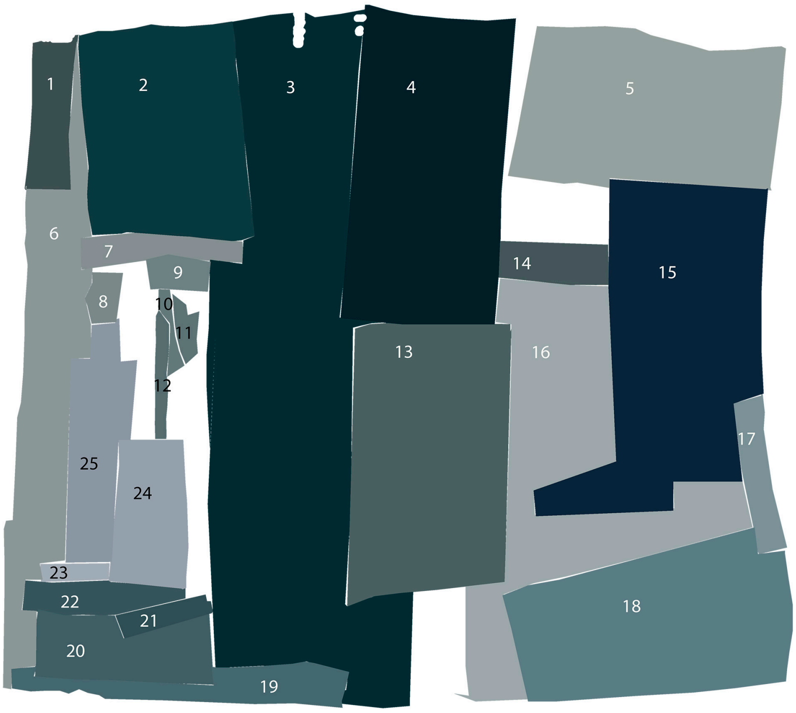
9 Appendices

9.1 Appendix 1 *Time Zero* examination and condition

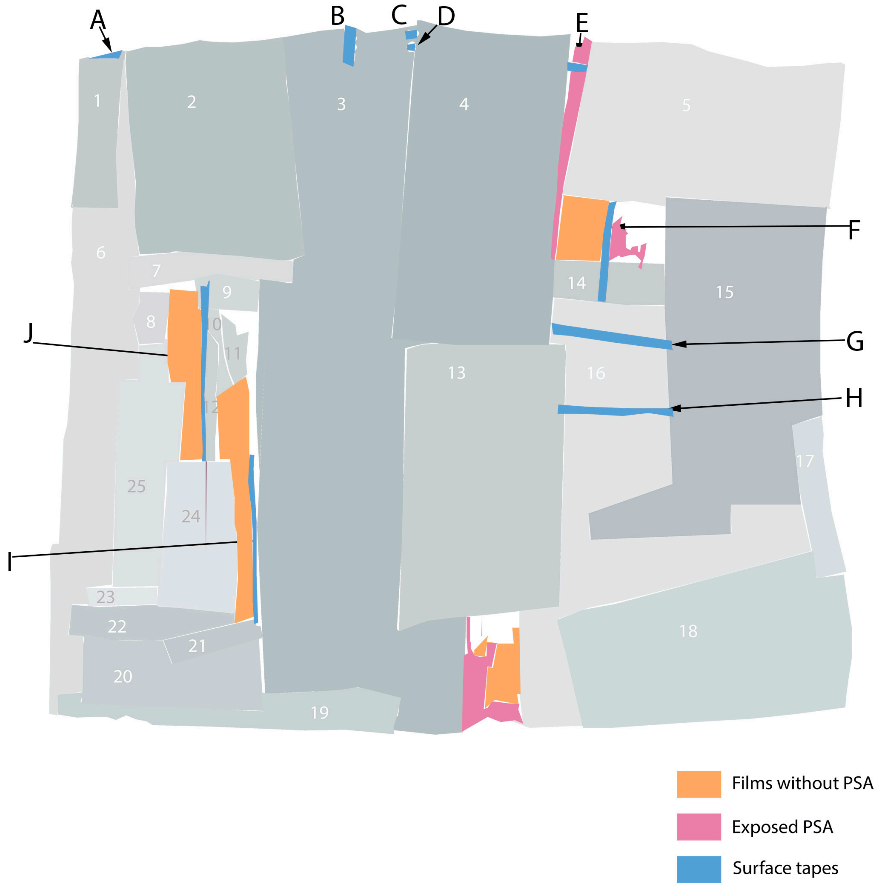


Appendix 9. 1 Time Zero front face in UV-light. Photo: Frode Larsen. National Museum of Art, archtecture and Design.

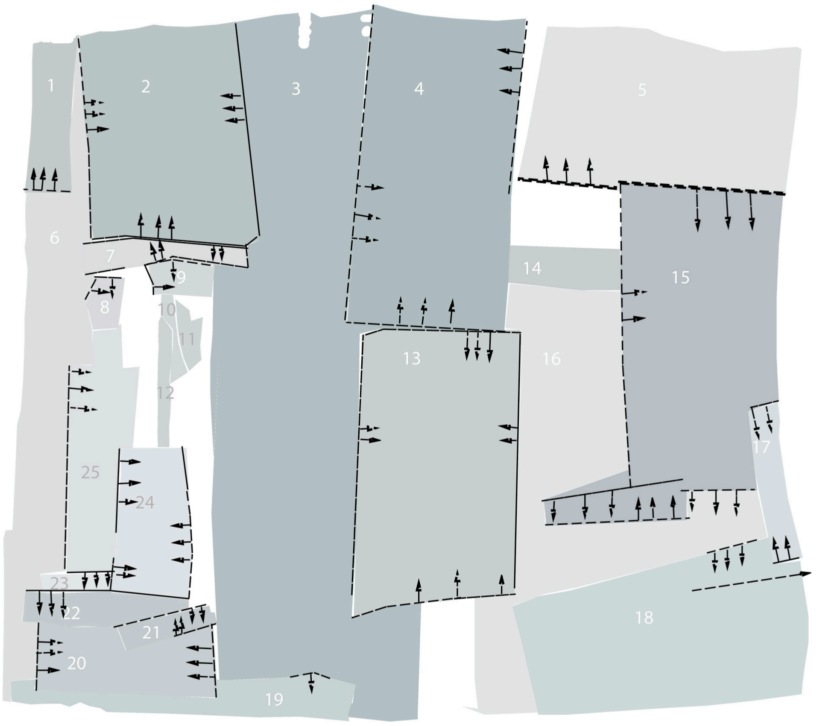
Appendix 9. 2 Time Zero front face. Map of condition



Appendix 9. 3 Time Zero front face. Map of surface films

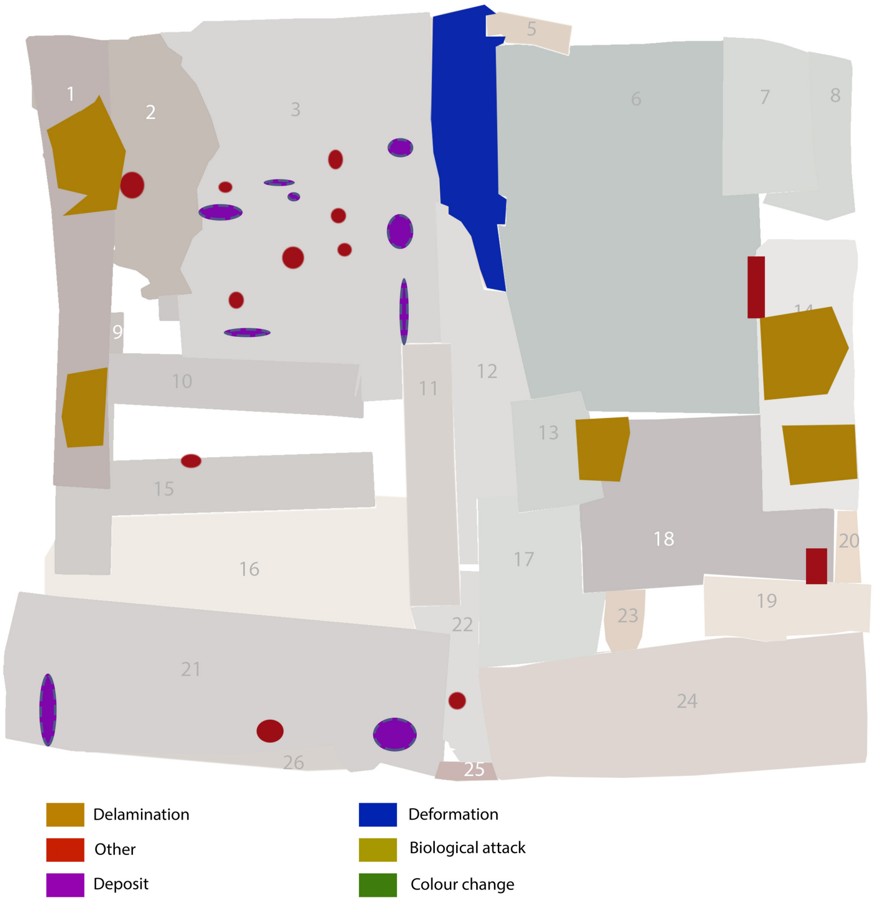


Appendix 9. 4 Time Zero front face. Map of other films and tapes

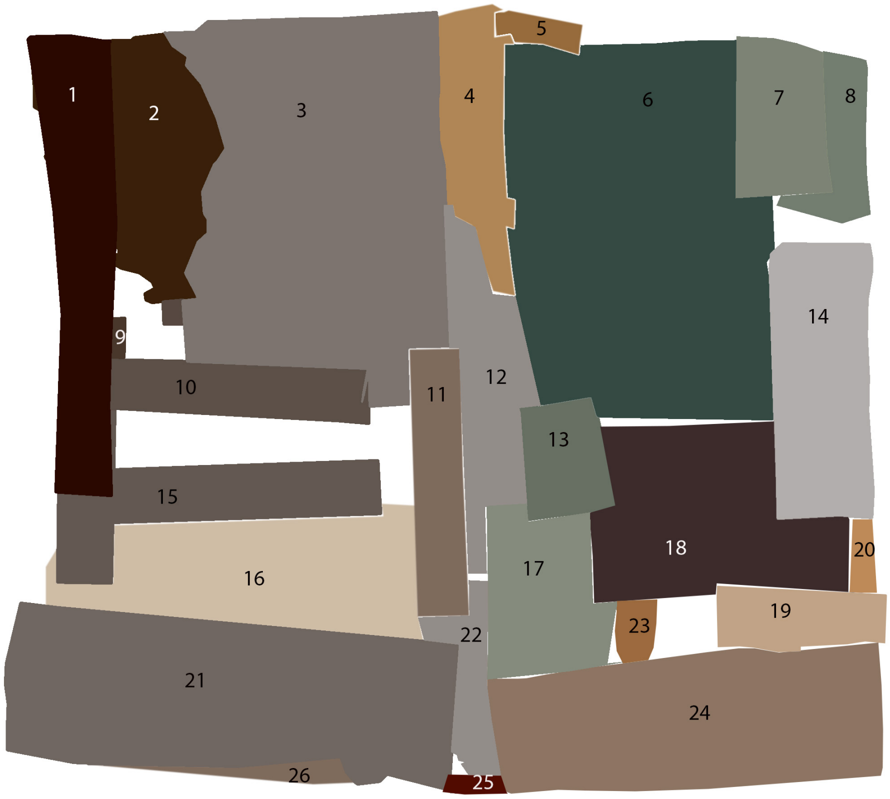


Appendix 9. 5 Time Zero front face adhesive tide-lines

Appendix 9. 6 Time Zero verso in UV-light. Photo: Frode Larsen, National Museum of Art, Architecture and Design



Appendix 9. 7 Time Zero verso. Map of condition



Appendix 9. 8 Time Zero verso. Map of surface films

Appendix 9. 9 Time Zero verso. Map of tapes and exposed paper

Appendix 9. 10 Time Zero verso. Adhesive tide lines

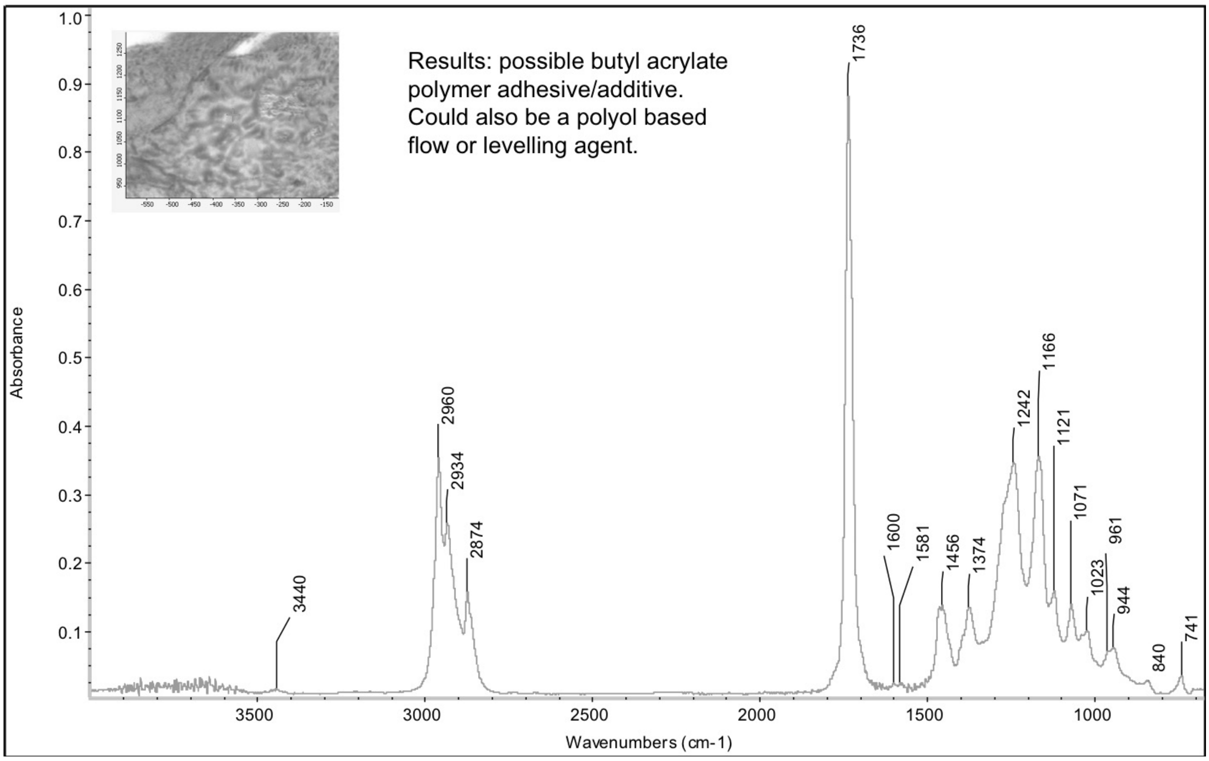
9.2 Appendix 2 Slettemark, *Time Zero* FTIR analysis report

Slettemark, Time Zero
FTIR analysis report

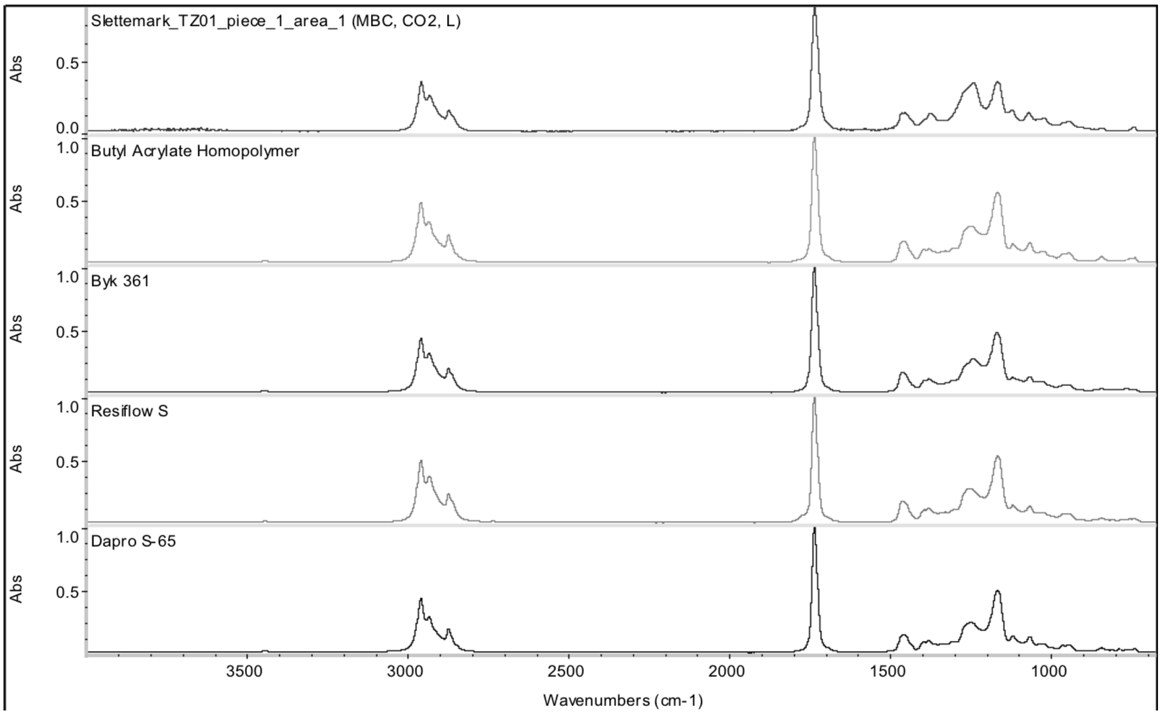
Anja Sandtrø, University of Oslo
Research Masters

Bronwyn Ormsby, Tate
October 2014

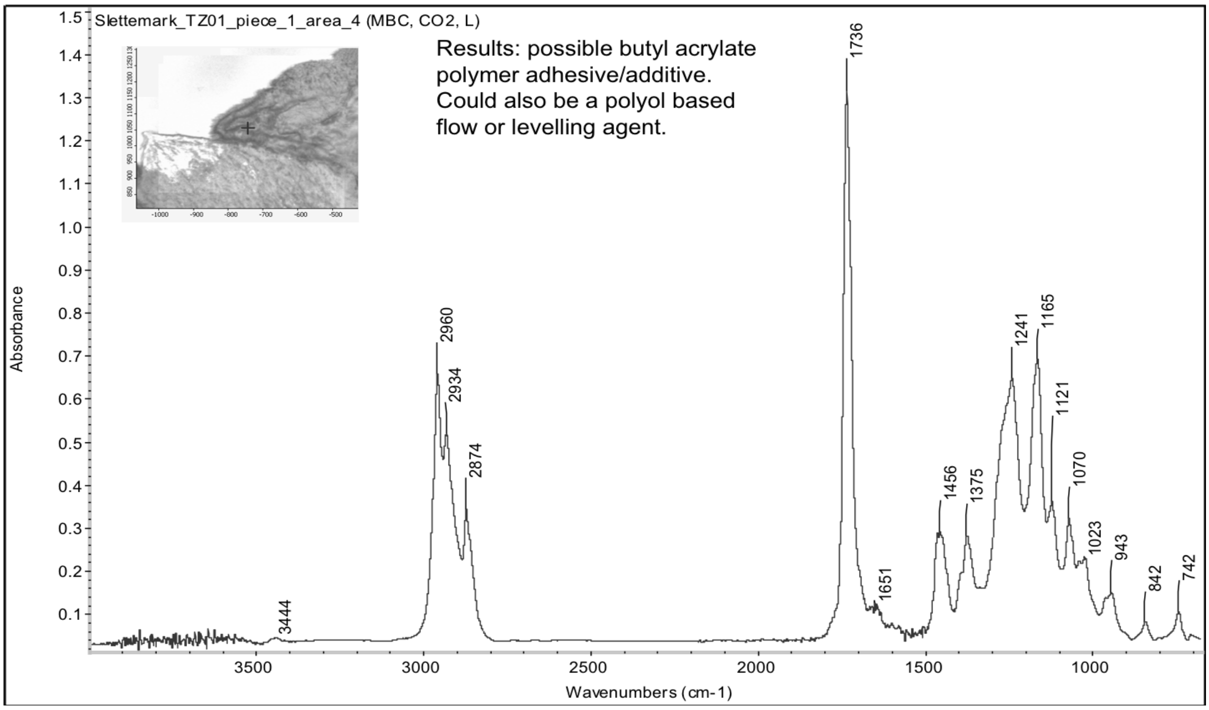
Slettemark_TZ01_piece_1_area_1: sticky/adhesive material: spectrum


Results: possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.

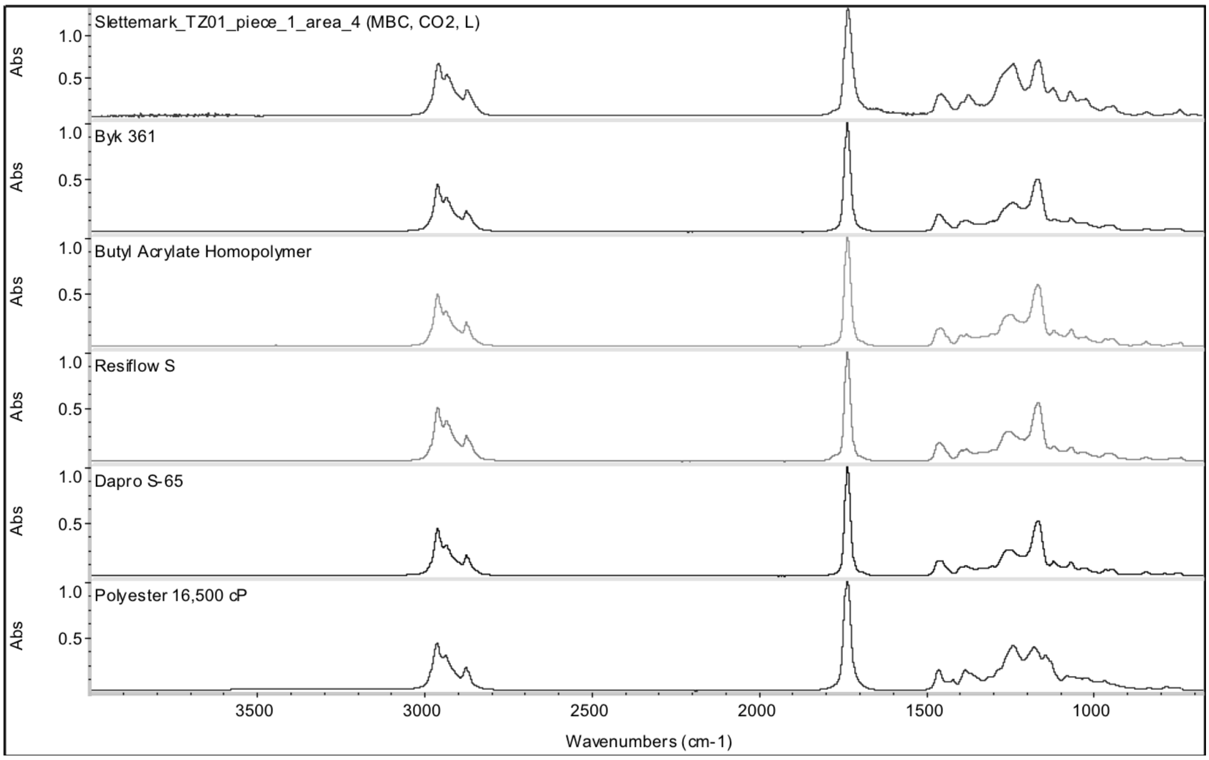
Slettemark_TZ01_piece_1_area_1: interpretation



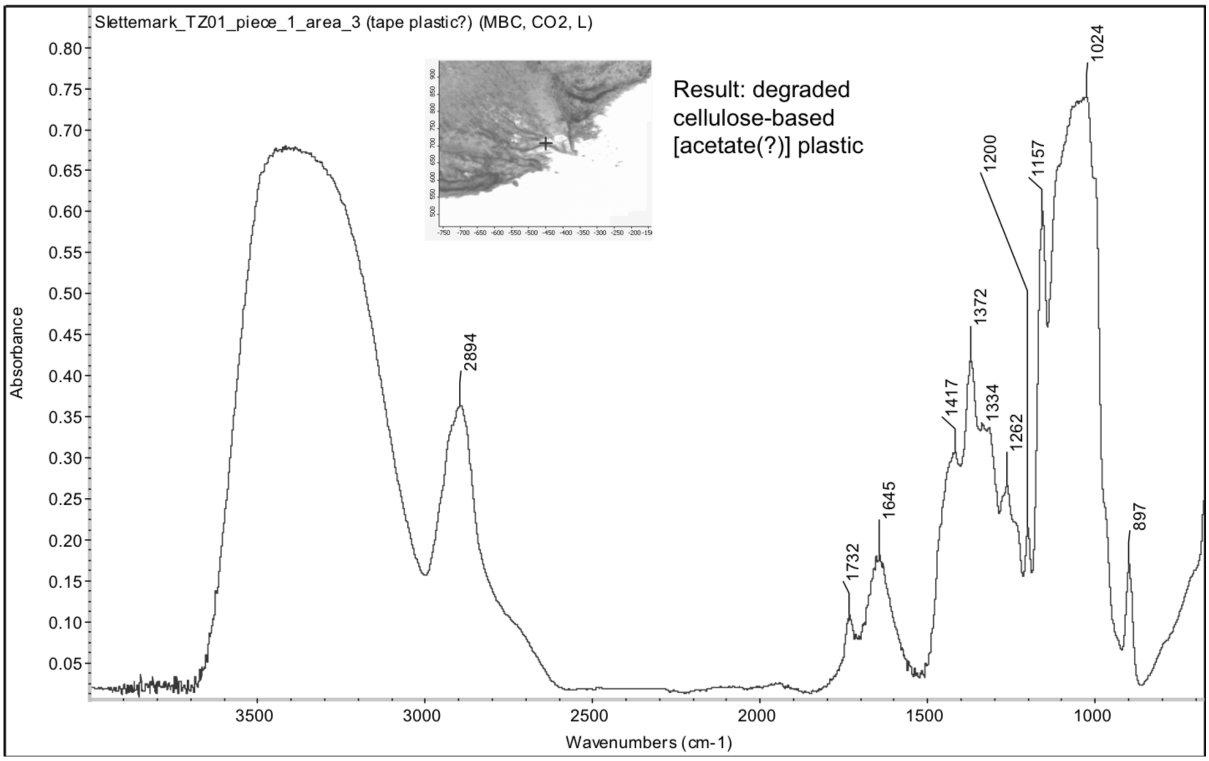
Slettemark_TZ01_piece_1_area_4: (sticky/adhesive) spectrum


Results: possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.

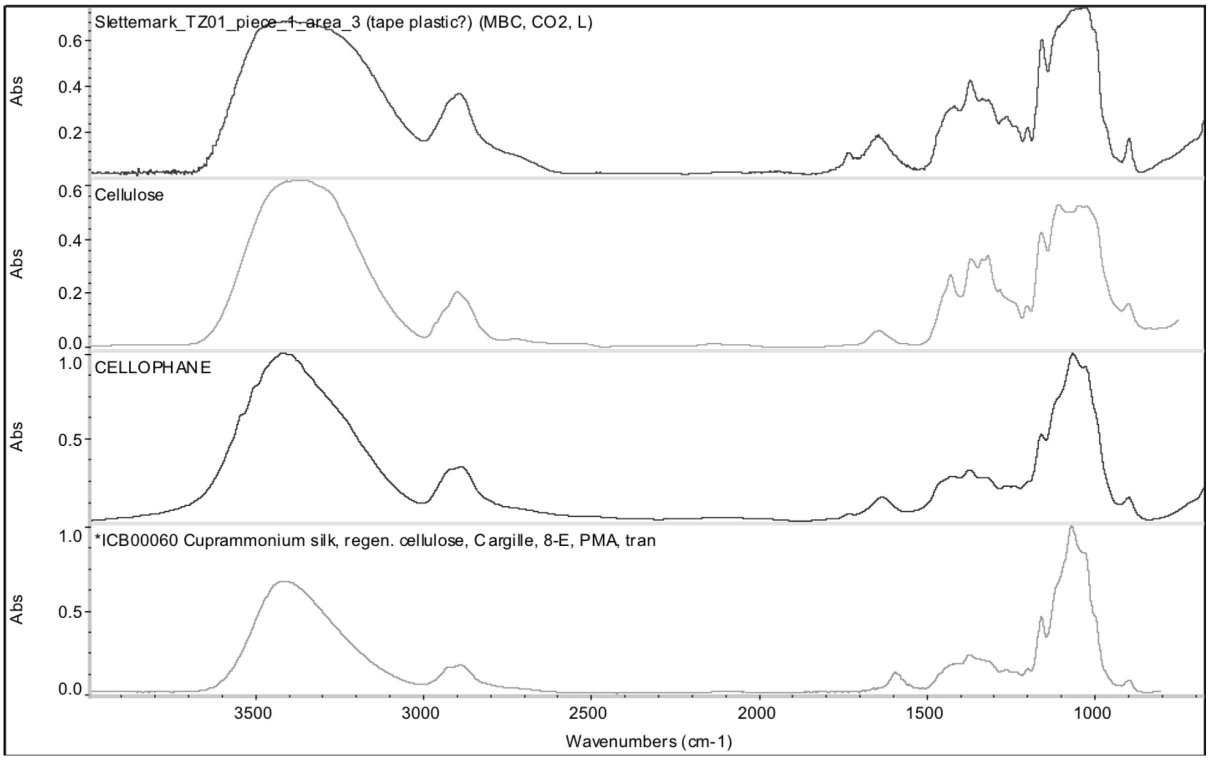
Slettemark_TZ01_piece_1_area_4: interpretation



Slettemark_TZ01_piece_1_area_3 (plastic): spectrum


Result: degraded cellulose-based [acetate(?)] plastic

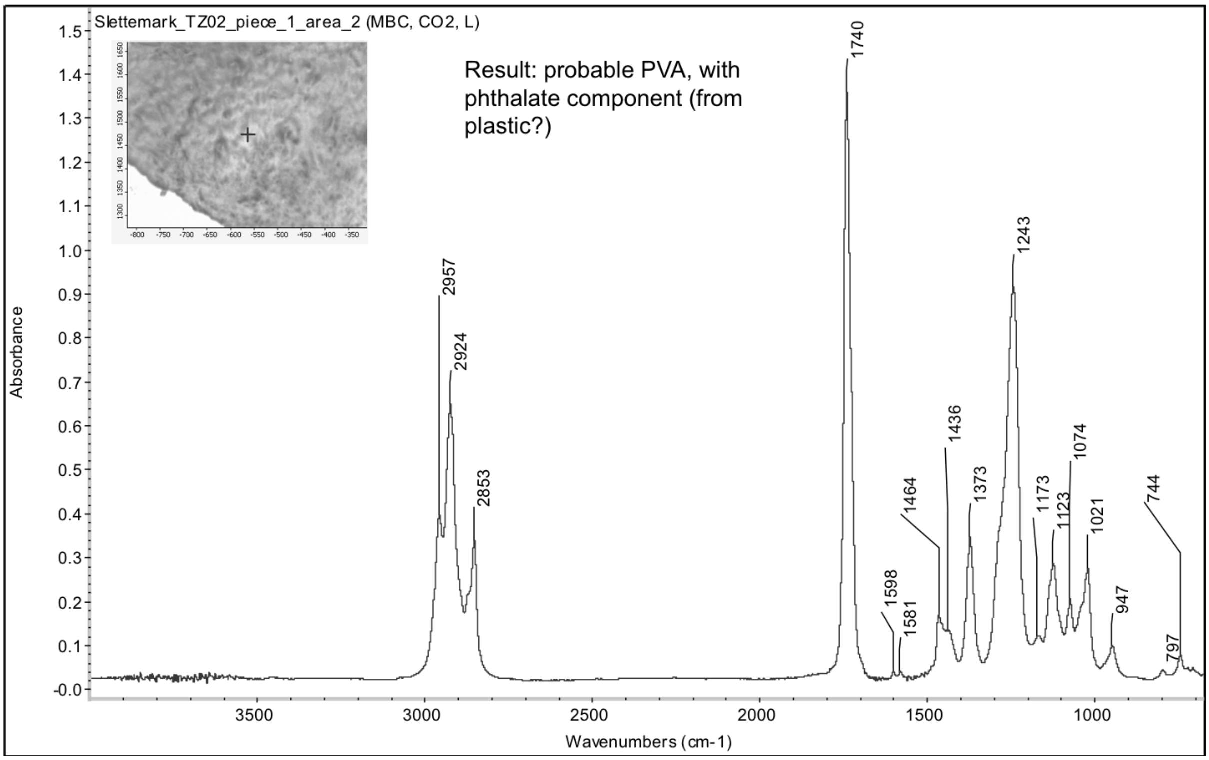
Slettemark_TZ01_piece_1_area_3 (plastic): interpretation



TZ01: FTIR result summary

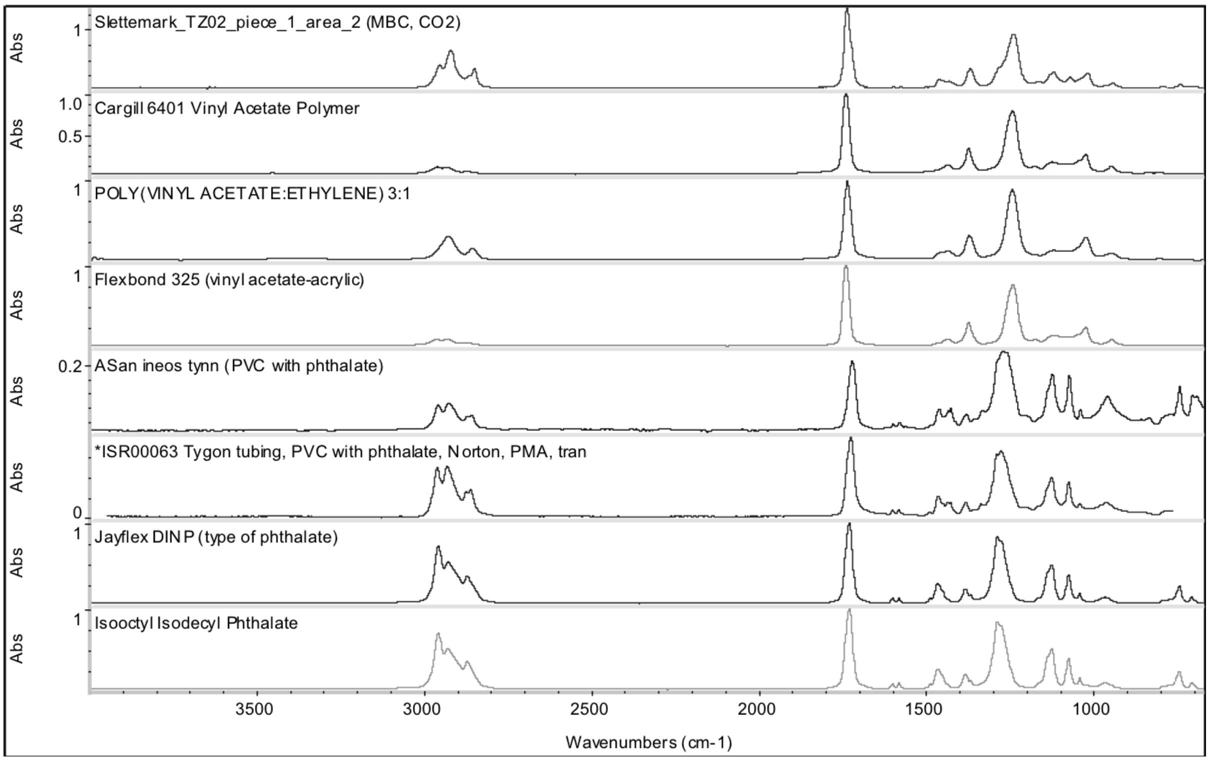
Piece and area No.	Description	Polymer ID	Other	Notes
1-1	Soft material, adhesive/additive	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent.	-	Acrylic-based adhesive and/or additive (flow or levelling agent?)
1-3	Harder plastic section	Cellulose-based plastic (acetate?)	-	Degraded cellulose-based plastic.
1-4	Soft material, adhesive/additive	Same as 1-1	-	Same as 1-1

Slettemark_TZ02_piece_1_area_2: spectrum (sticky adhesive)

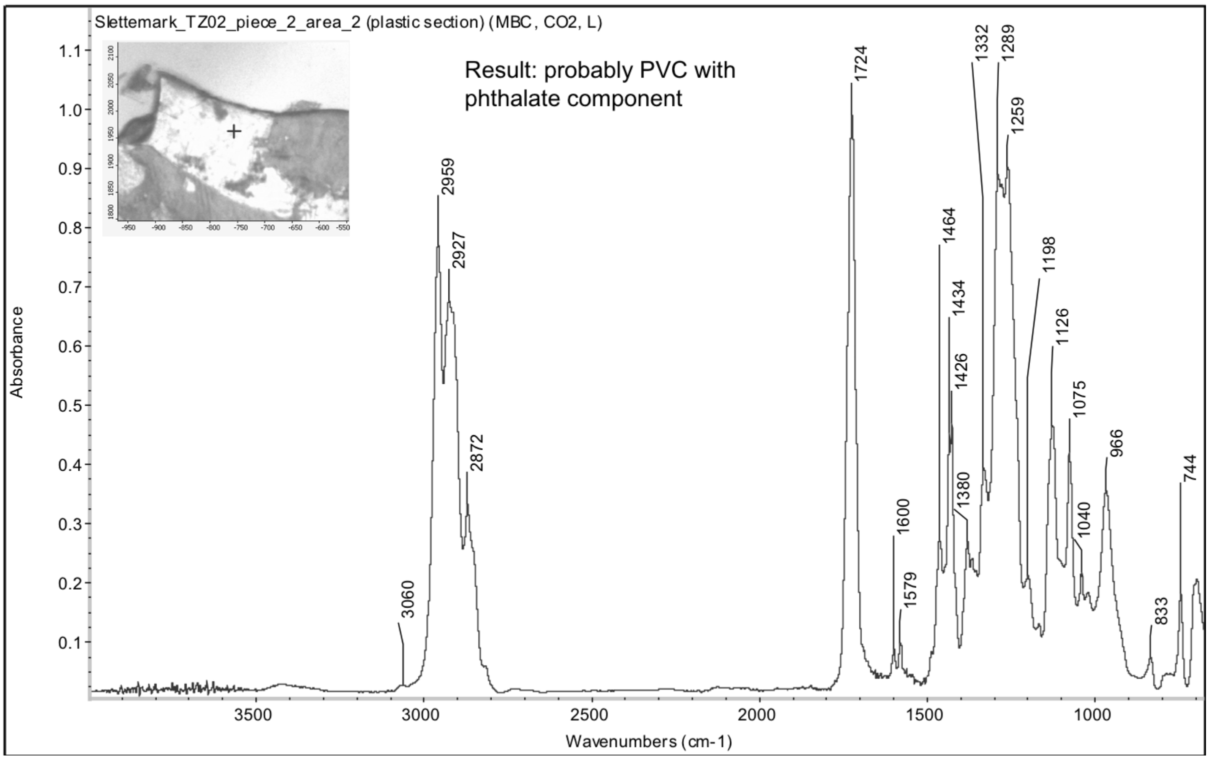


Result: probable PVA, with phthalate component (from plastic?)

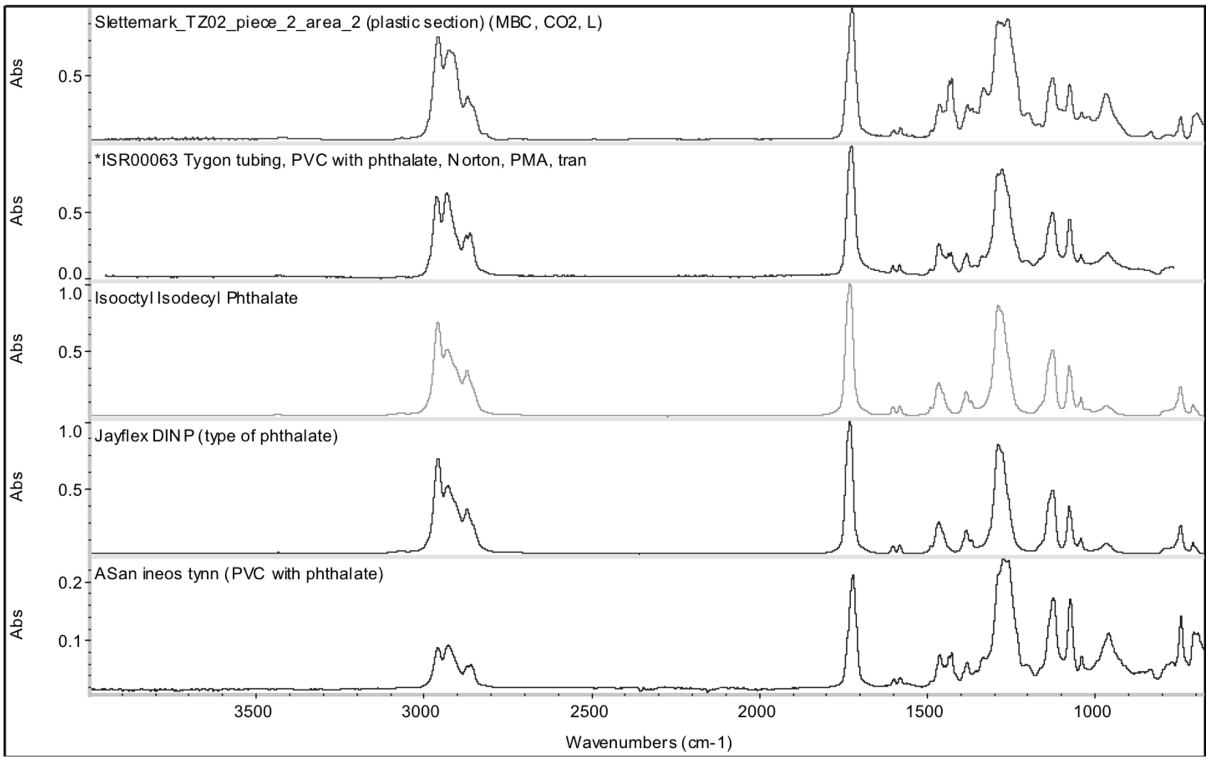
Slettemark_TZ02_piece_1_area_2: (sticky adhesive): interpretation



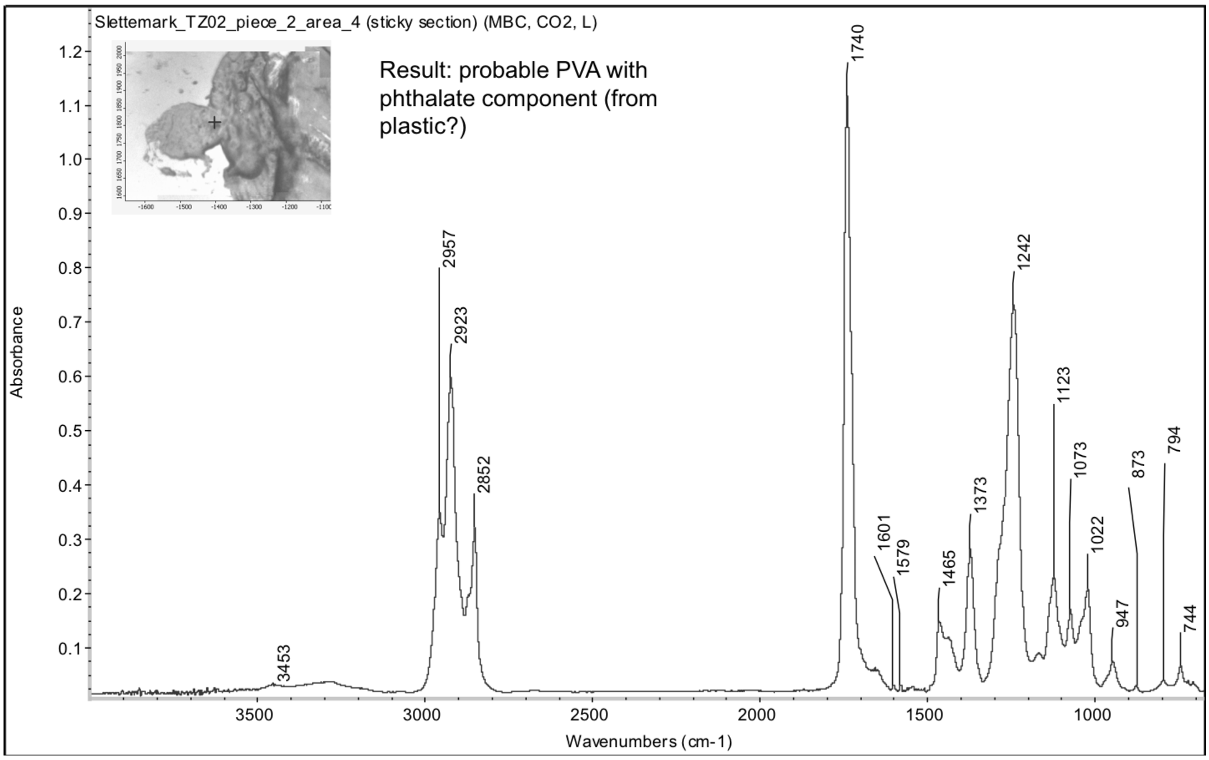
Slettemark_TZ02_piece_2_area_2 (plastic section): spectrum



Slettemark_TZ02_piece_2_area_2 (plastic section): interpretation

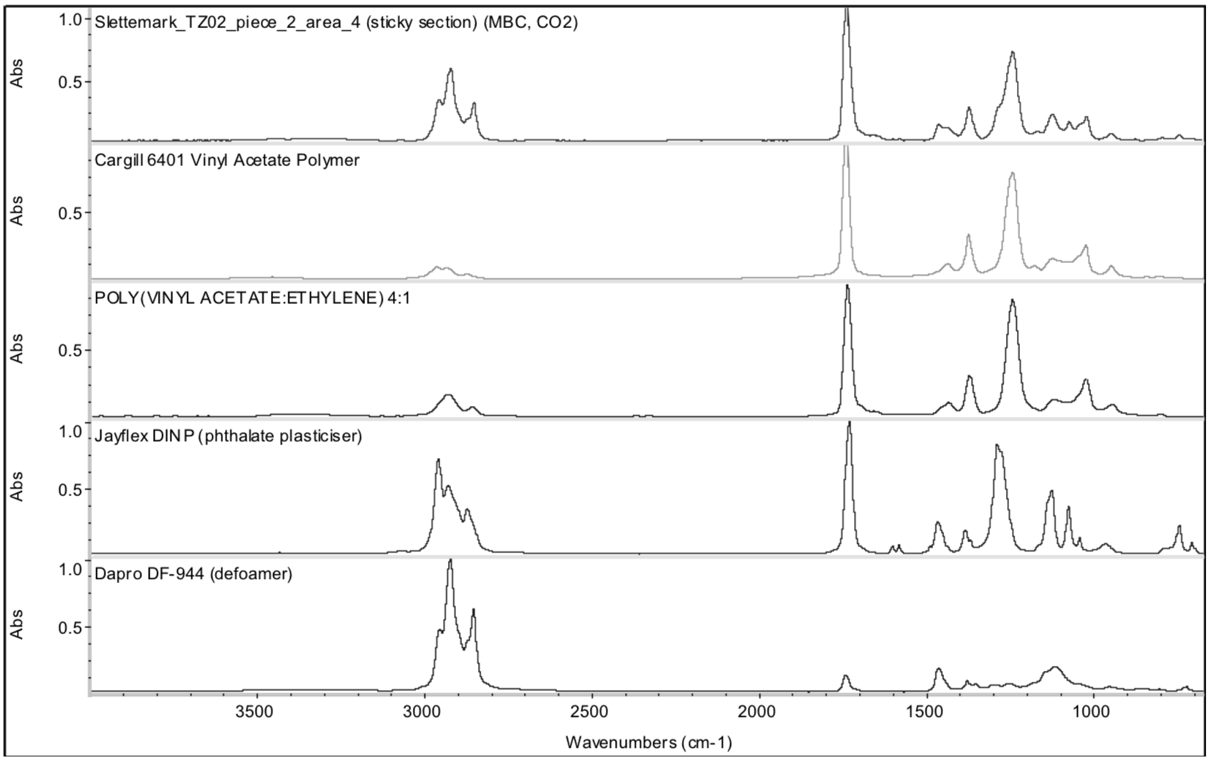


Slettemark_TZ02_piece_2_area_4 (sticky material): spectrum



Result: probable PVA with phthalate component (from plastic?)

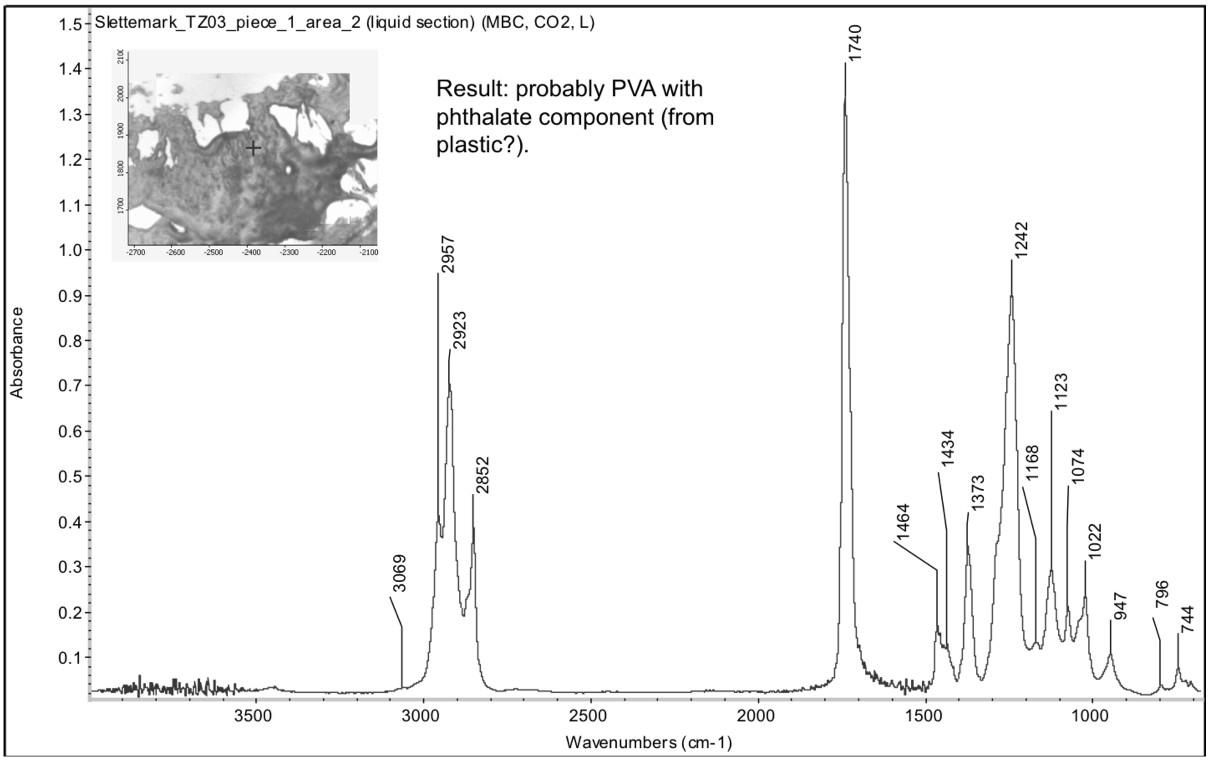
Slettemark_TZ02_piece_2_area_4 (sticky section): interpretation



TZ02: FTIR result summary

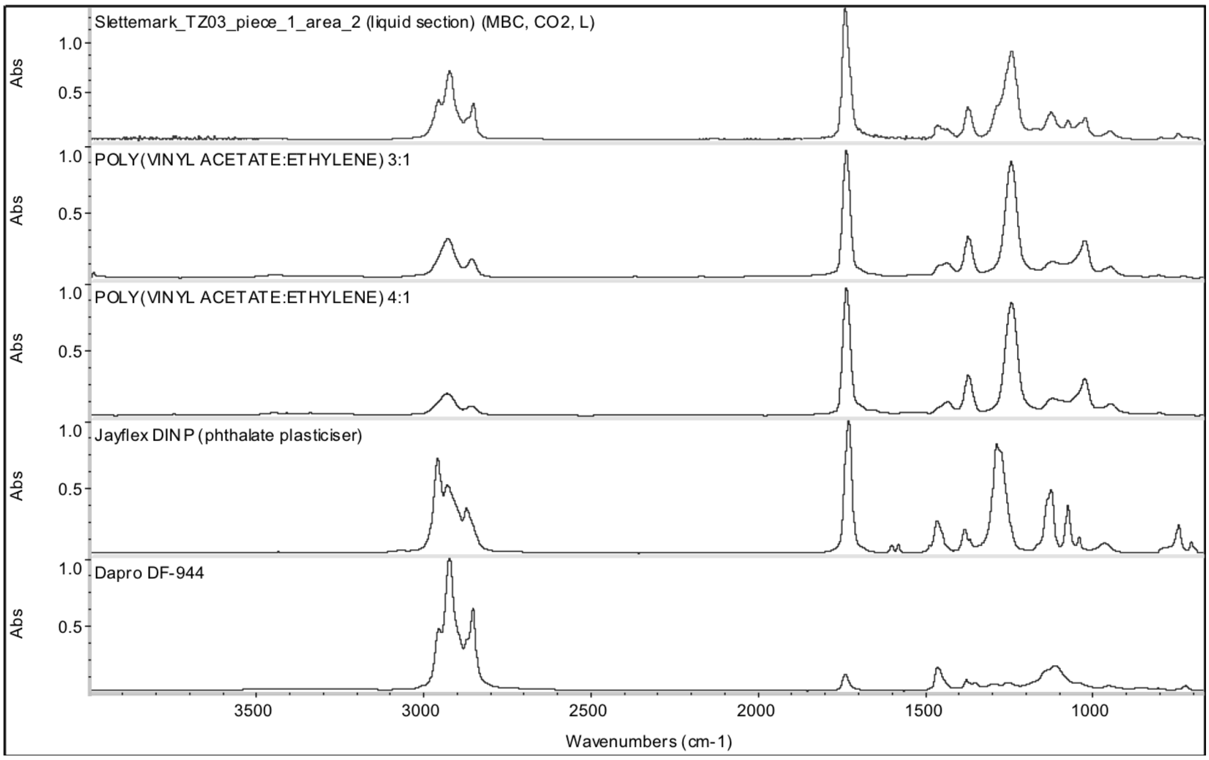
Piece and area No.	Description	Polymer ID	Other	Notes
1-2	Soft material, adhesive/additive	Probable PVA, with phthalate component (from plastic?)	-	
2-2	Harder plastic section	Result: probably PVC with phthalate component	-	
2-4	Soft material, adhesive/additive	Probable PVA, with phthalate component (from plastic?)	-	

Slettemark_TZ03_piece_1_area_2 (liquid section): spectrum

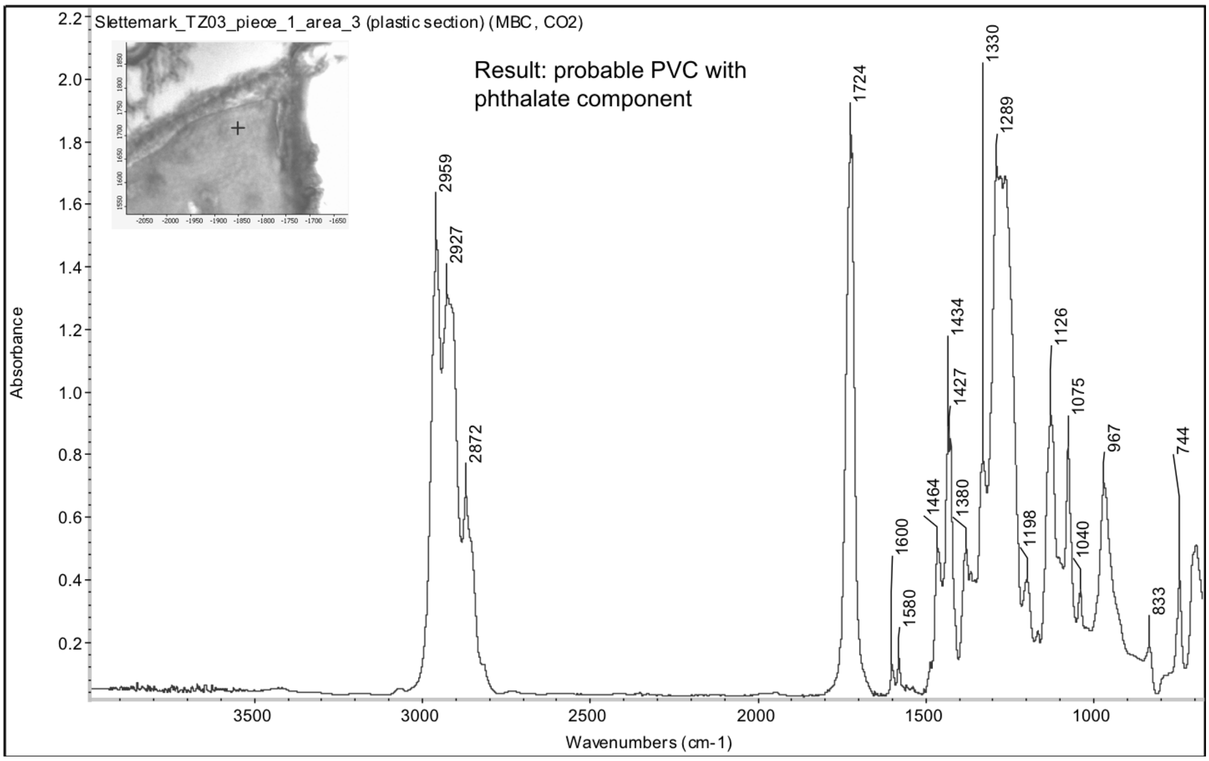


Result: probably PVA with phthalate component (from plastic?).

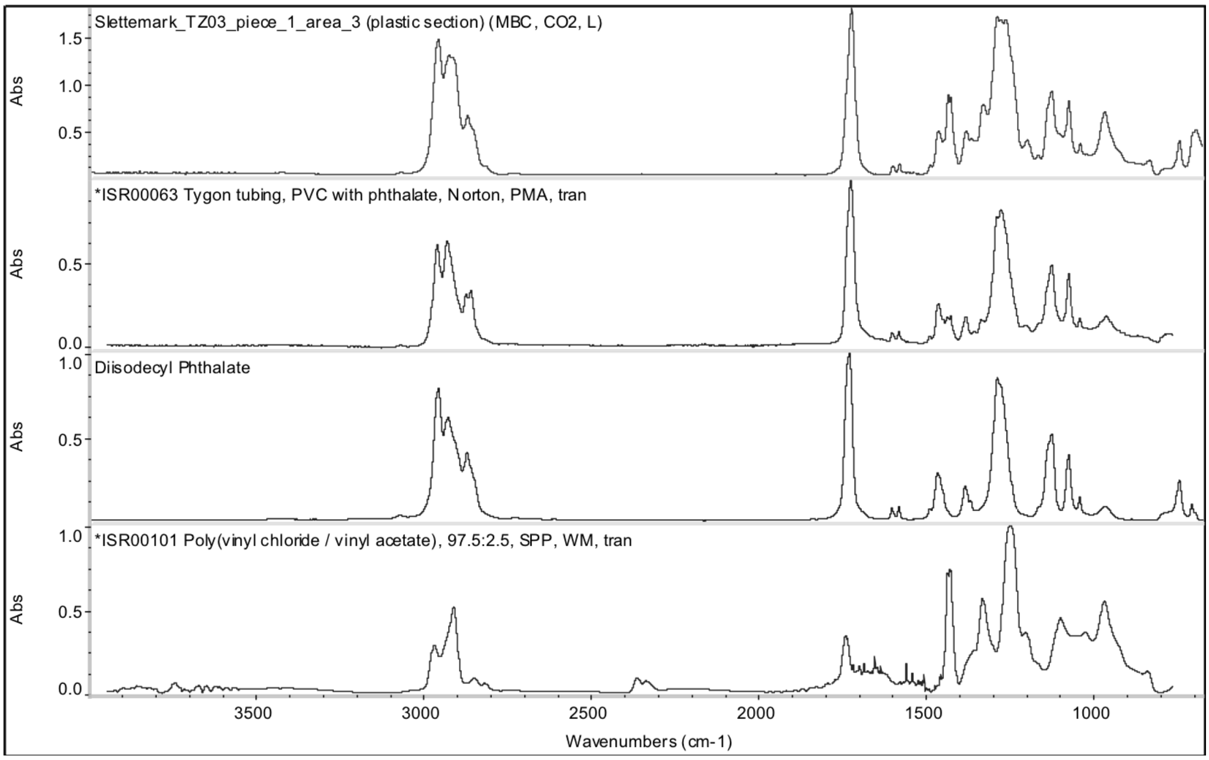
Slettemark_TZ03_piece_1_area_2 (liquid section): interpretation



Slettemark_TZ03_piece_1_area_3 (plastic section): spectrum


Result: probable PVC with phthalate component

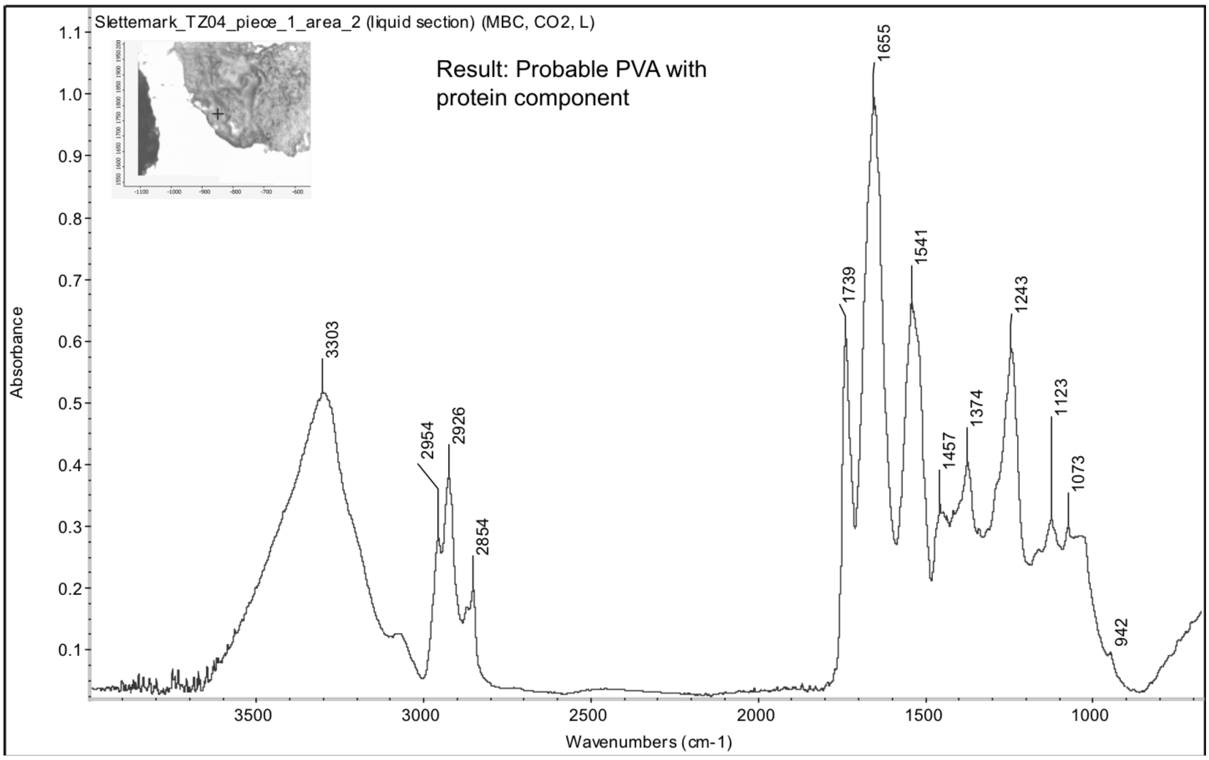
Slettemark_TZ03_piece_1_area_3 (plastic section): interpretation



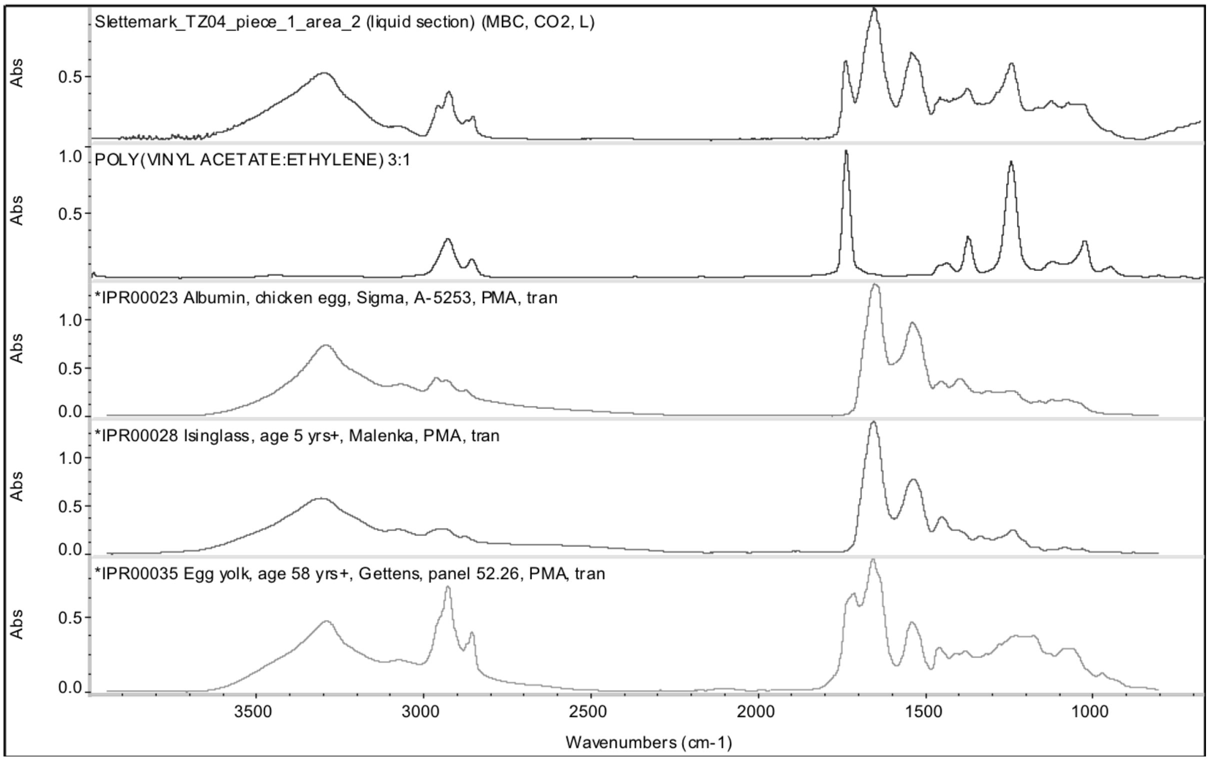
TZ03: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
1-2	Soft material, adhesive/additive	Probably PVA with minor phthalate component (from plastic?)	-	PyGCMS useful?
1-3	Harder plastic section	Probable PVC with phthalate component	-	

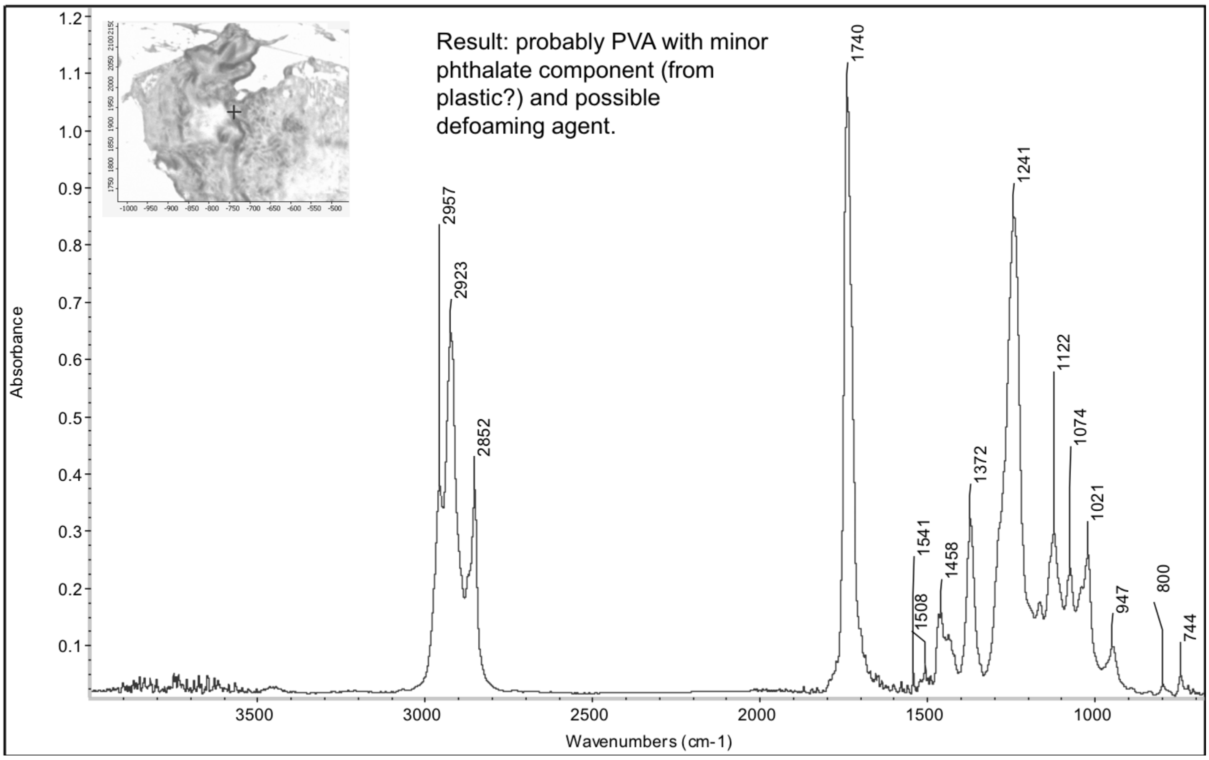
Slettemark_TZ04_piece_1_area_2 (liquid material, at edge): spectrum



Slettemark_TZ04_piece_1_area_2 (liquid gel material, edge area): interpretation

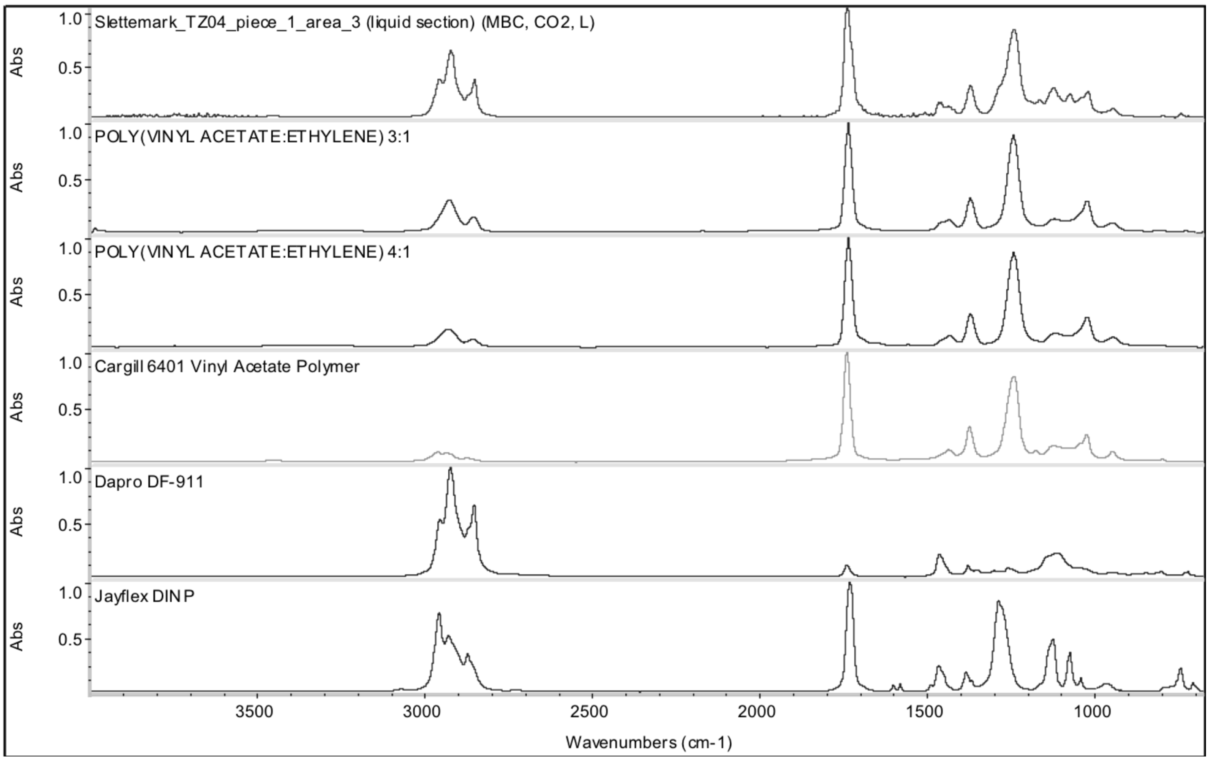


Slettemark_TZ04_piece_1_area_3 (liquid gel material): spectrum

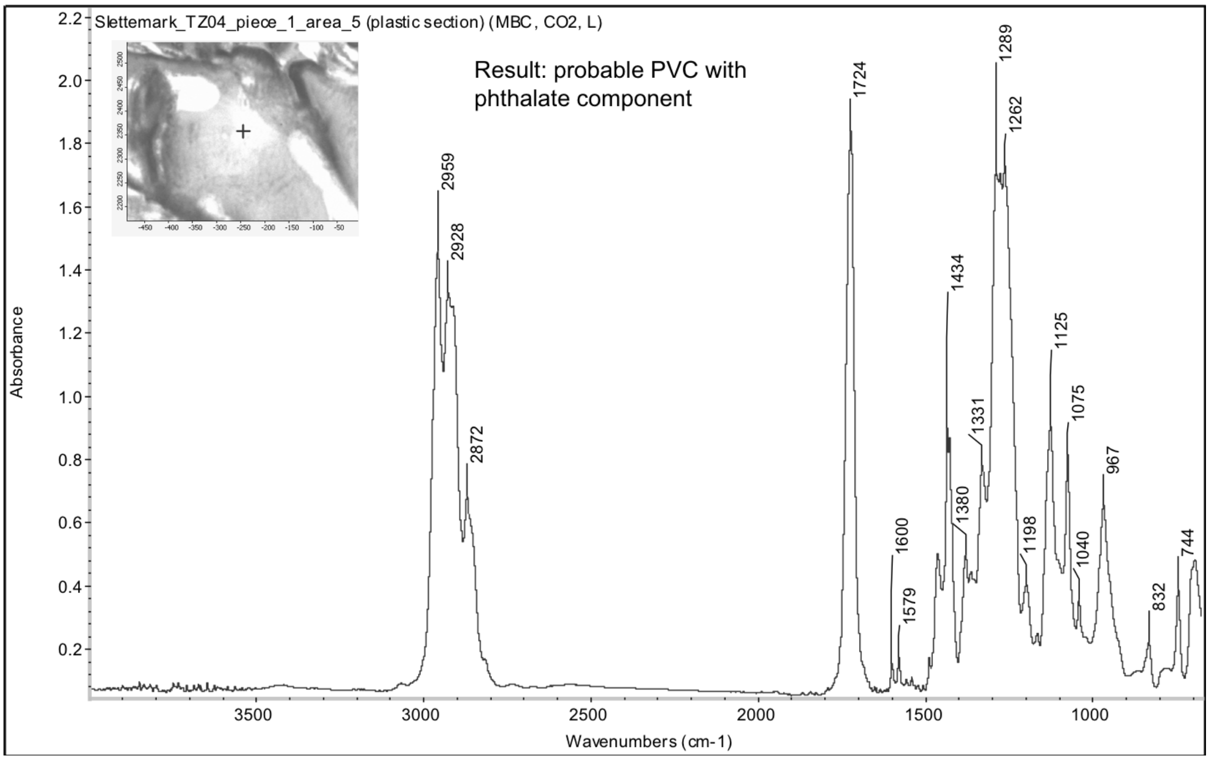


Result: probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.

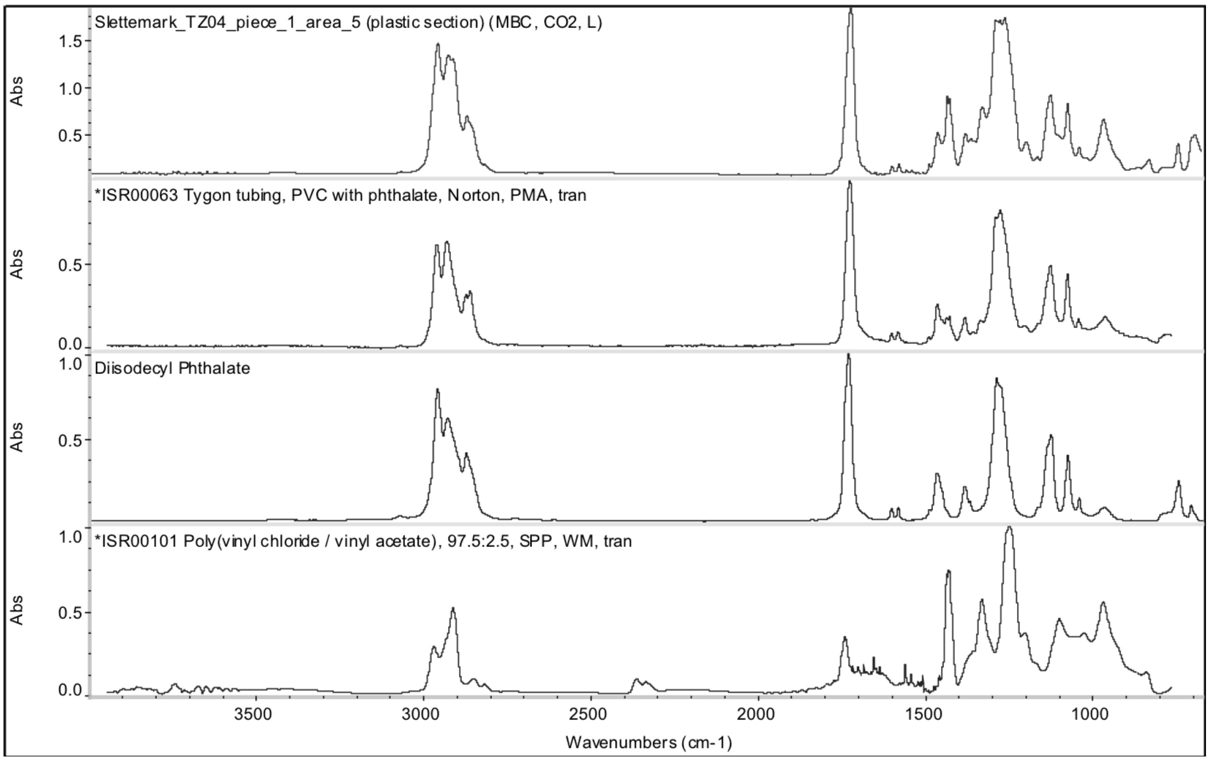
Slettemark_TZ04_piece_1_area_3 (liquid gel material): interpretation



Slettemark_TZ04_piece_1_area_5 (plastic section): spectrum



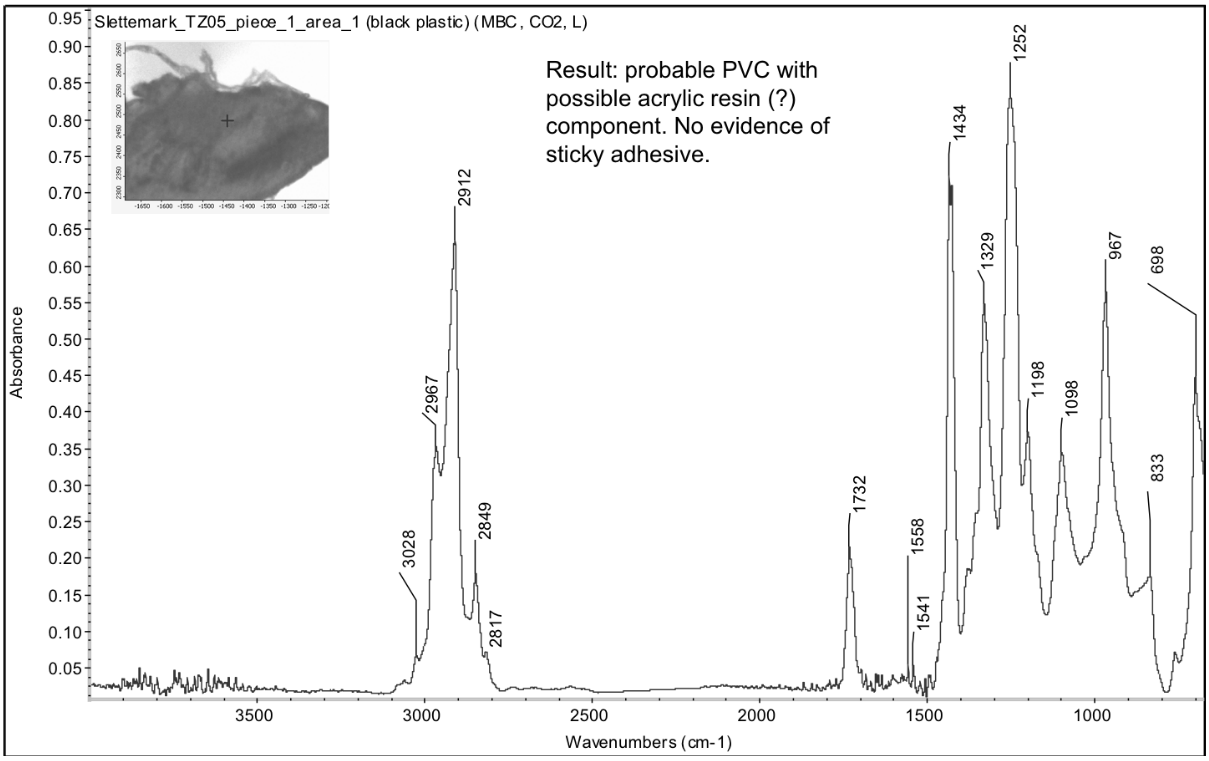
Slettemark_TZ04_piece_1_area_5 (plastic section): interpretation



TZ04: FTIR result summary

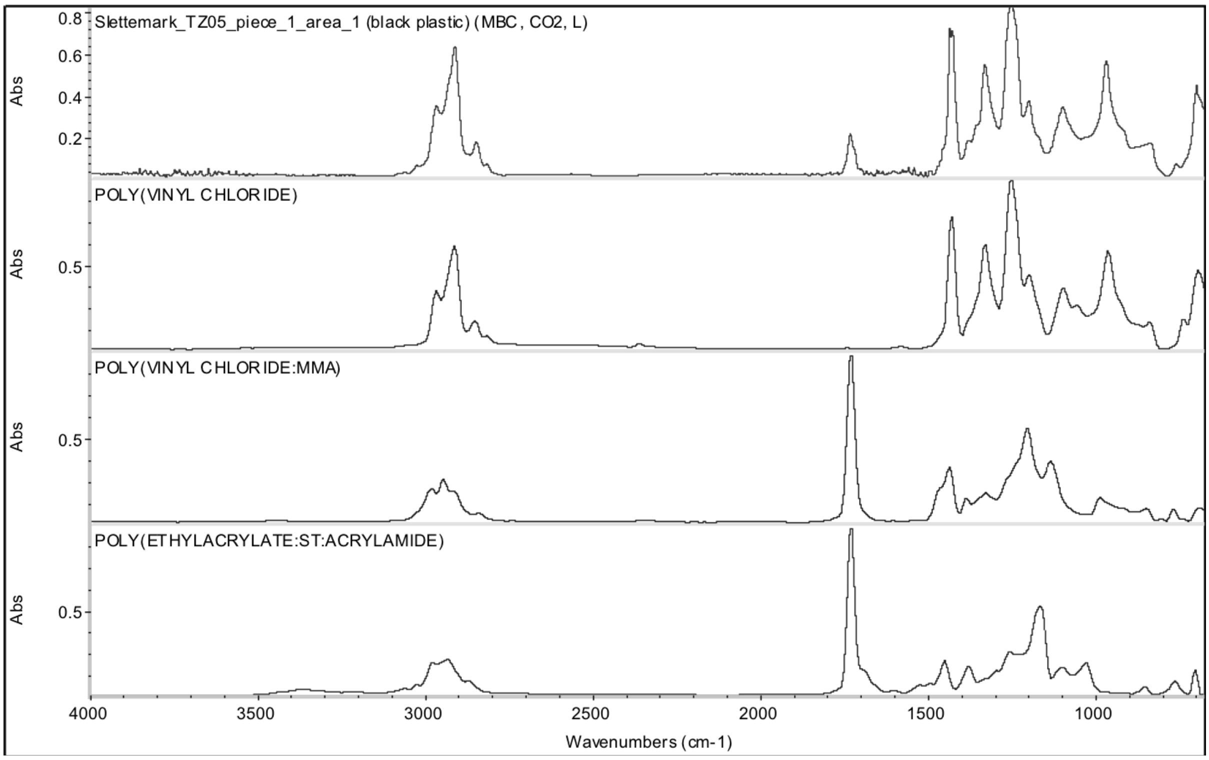
Piece and area No.	Description	Polymer ID	Other	Notes
1-2	Soft material, adhesive/ additive	Probably PVA with protein component.	-	Where could protein be coming from?
1-3	Soft material, adhesive/ additive	Probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.	-	Check defoaming agent attribution and in all other samples
1-5	Harder plastic section	Probable PVC with phthalate component	-	

Slettemark_TZ05_piece_1_area_1 (black plastic): spectrum



Result: probable PVC with possible acrylic resin (?) component. No evidence of sticky adhesive.

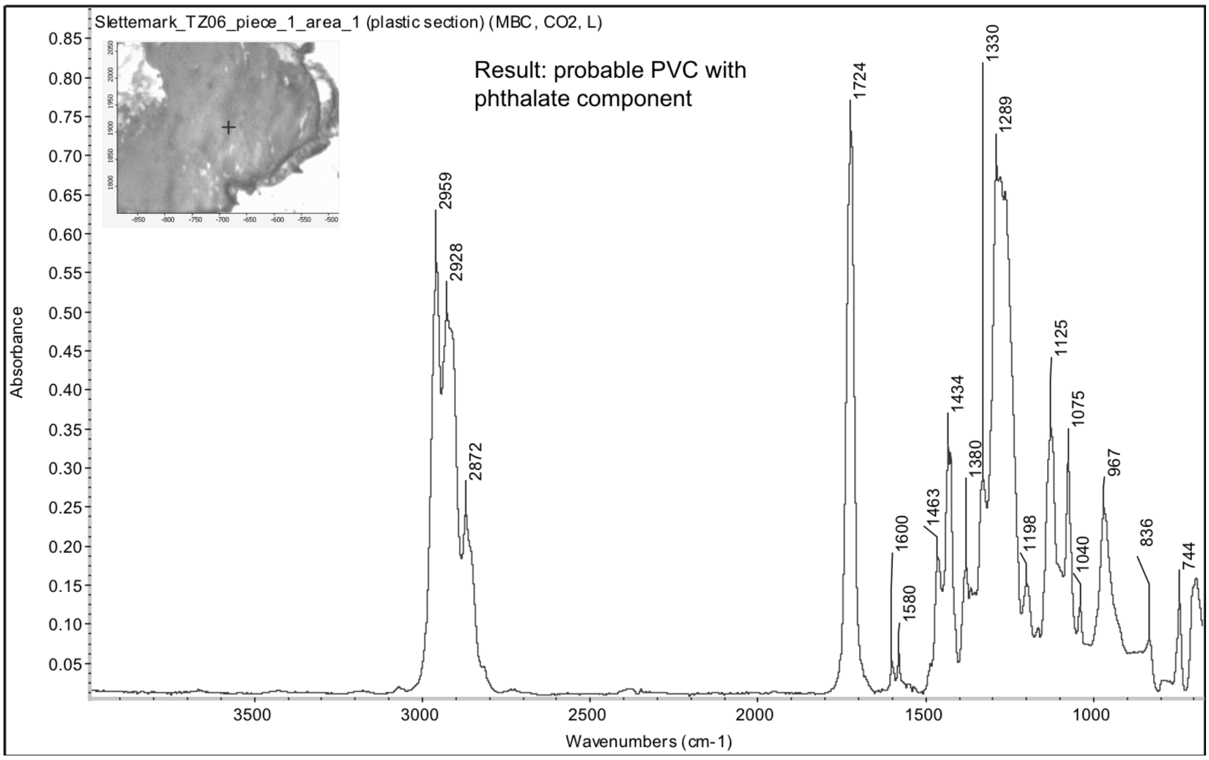
Slettemark_TZ05_piece_1_area_1 (black plastic): interpretation



TZ05: FTIR result summary

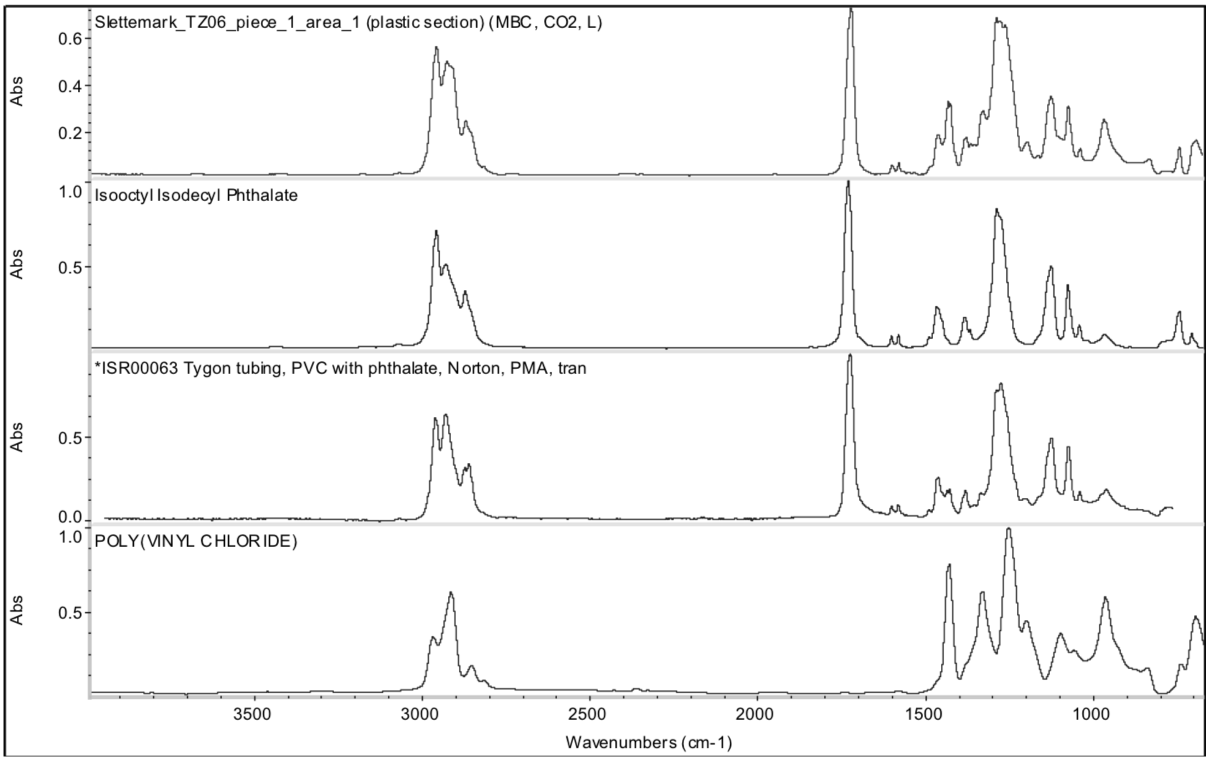
Piece and area No.	Description	Polymer ID	Other	Notes
5-1	Black plastic, no obvious sticky adhesive/ residue	Probable PVC with possible acrylic component.	-	PyGCMS may be useful

Slettemark_TZ06_piece_1_area_1 (plastic section): spectrum

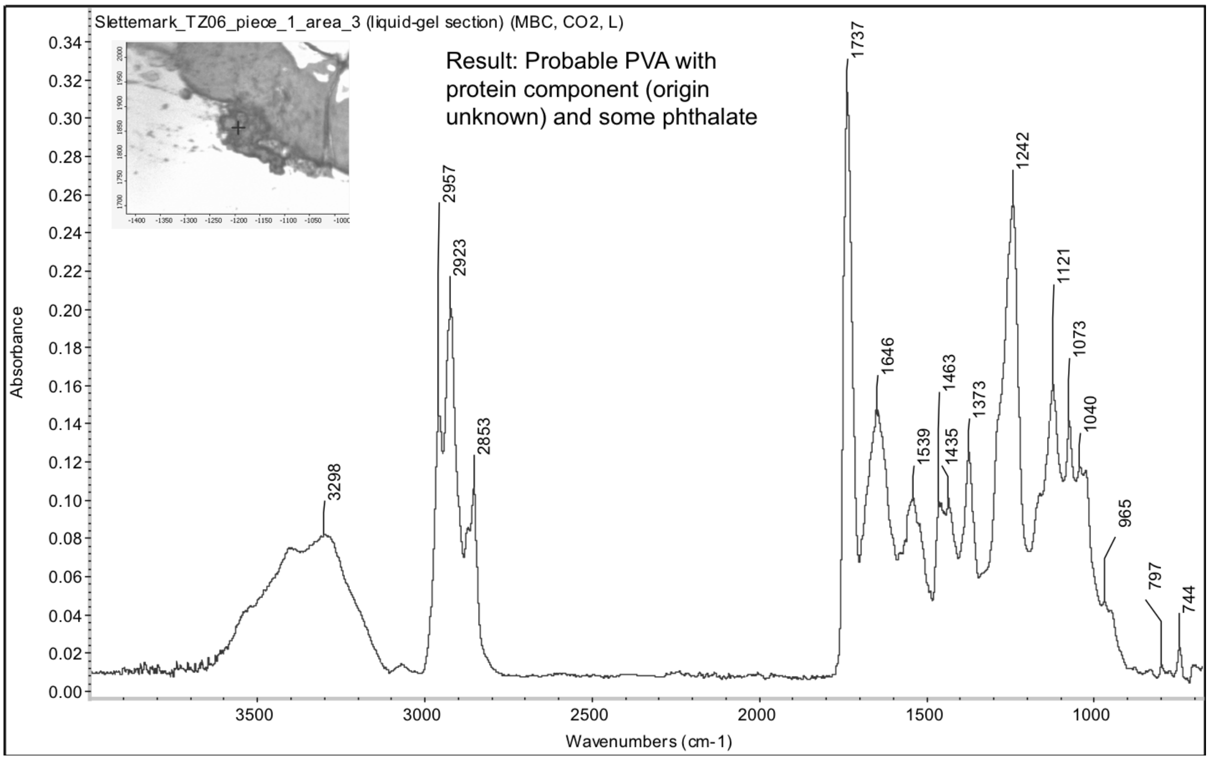


Result: probable PVC with phthalate component

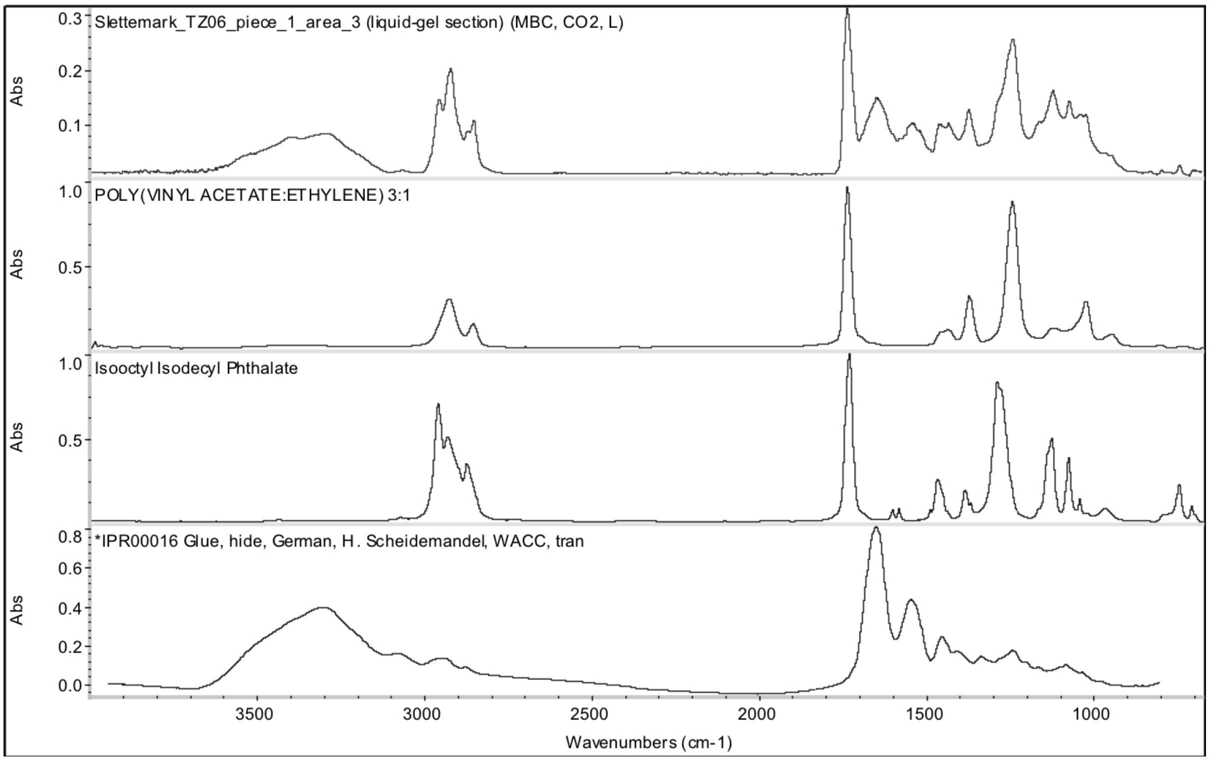
Slettemark_TZ06_piece_1_area_1 (plastic section): interpretation



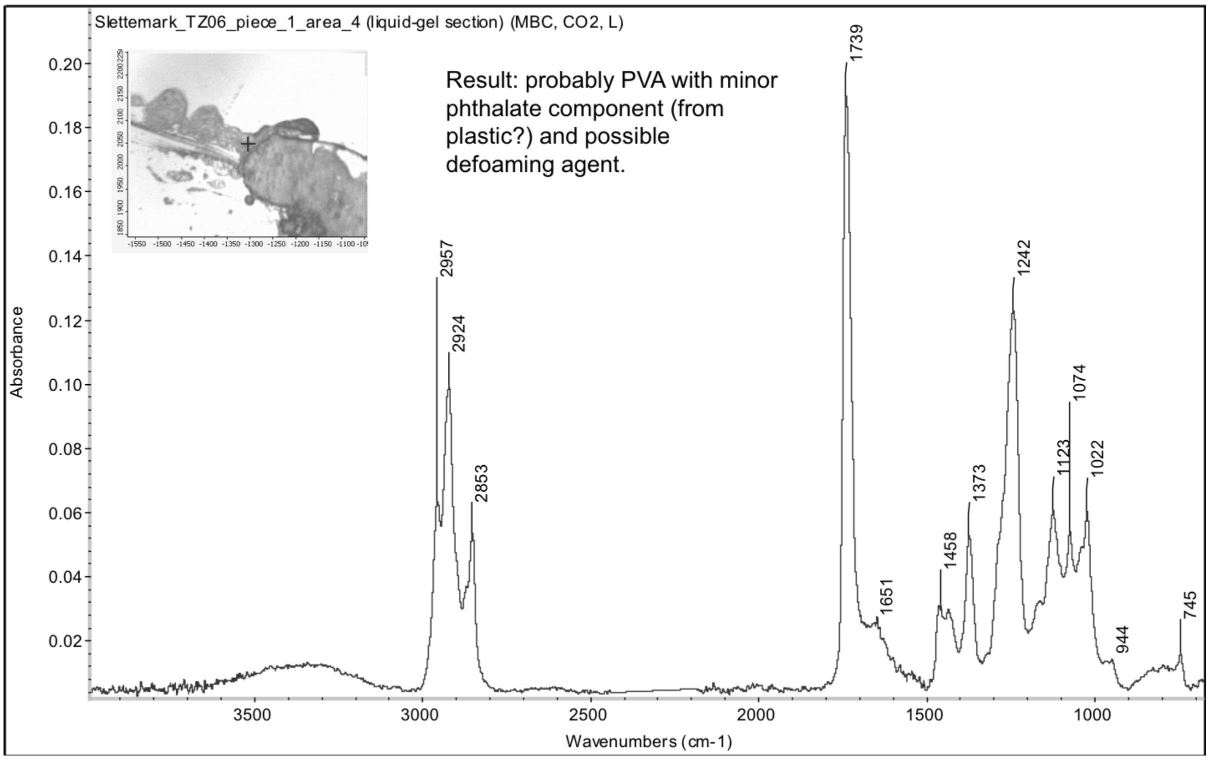
Slettemark_TZ06_piece_1_area_3 (liquid-gel section [with plastic?]): spectrum


Result: Probable PVA with protein component (origin unknown) and some phthalate

Slettemark_TZ06_piece_1_area_3 (liquid-gel section [with plastic?]): interpretation

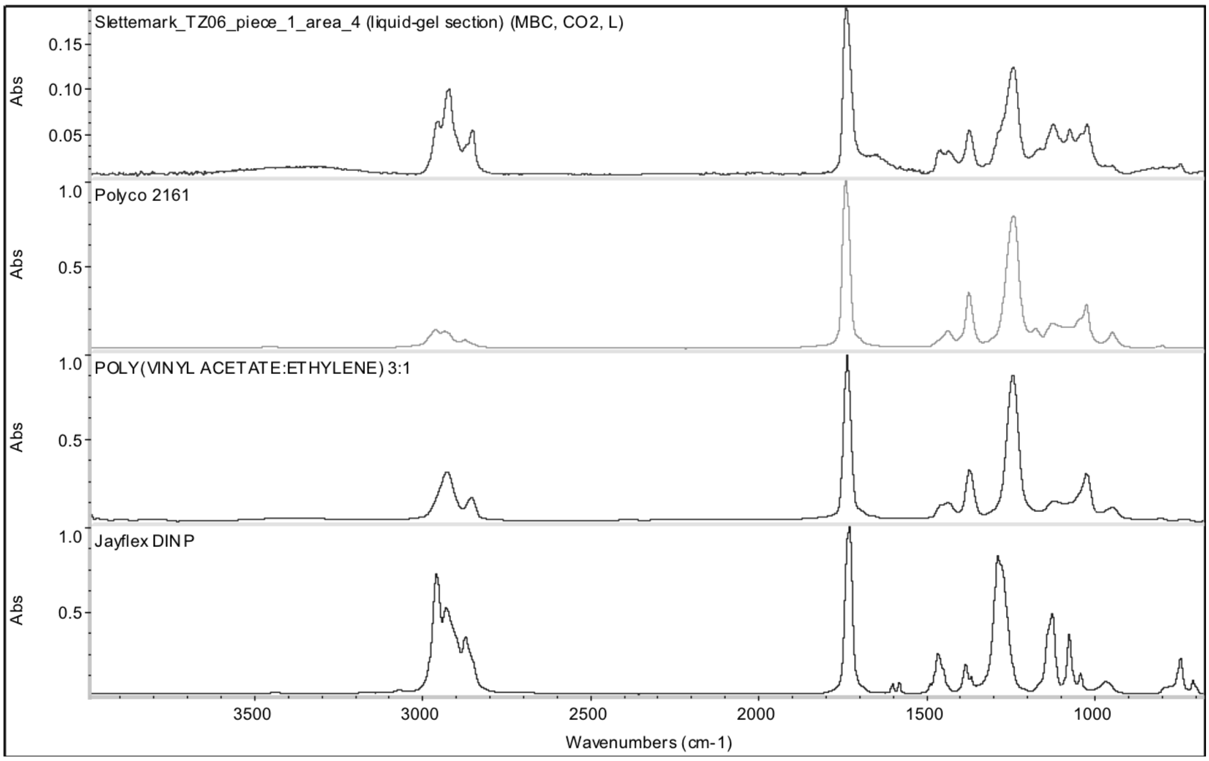


Slettemark_TZ06_piece_1_area_4 (liquid-gel section): spectrum



Result: probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.

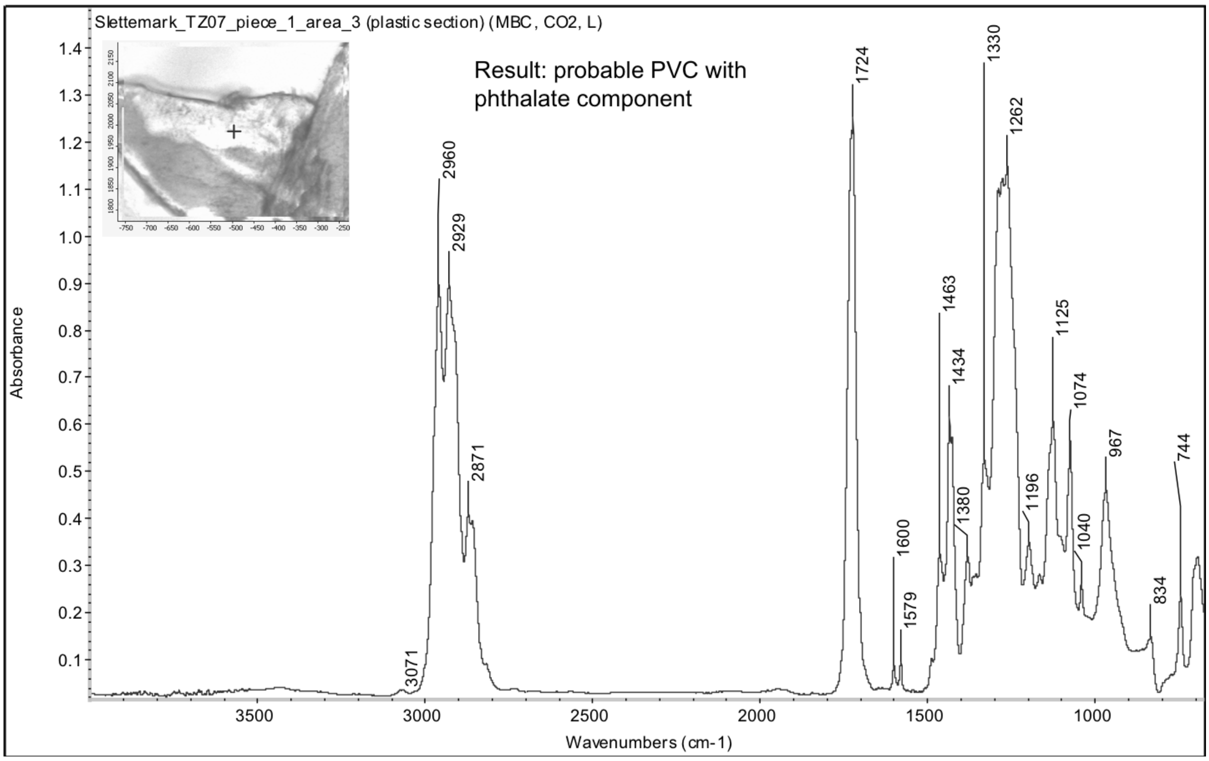
Slettemark_TZ06_piece_1_area_4 (liquid-gel section): spectrum



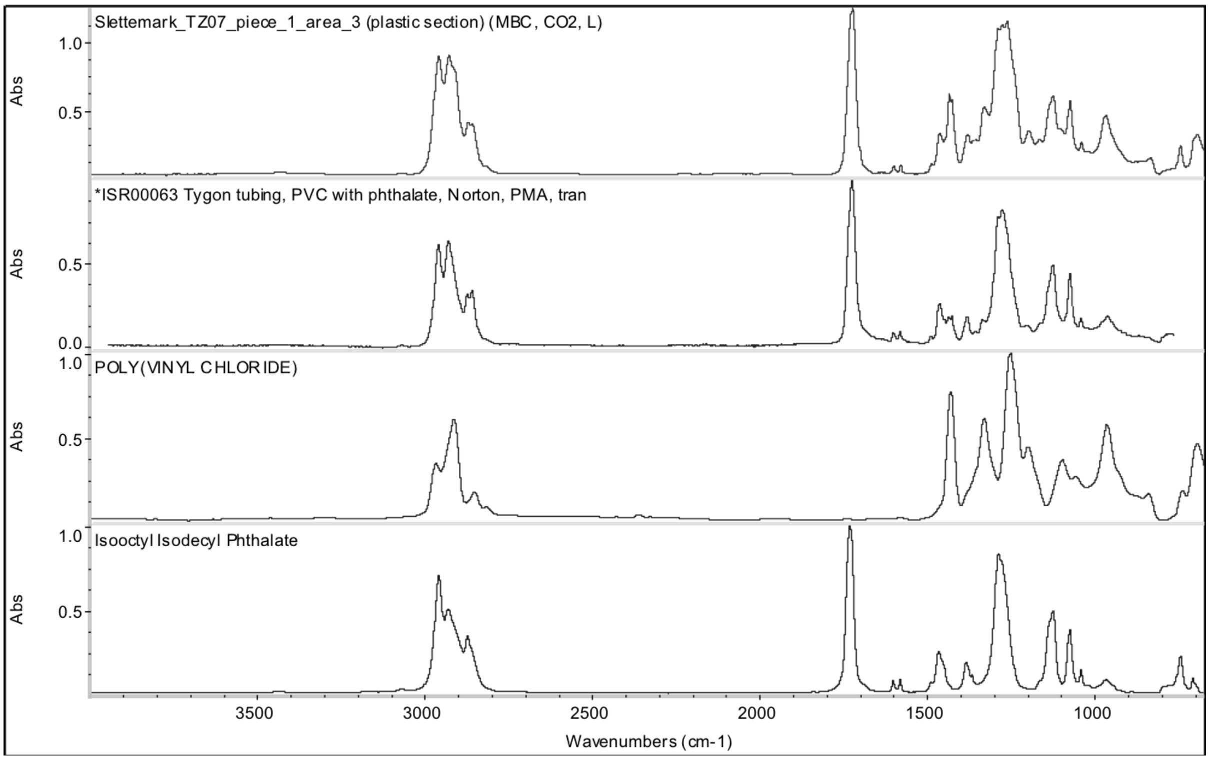
TZ06: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
6-1	Plastic section (transparent)	Probably PVC with phthalate component	-	
6-3	Soft material	Probably PVA with minor phthalate component (from plastic?) and some protein component.	-	What would the source of protein be?
6-4	Soft material	Probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.	-	

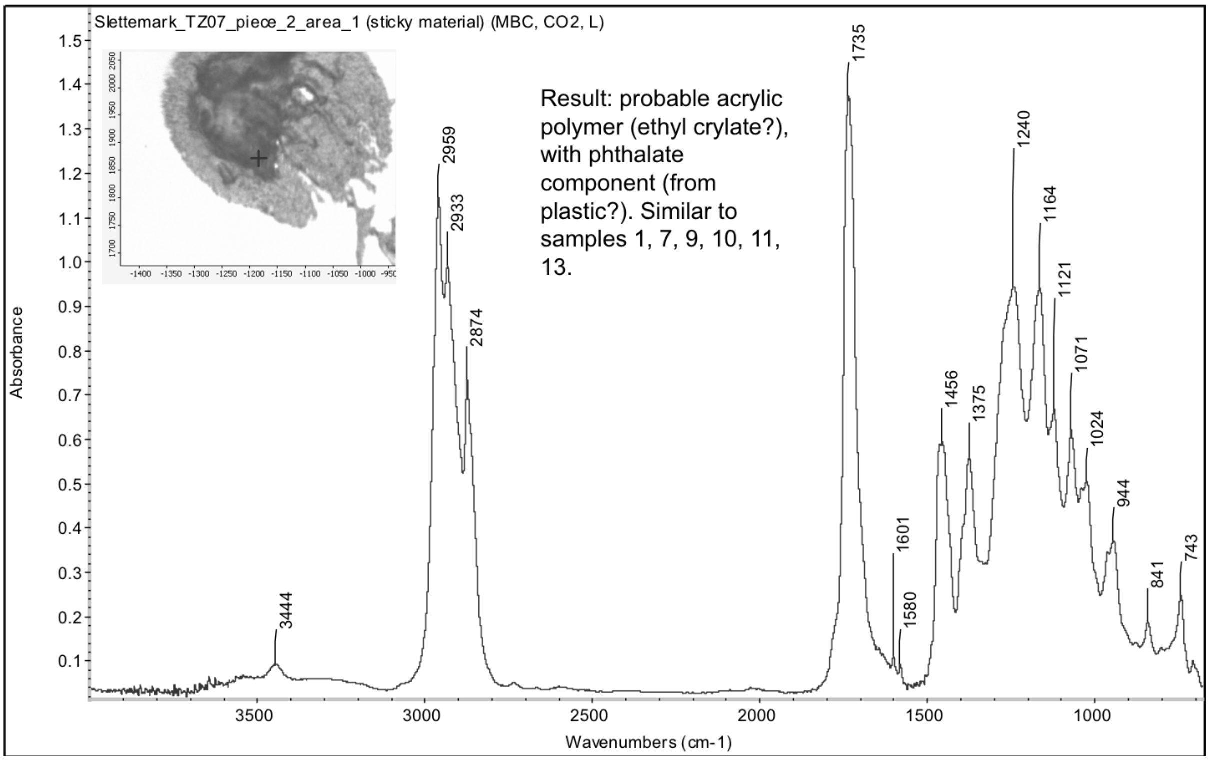
Slettemark_TZ07_piece_1_area_3 (plastic section): spectrum



Slettemark_TZ07_piece_1_area_3 (plastic section): interpretation

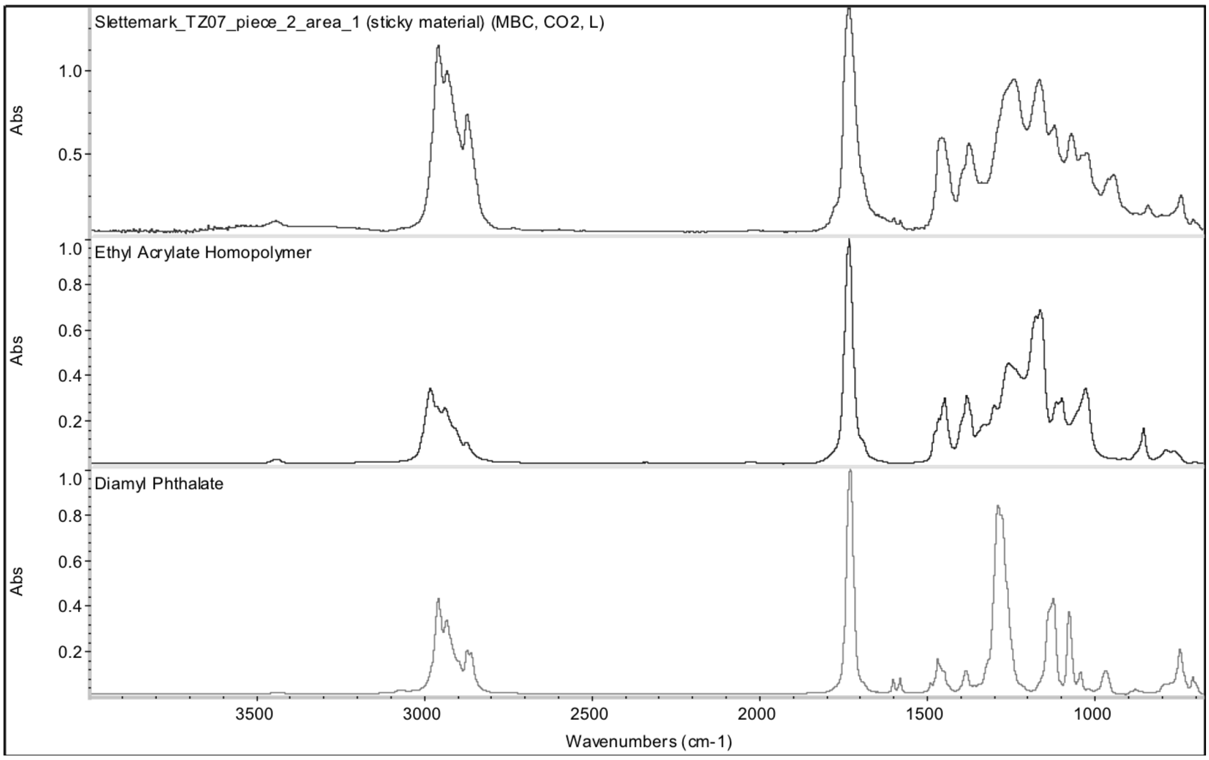


Slettemark_TZ07_piece_2_area_2 (sticky material): spectrum



Result: probable acrylic polymer (ethyl crylate?), with phthalate component (from plastic?). Similar to samples 1, 7, 9, 10, 11, 13.

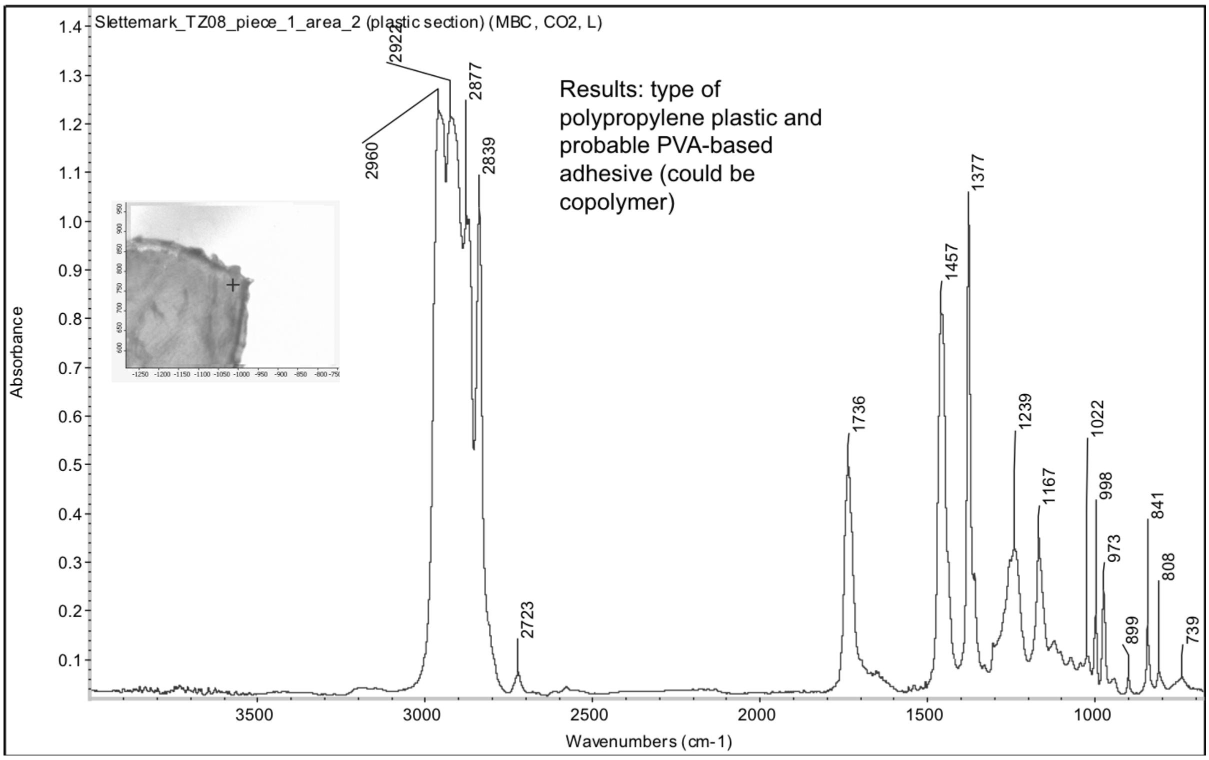
Slettemark_TZ07_piece_2_area_2 (sticky material): interpretation



TZ07: FTIR result summary

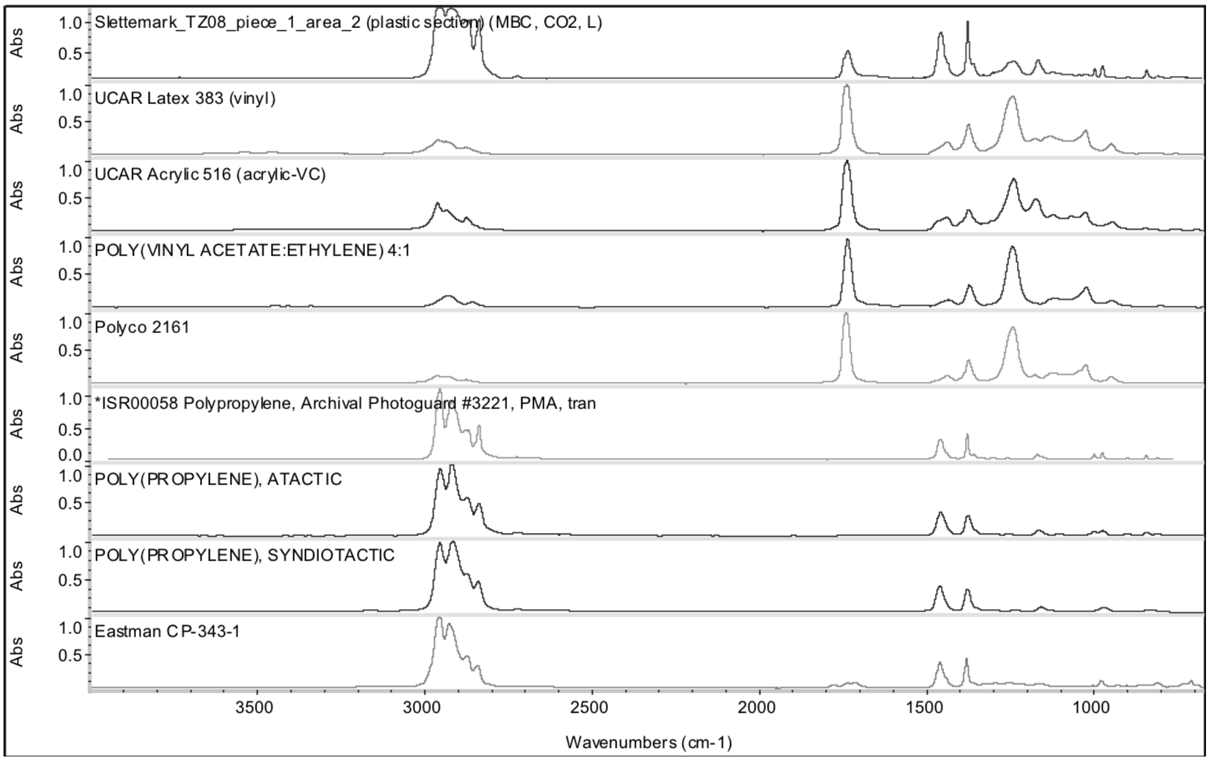
Piece and area No.	Description	Polymer ID	Other	Notes
1-3	Plastic section (transparent)	Result: probable PVC with phthalate component	-	
2-2	Soft material, adhesive	Probable acrylic (ethyl acrylate?) polymer, with phthalate component (from plastic?)	-	Plasticiser likely to be from plastic. This was a thick area of the adhesive. Similar to samples 1, 7, 9, 10, 11, 13 (may be butyl acrylate).

Slettemark_TZ08_piece_1_area_2 (plastic section): spectrum



Results: type of polypropylene plastic and probable PVA-based adhesive (could be copolymer)

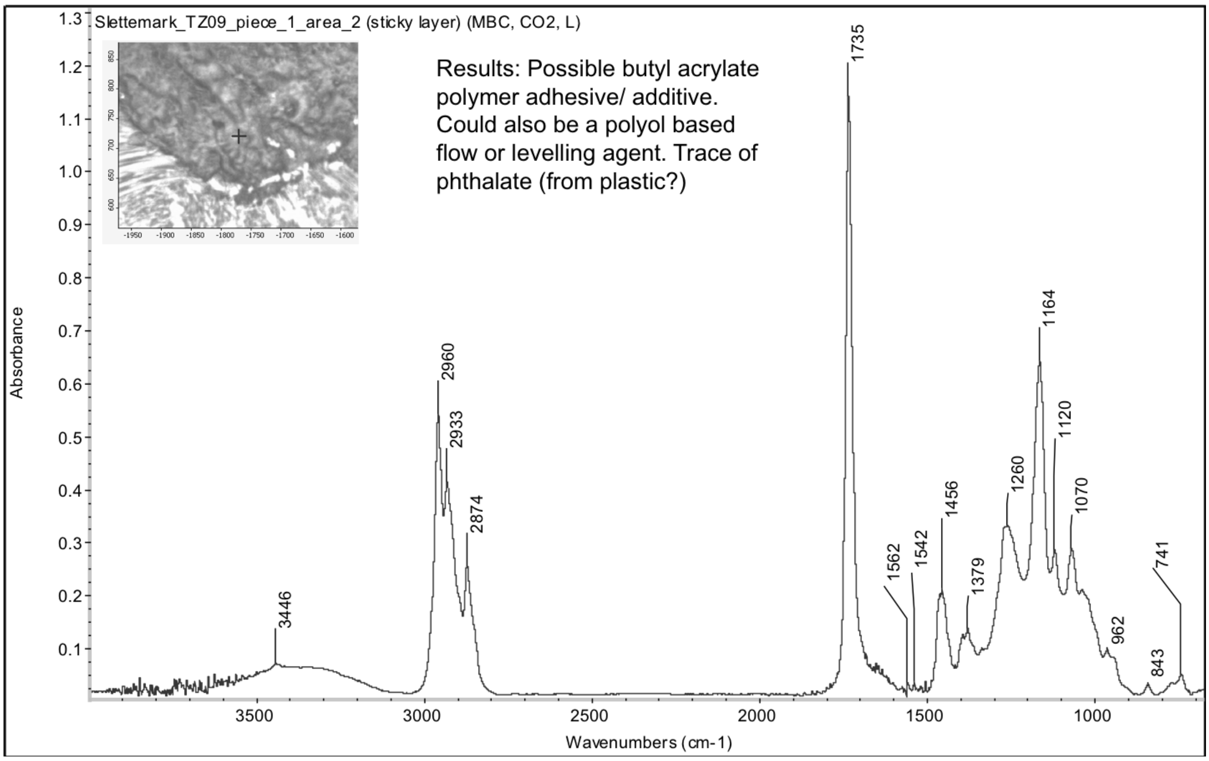
Slettemark_TZ08_piece_1_area_2 (plastic section): interpretation



TZ08: FTIR result summary

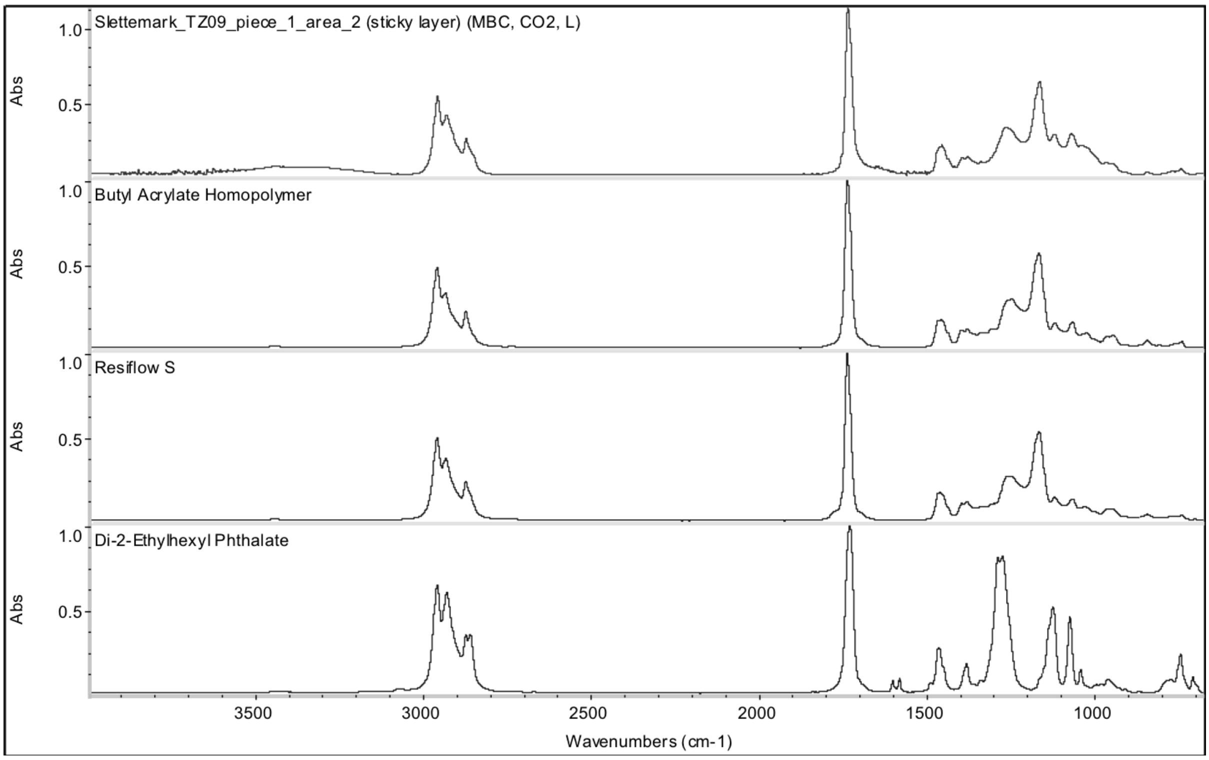
Piece and area No.	Description	Polymer ID	Other	Notes
1-2	Plastic section (transparent)	Type of polypropylene with possible PVA or PVA-copolymer adhesive	-	No noticeable sticky residue on this sample.

Slettemark_TZ09_piece_1_area_2 (sticky liquid section): spectrum

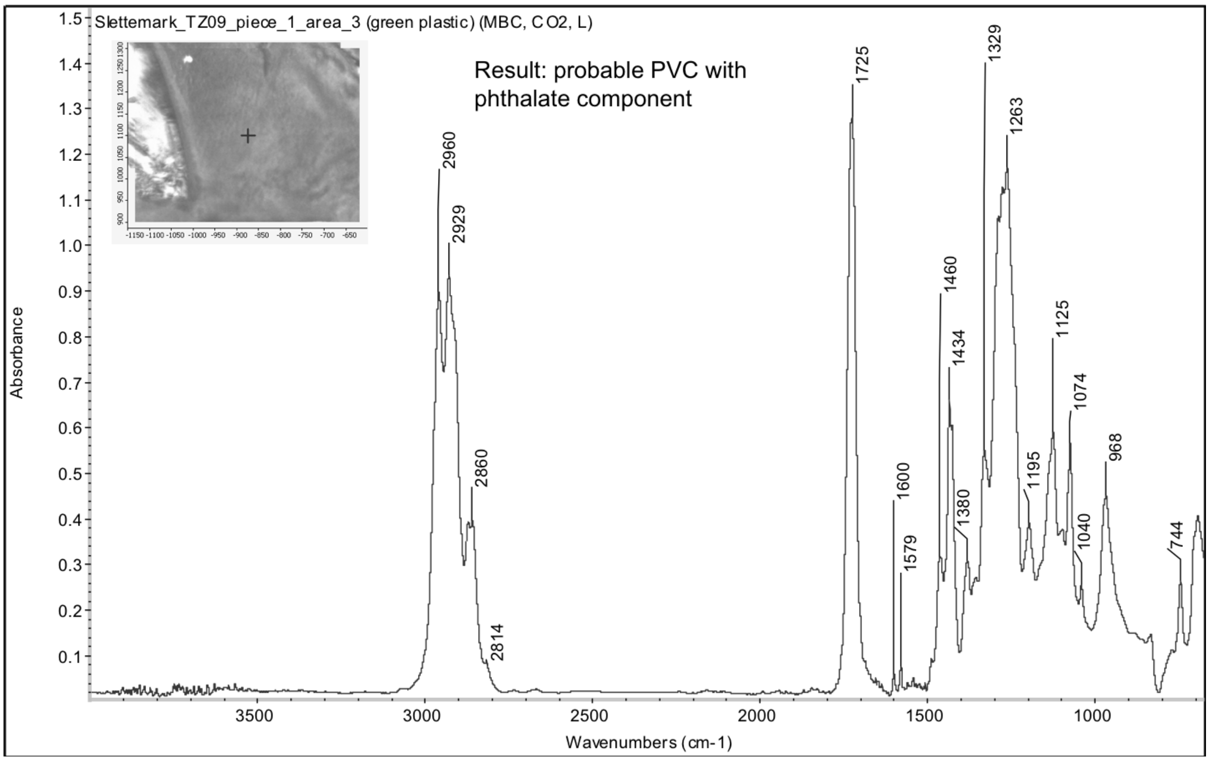


Results: Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)

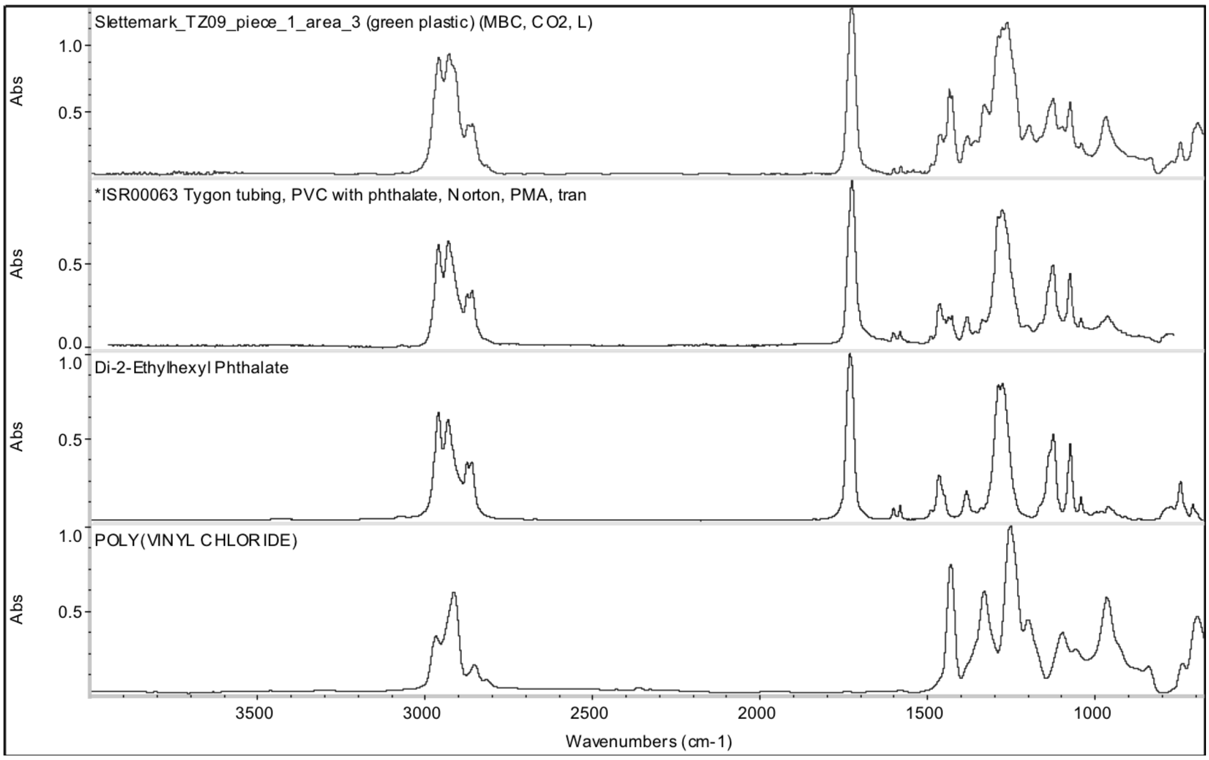
Slettemark_TZ09_piece_1_area_2 (sticky liquid section): interpretation



Slettemark_TZ09_piece_1_area_3 (green plastic): spectrum



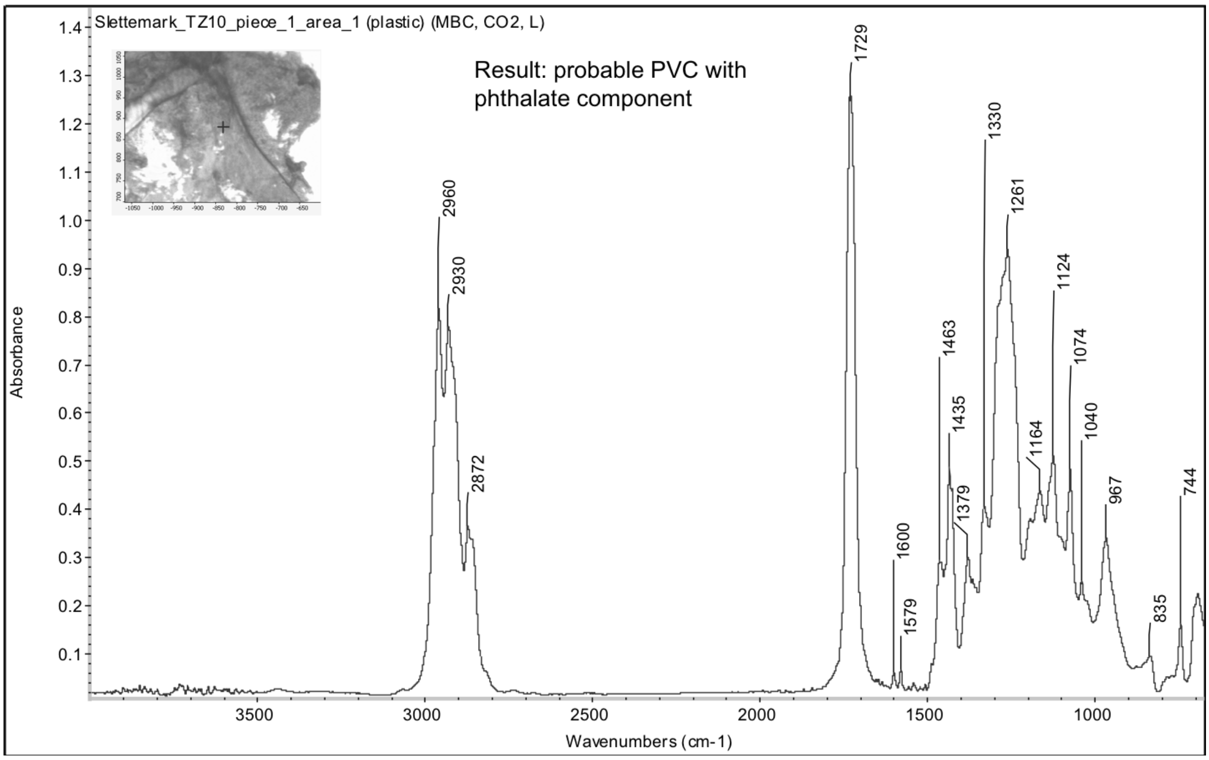
Slettemark_TZ09_piece_1_area_3 (green plastic): interpretation



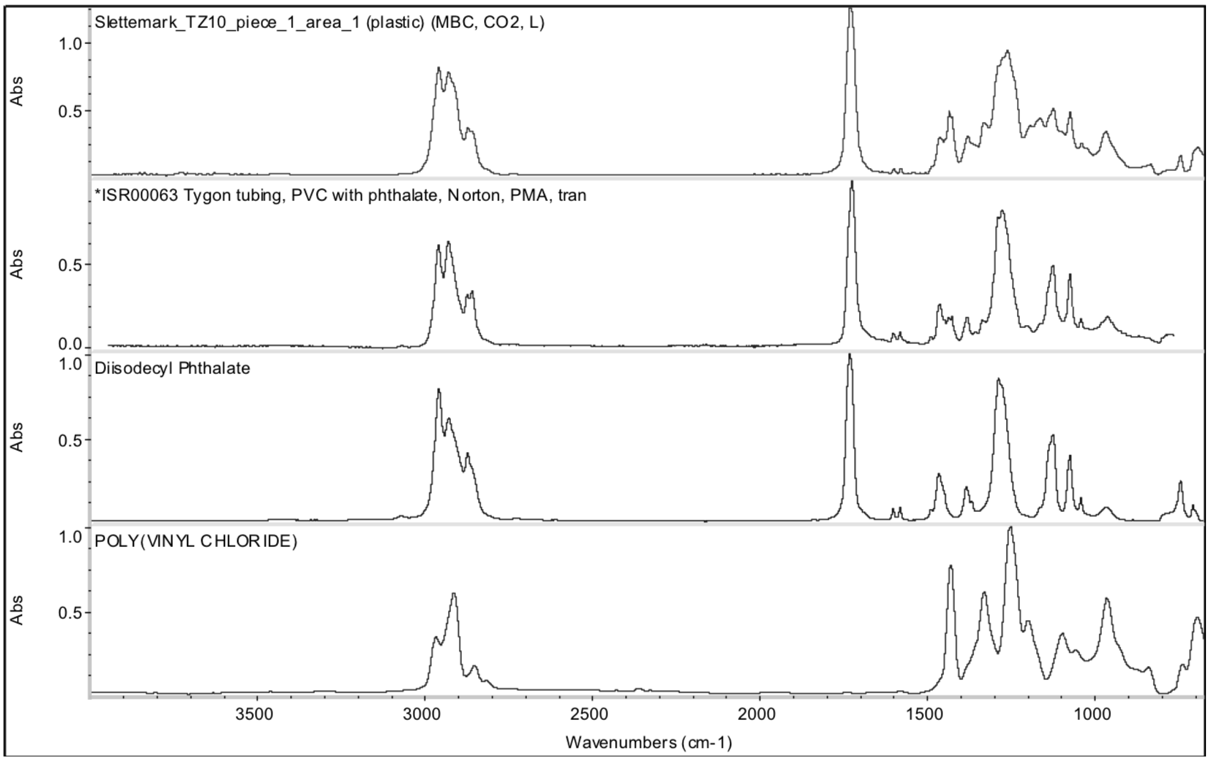
TZ09: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
9-2	Soft material, adhesive/ additive	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)	-	Very sticky layer on the green plastic.
9-3	Plastic section (green)	Probable PVC with phthalate component	-	

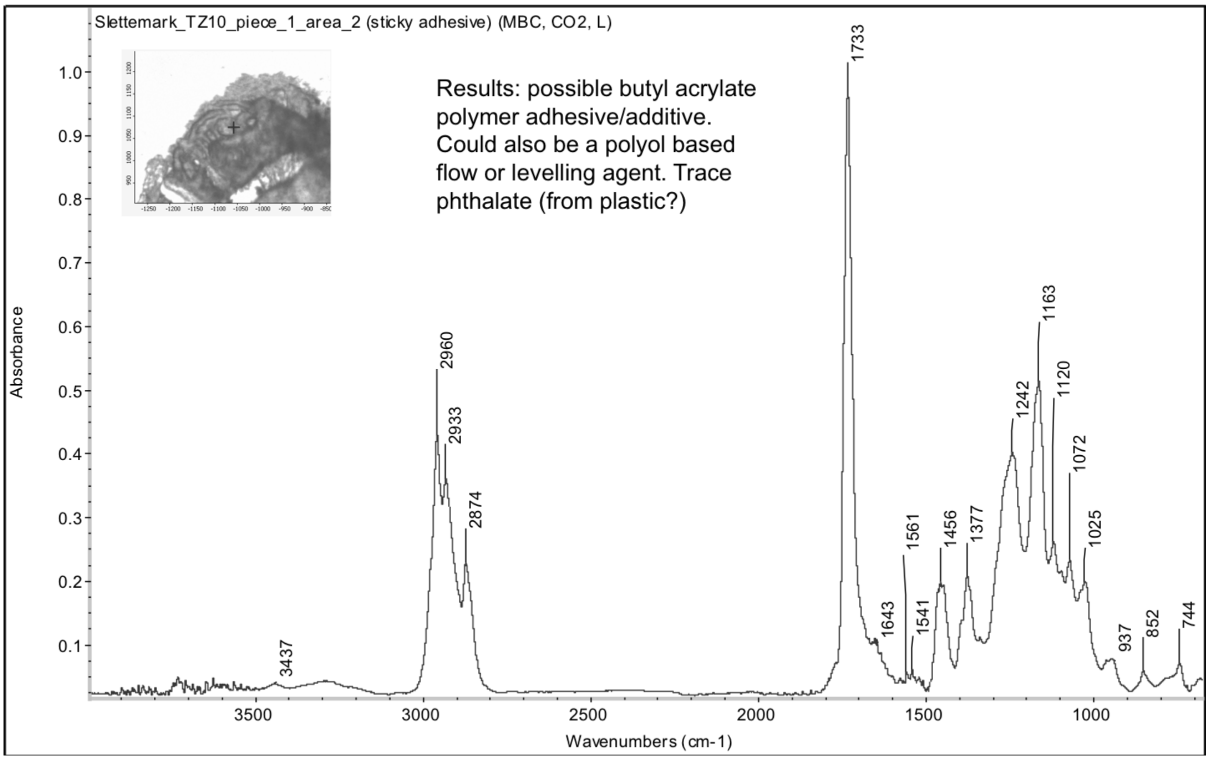
Slettemark_TZ10_piece_1_area_1 (plastic): spectrum



Slettemark_TZ10_piece_1_area_1 (plastic): interpretation

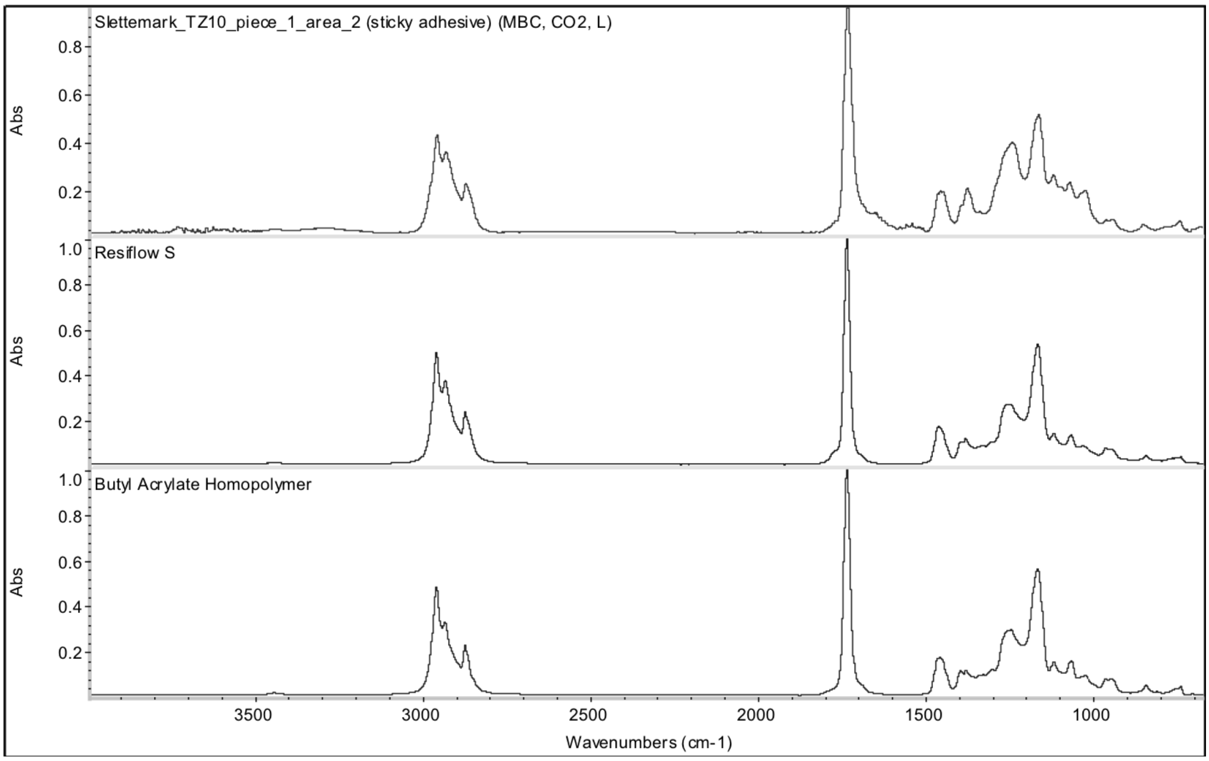


Slettemark_TZ10_piece_1_area_2 (sticky adhesive): spectrum



Results: possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace phthalate (from plastic?)

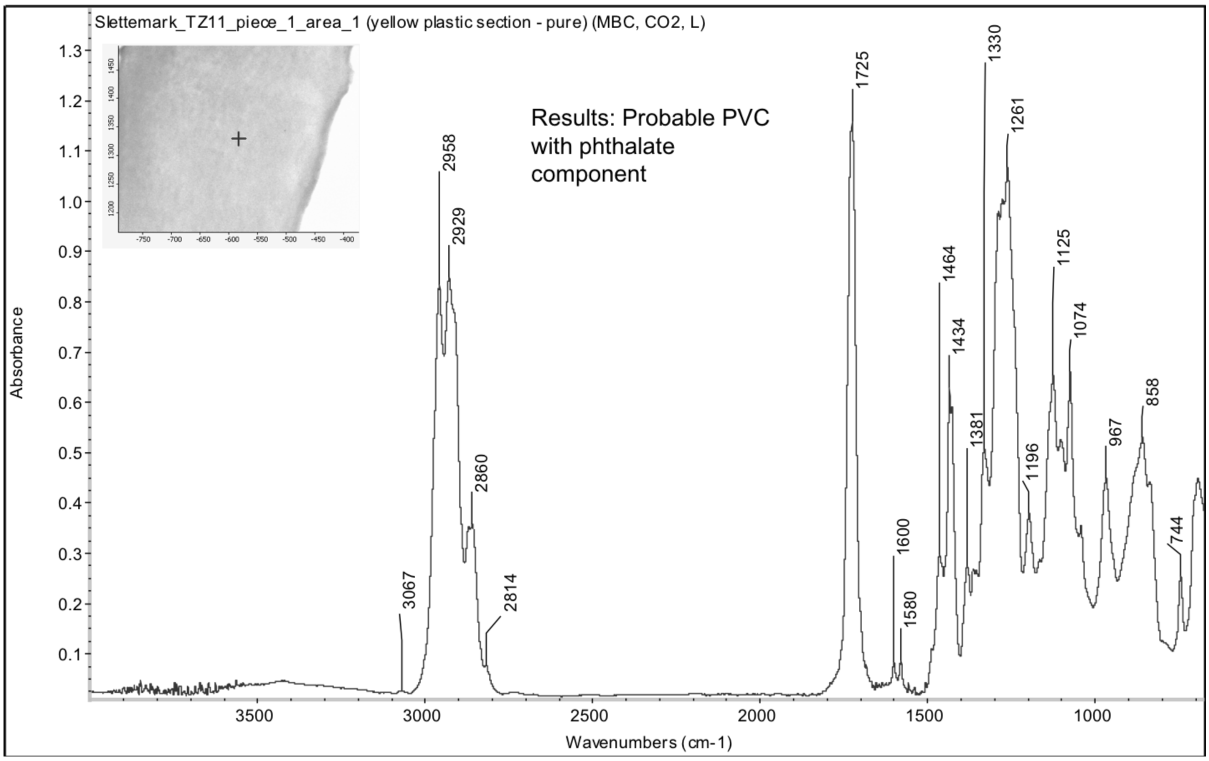
Slettemark_TZ10_piece_1_area_2 (sticky adhesive): interpretation



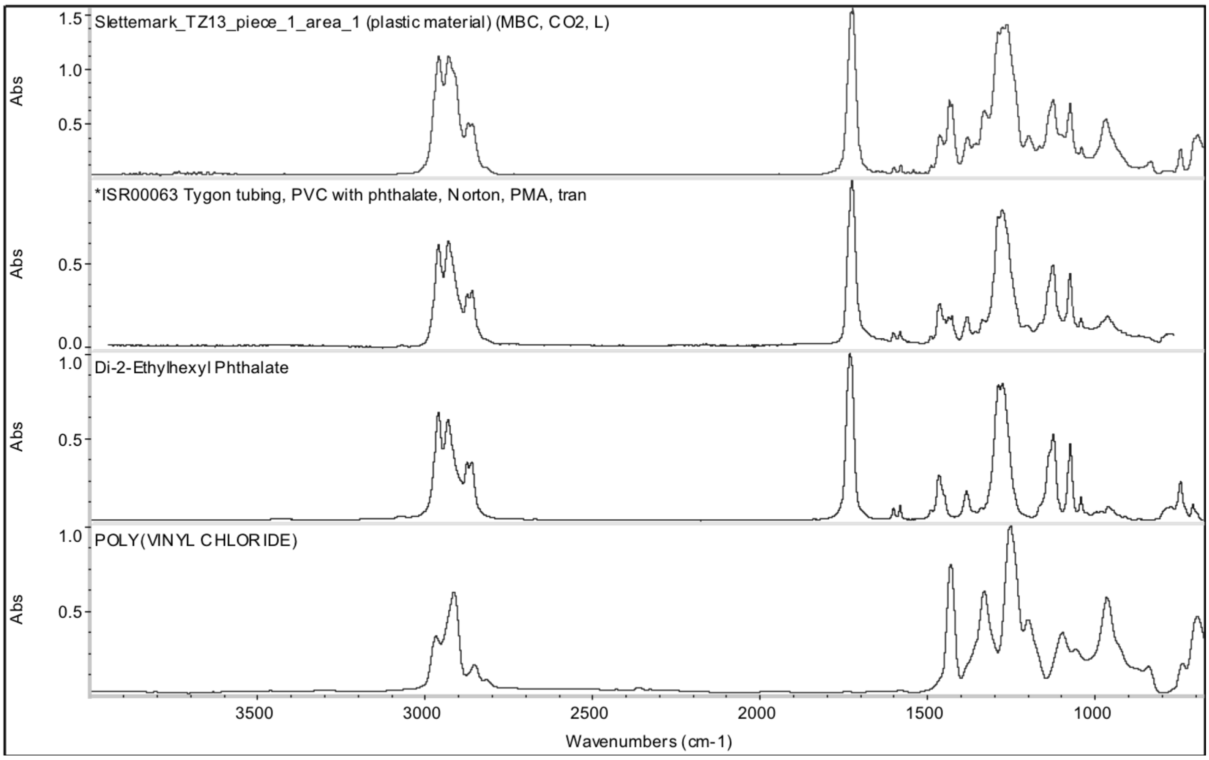
TZ10: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
10-1	Plastic section (transparent)	Probable PVC with phthalate component	-	
10-2	Soft material, adhesive/ additive	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace phthalate (from plastic?)	-	

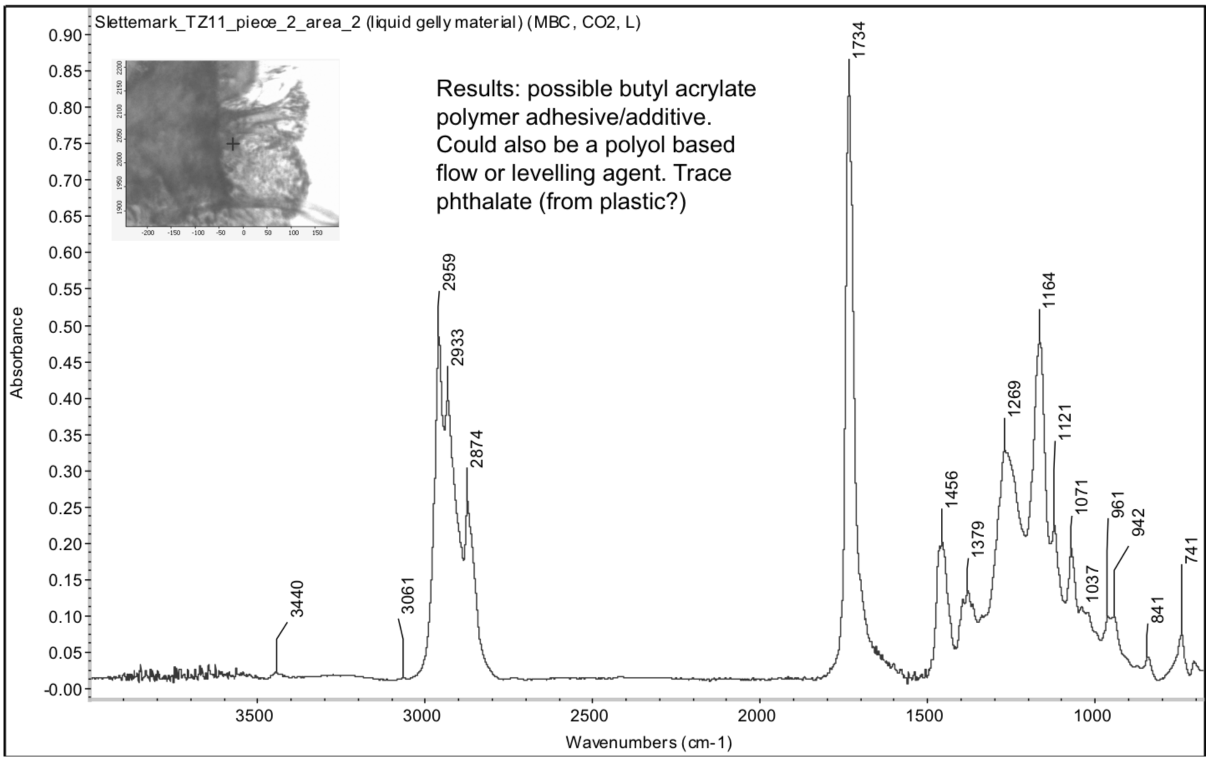
Slettemark_TZ11_piece_1_area_2 (yellow plastic section - pure): spectrum



Slettemark_TZ13_piece_1_area_1 (plastic material): interpretation

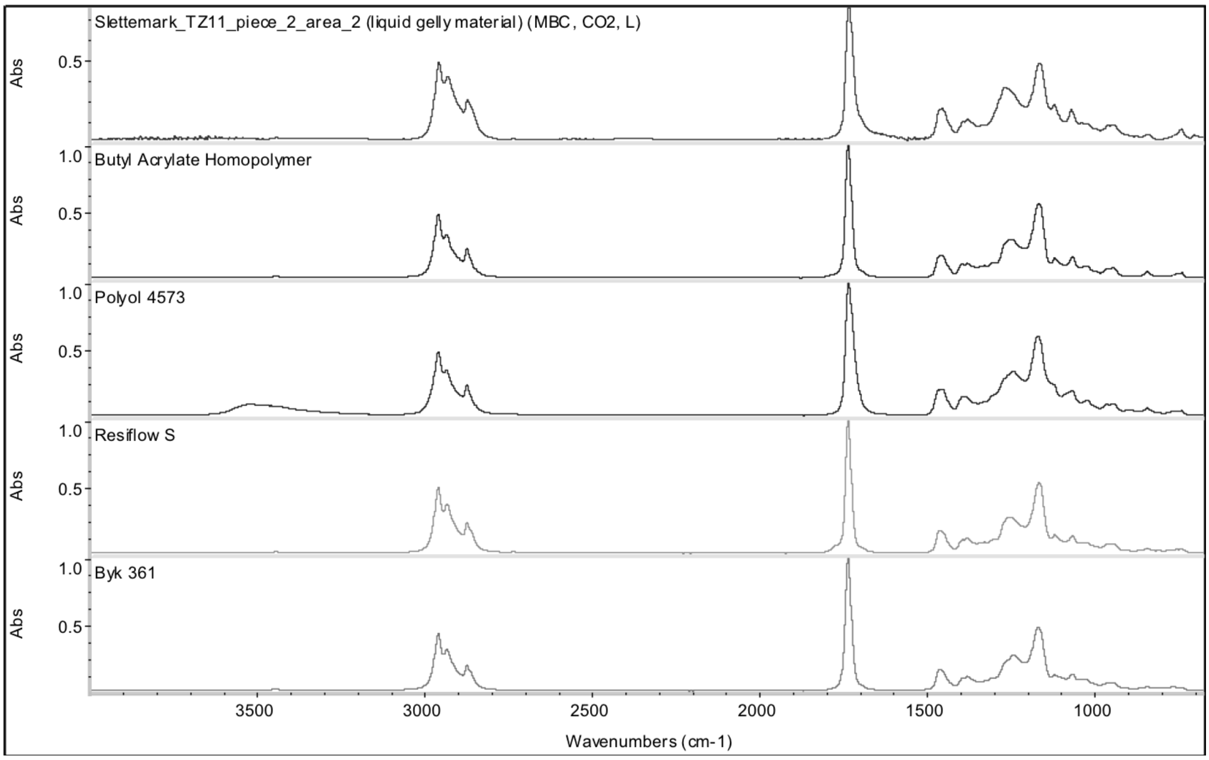


Slettemark_TZ11_piece_2_area_2 (liquid gel material): spectrum



Results: possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace phthalate (from plastic?)

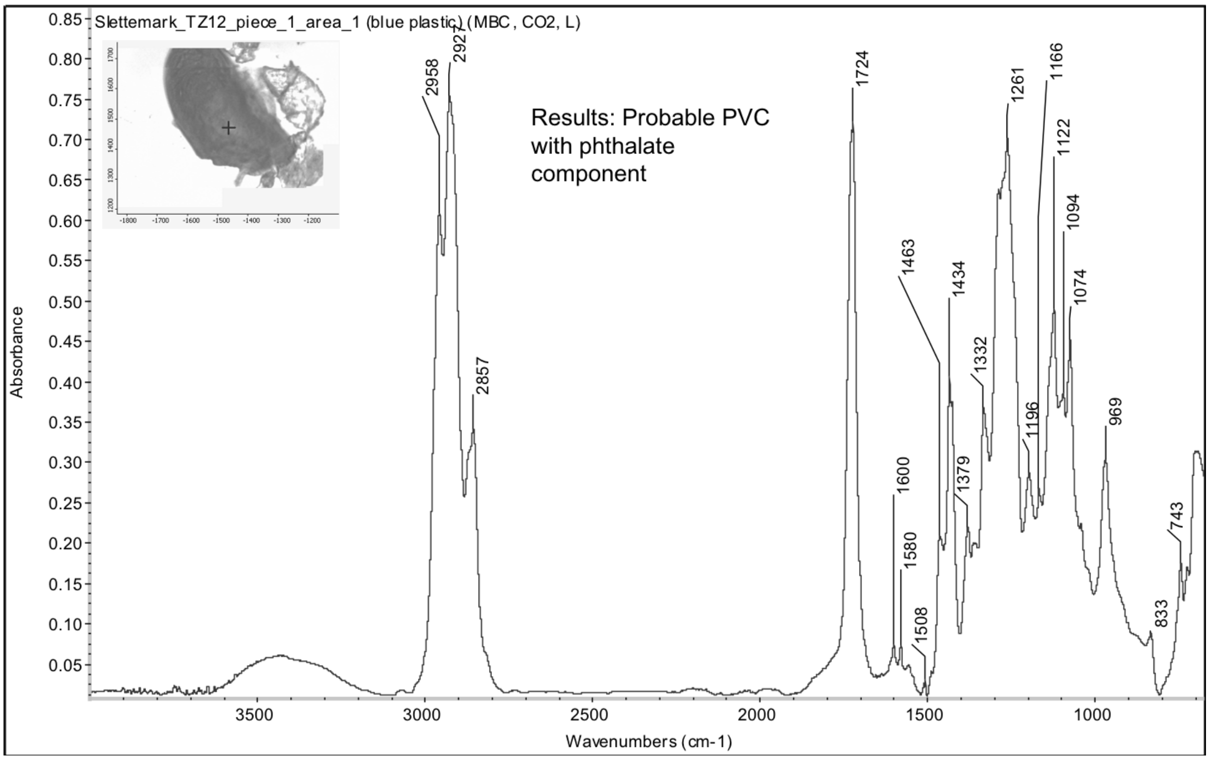
Slettemark_TZ11_piece_2_area_2 (liquid gel material): interpretation



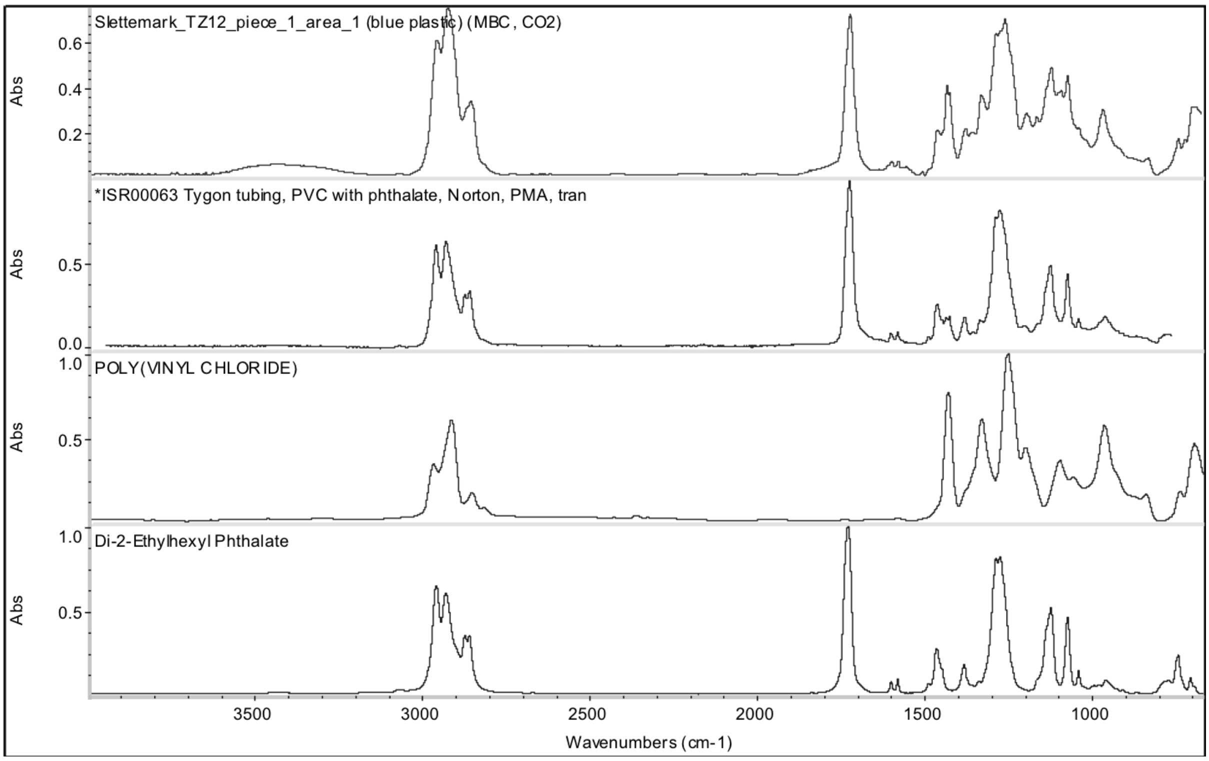
TZ11: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
11-1-2	Plastic section (yellow)	Probable PVC with phthalate component	-	
11-2-2	Soft material, adhesive/ additive	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace phthalate (from plastic?)	-	

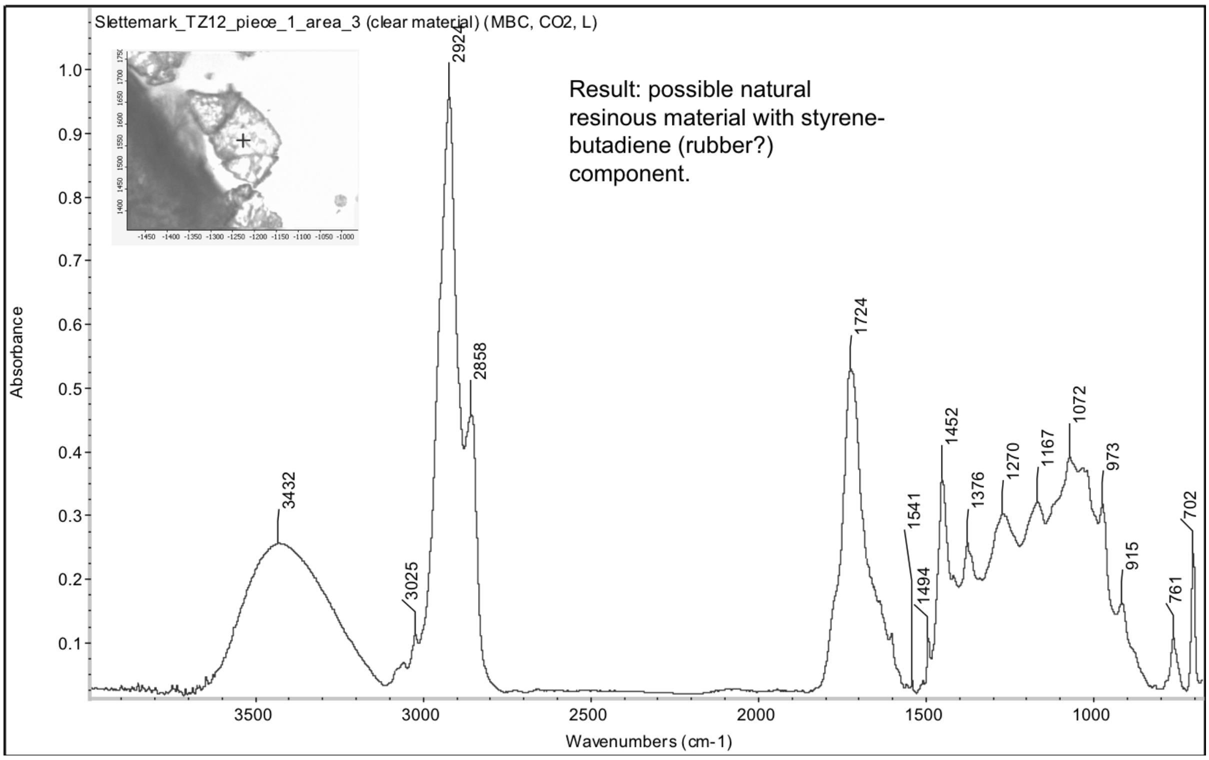
Slettemark_TZ12_piece_1_area_1 (blue plastic): spectrum



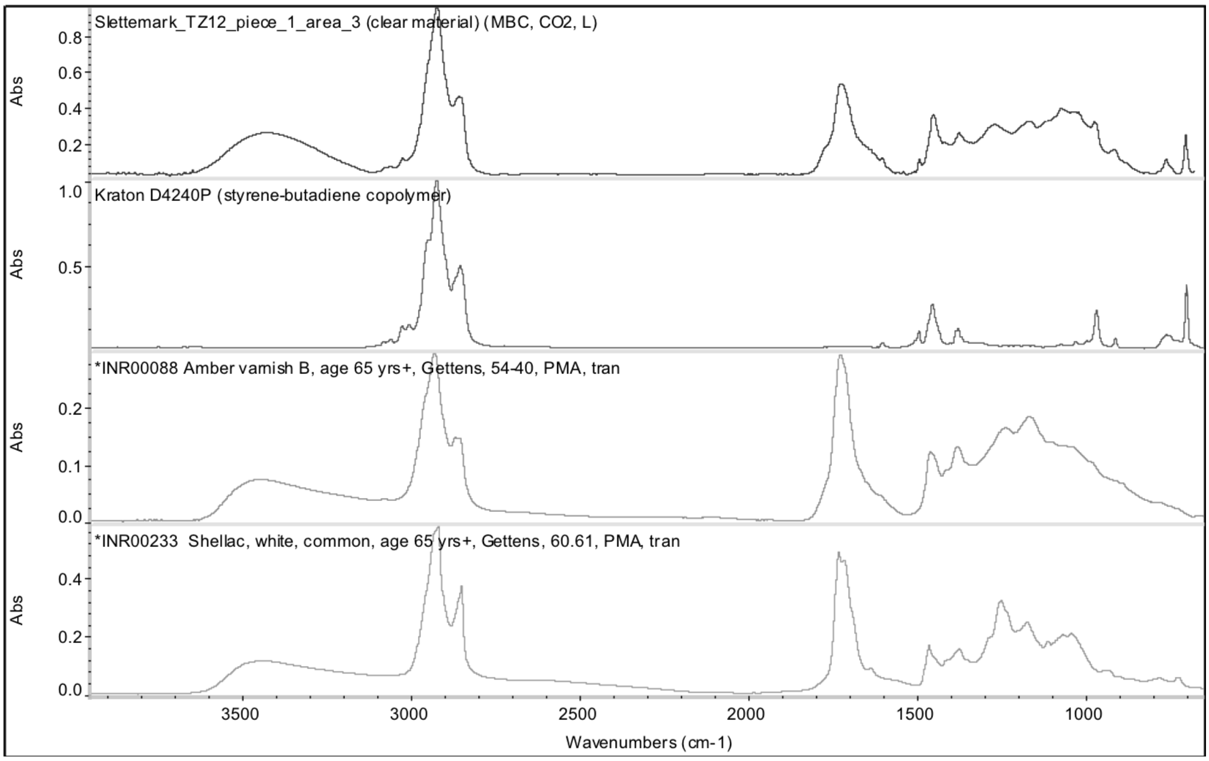
Slettemark_TZ12_piece_1_area_1 (blue plastic): intrepretation



Slettemark_TZ12_piece_1_area_3 (clear material): spectrum



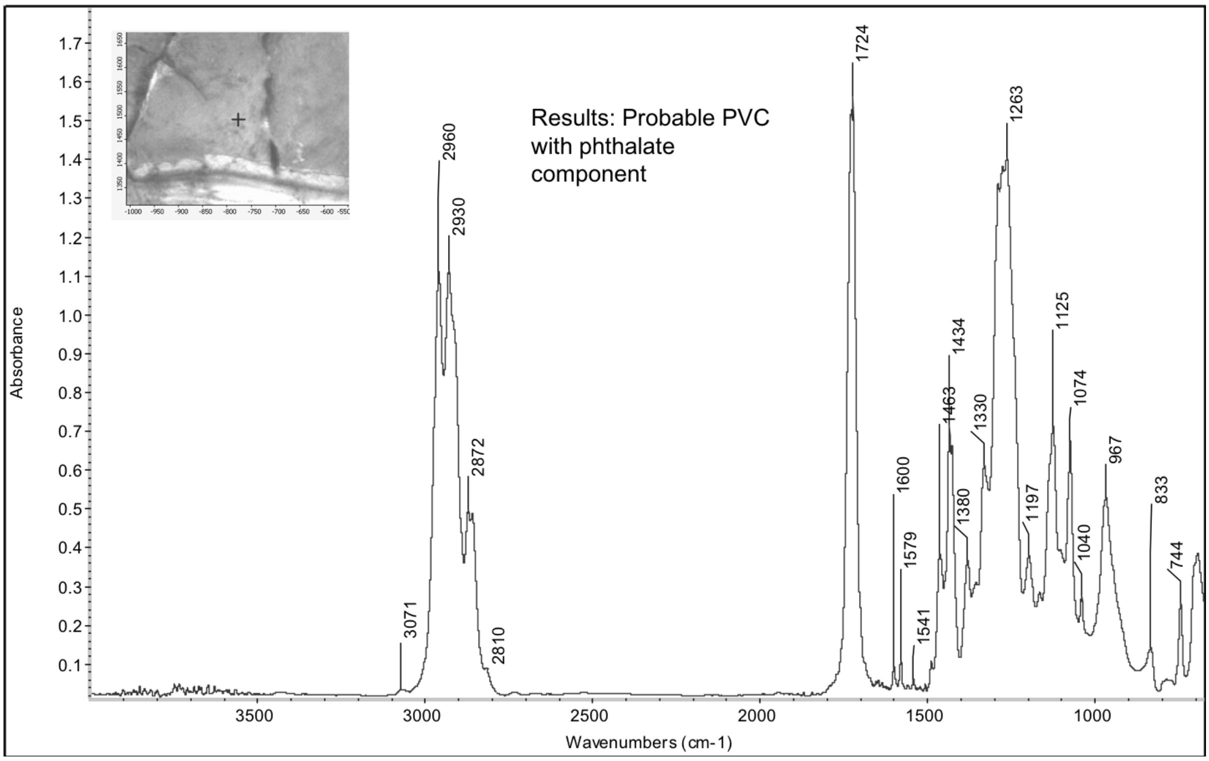
Slettemark_TZ12_piece_1_area_3 (clear material): interpretation



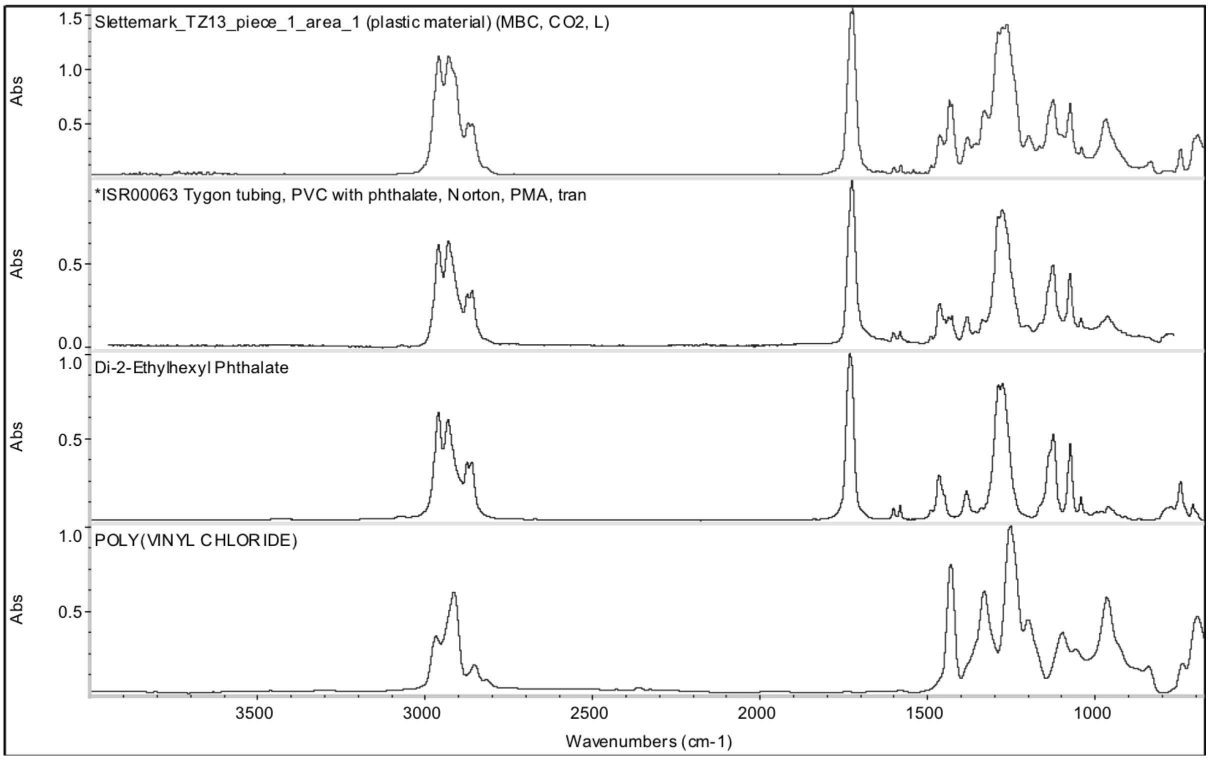
TZ12: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
1-1	Blue plastic	Probable PVC with phthalate component	-	
1-3	Clear adhesive/coating material	Possible natural resinous material with styrene-butadiene (rubber?) component.	-	Would it be unusual to have a hot-melt/heal seal adhesive here?

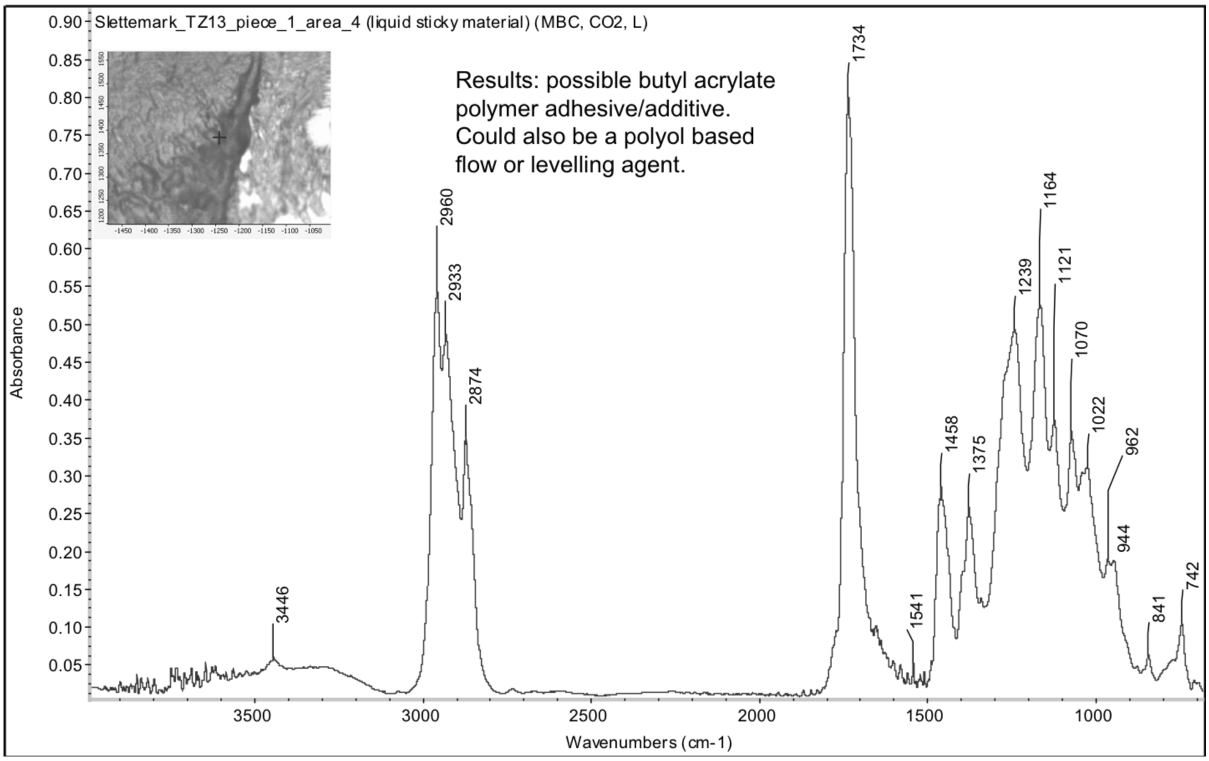
Slettemark_TZ13_piece_1_area_1 (plastic material): spectrum



Slettemark_TZ13_piece_1_area_1 (plastic material): interpretation

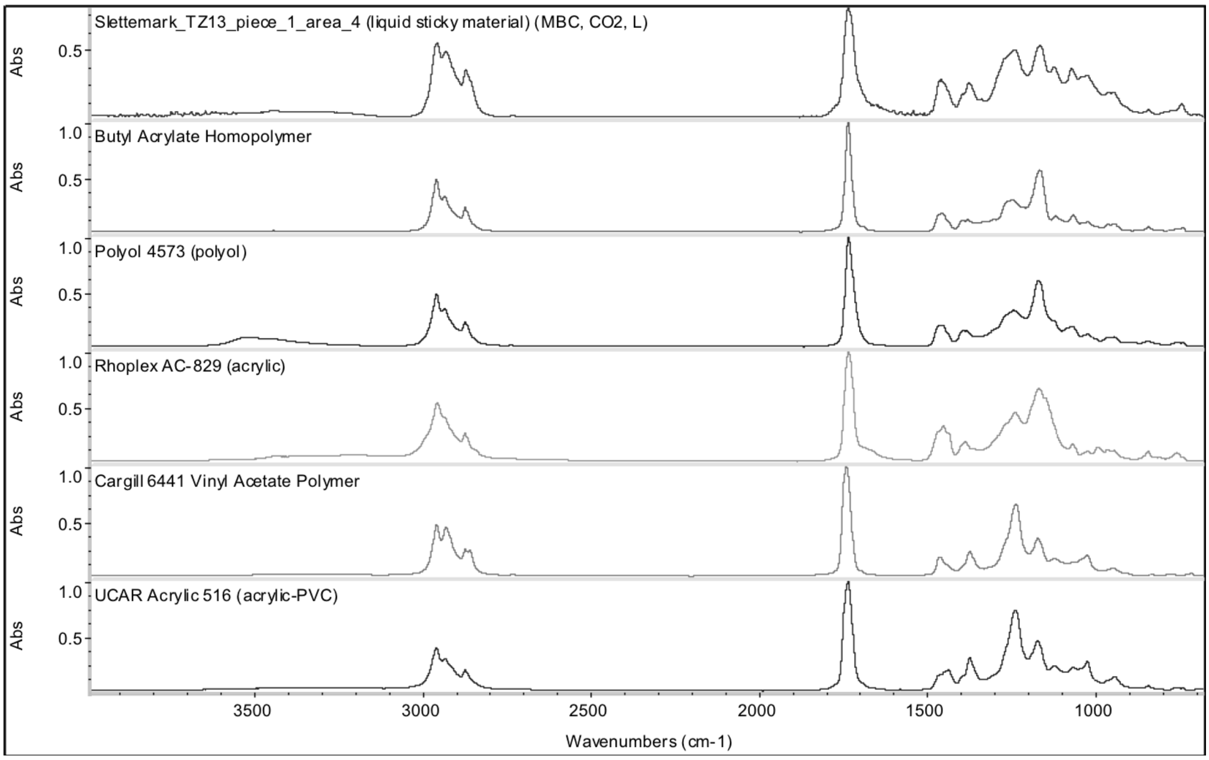


Slettemark_TZ13_piece_1_area_4 (liquid sticky material): spectrum



Results: possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.

Slettemark_TZ13_piece_1_area_4 (liquid sticky material): interpretation



TZ13: FTIR result summary

Piece and area No.	Description	Polymer ID	Other	Notes
13-1-1	Plastic material (transparent)	Probable PVC with a phthalate plasticiser	-	
13-1-4	Clear, sticky adhesive/coating material	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent.	-	

No	FTIR plastic	FTIR liquid/gel material	Notes
1	Result: degraded cellulose-based [acetate(?)] plastic	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.	Possible polyol, similar spectra for flow agents and levelling agents.
2	Probable PVC with phthalate	Probably PVA, with phthalate component (from plastic?)	
3	Probable PVC with phthalate	Probably PVA with phthalate component (from plastic?).	
4	Probable PVC with phthalate	Probably PVA with protein component	Where could protein (e.g. animal glue) be coming from?
		Probably PVA with phthalate component (from plastic?) and possible defoaming agent.	Check presence of possible defoaming agent in other samples
5	Probable PVC with possible acrylic.		No evidence of any softened/liquid/adhesive material on this sample.
6	Probable PVC with phthalate	Probably PVA with protein component and some phthalate (from plastic?)	Where could protein (e.g. animal glue) be coming from? Conservation?
		Probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.	
7	Probable PVC with phthalate	Probable acrylic polymer (ethyl acylate?) with phthalate (from plastic?)	Plasticiser likely to be from plastic. This was a thick area of adhesive. Similar to samples 1, 9, 10, 11, 13 (may be butyl acrylate).
8	Type of polypropylene plastic and probable PVA-or PVA-copolymer adhesive		No noticeable sticky residue on this sample.
9	Probable PVC with phthalate	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)	Green plastic, with very sticky layer of material.
10	Probable PVC with phthalate	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)	
11	Probable PVC with phthalate	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)	
12	Probable PVC with phthalate	Possible natural resinous material with styrene-butadiene (rubber?) component.	Hot melt adhesive possible?
13	Probable PVC with phthalate	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.	Simlar to samples 11, 10, 9, 1 and possibly 7.

Transmission µFTIR spectroscopy

Transmission FTIR spectroscopic analysis was carried out on a Thermoscientific Nicolet iN10 MX microscope using a single diamond cell. 64 scans were collected at a resolution of 4 cm^{-1} across a wavenumber range of 4000 to 600 cm^{-1}. Data was processed using Omnic 8 software.

If any of the information contained in this report is to be published/ presented, please contact Bronwyn Ormsby at Tate via:
email: bronwyn.ormsby@tate.org.uk or
telephone: +44 (0)20 7887 3980.

This file is not to be distributed without permission from Tate.

9.3 Appendix 3. FTIR summary of results

Sample: TZ01			Transparent. Matte. Front. Bottom rigth corner.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Result: degraded cellulose-based [acetate(?)] plastic	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.	Possible polyol, similar spectra for flow agents and levelling agents.	Probable celllulose nitrate (degraded) with phthalate component		Cellulose nitrate

Sample: TZ02			Transparent. Dirt. Back. Bottom right corner.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Probably PVA, with phthalate component (from plastic?)		Probable PVC with phthalate component , trace of talc filler.	Probably PVA polymer or PVA-copolymer with phthalate component (from plastic).	

Sample: TZ03			Transparent. Not in contact with background. Front?		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Probably PVA with phthalate component (from plastic?).		Probable PVC with phthalate component	Probably PVA polymer or PVA-copolymer with phthalate component (from plastic).	

Sample: TZ04			Transparent. Creep? Front		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Probably PVA with protein component. Probably PVA with phthalate component (from plastic?) and possible defoaming agent.	Where could protein (e.g. animal glue) be coming from? Treatment?	Probable PVC with phthalate component.	Probably PVA polymer or PVA-copolymer with phthalate component (from plastic).	

Sample: TZ05			Black. Hard. No adhesive layer. Front. Right hand side. Upper half.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with possible acrylic component.		No evidence of any softened/liquid/adhesive material on this sample.	Probable PVC or PVC copolymer, phthalate component and kaolin (aluminium silicate).		Kaolin not noted in transmission sample. Could be used as insulating material.

Sample: TZ06			Transparent. Front. Upper left hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Probably PVA with protein component and some phthalate (from plastic?) Probably PVA with minor phthalate component (from plastic?) and possible defoaming agent.	Where could protein (e.g. animal glue) be coming from? Conservation?	Plastic probably PVC with phthalate component	Probably PVA polymer or PVA-copolymer with minor phthalate and PVC component (from plastic).	

Sample: TZ07			Transparent. Matte. Presumably stable. Front. Upper left hand side/ center.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Probable acrylic polymer (ethyl acylate?) with phthalate (from plastic?)	Plasticiser likely to be from plastic. This was a thick area of adhesive. Similar to samples 1, 9, 10, 11, 13 (may be butyl acrylate).	Probable PVC with phthalate component	An acrylic polymer, possibly modified, with some PVC and phthalate (from plastic)	

Sample: TZ08			Transparent. Clear. Front. Right hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Type of polypropylene plastic and probable PVA-or PVA-copolymer adhesive		No noticeable sticky residue on this sample.			

Sample: TZ09			Green. Front. Right hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Possible butyl acrylate polymer adhesive/ additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)	Green plastic, with very sticky layer of material.			

Sample: TZ10			Transparent. Thin. Slightly soft/ sticky. Front. Left hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)				

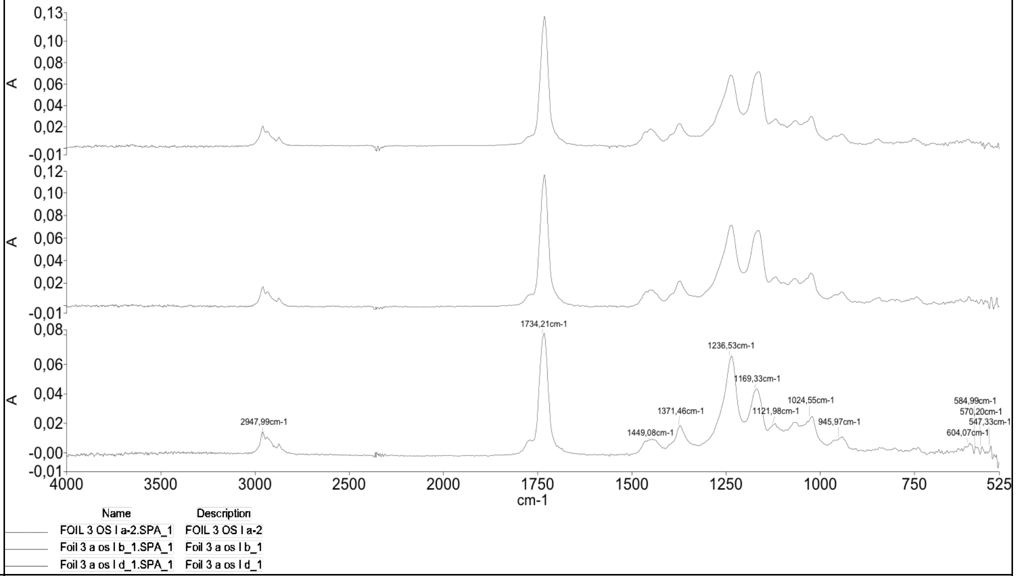
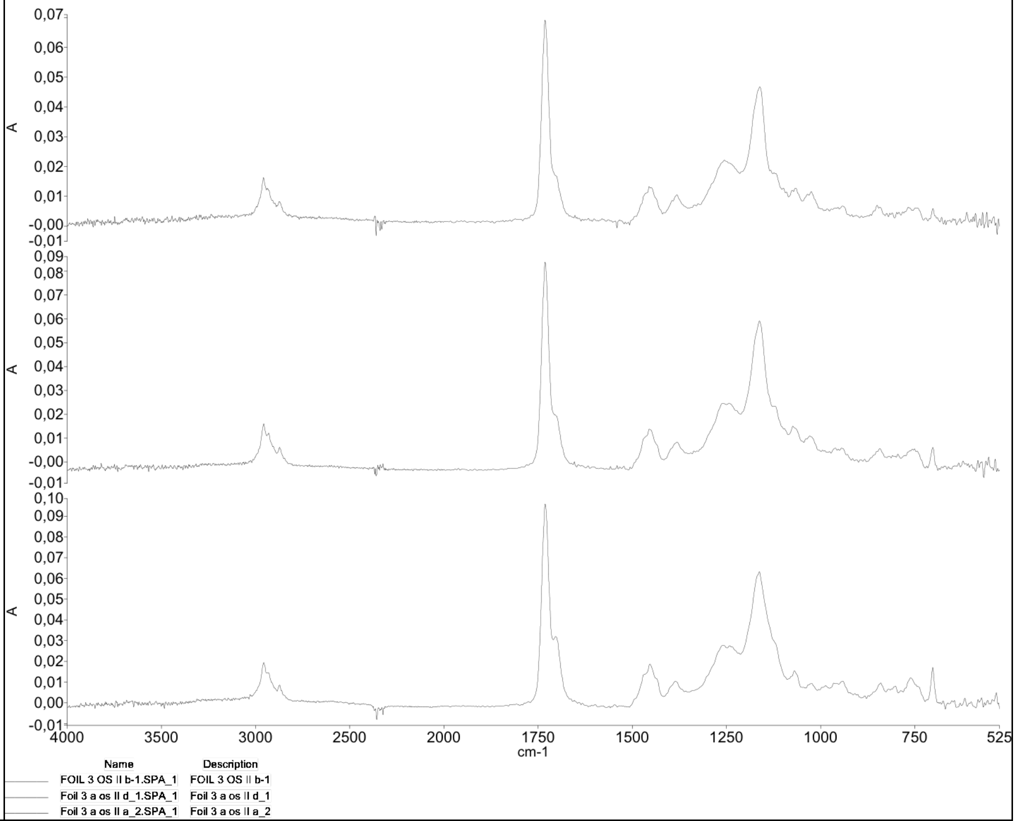
Sample: TZ11			Yellow. Back. Left hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent. Trace of phthalate (from plastic?)				

Sample: TZ12			Blue. Hardened? Fragile. Back. Left hand side.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Possible natural resinous material with styrene-butadiene (rubber?) component.	Hot melt adhesive possible?			

Sample: TZ13			Transparent. Matte. Thick. Front. Centre/ left.		
Transmission FTIR (Results from Tate/ Bronwyn Ormsby)			FTIR-ATR (Results from Oslo University/ Anja Sandtrø		
FTIR plastic	**FTIR liquid/gel material**	**Notes**	**FTIR plastic**	**FTIR liquid/gel material/adhesive**	**Notes**
Probable PVC with phthalate component	Possible butyl acrylate polymer adhesive/additive. Could also be a polyol based flow or levelling agent.	Simlar to samples 11, 10, 9, 1 and possibly 7.			

Sample	Description	Location	Note
BT01	Green	Back. Close to left hand side	Chlorine present
BT02	Transparent. Glossy.	Back. Left hand side. Bottom half.	Chlorine present
BT03	Transparent. Matte.	Front. Top centre.	Chlorine present

9.4 Appendix 4. FTIR results. Adhesive side of PVC carrier mock-ups

<table>
<tr><td>Acronal D500
Before ageing
Natural ageing in the dark
Light ageing</td><td>
</td></tr>
<tr><td>Primal WS24
Before ageing
Natural ageing in the dark
Light ageing</td><td>
</td></tr>
<tr><td></td><td></td></tr>
</table>

<table>
<tr>
<td>

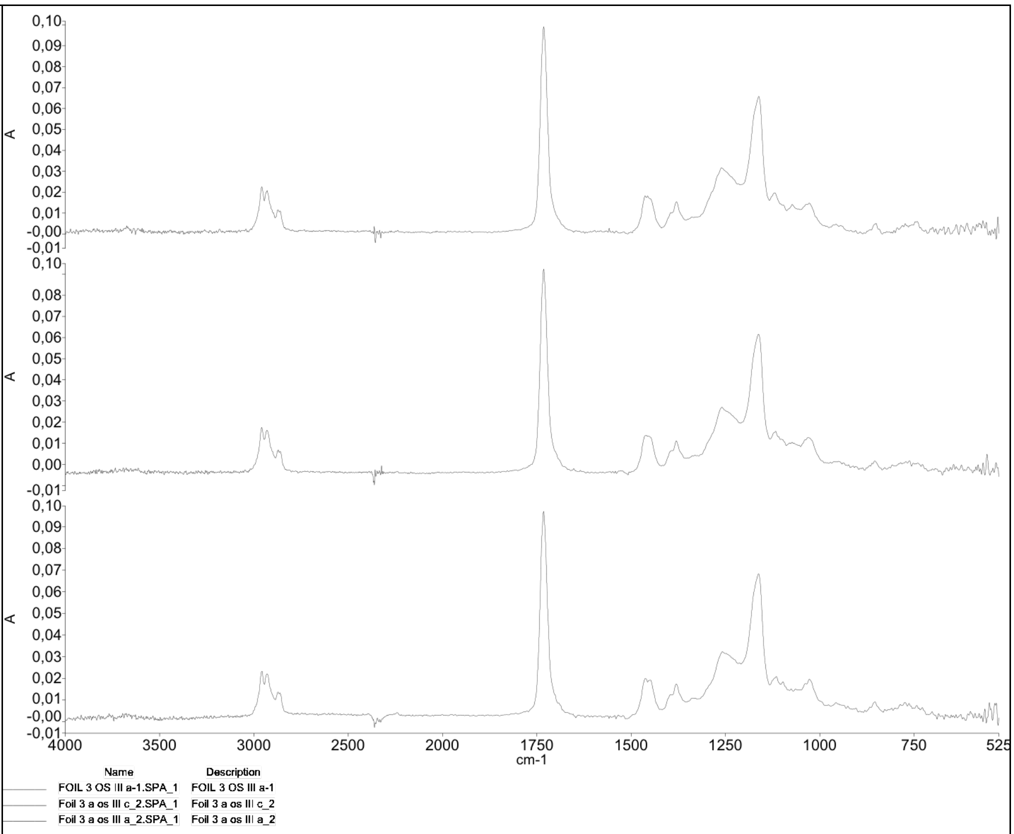
Dispersion K 360

Before ageing

Natural ageing in the dark

Light ageing

</td>
<td>



</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>

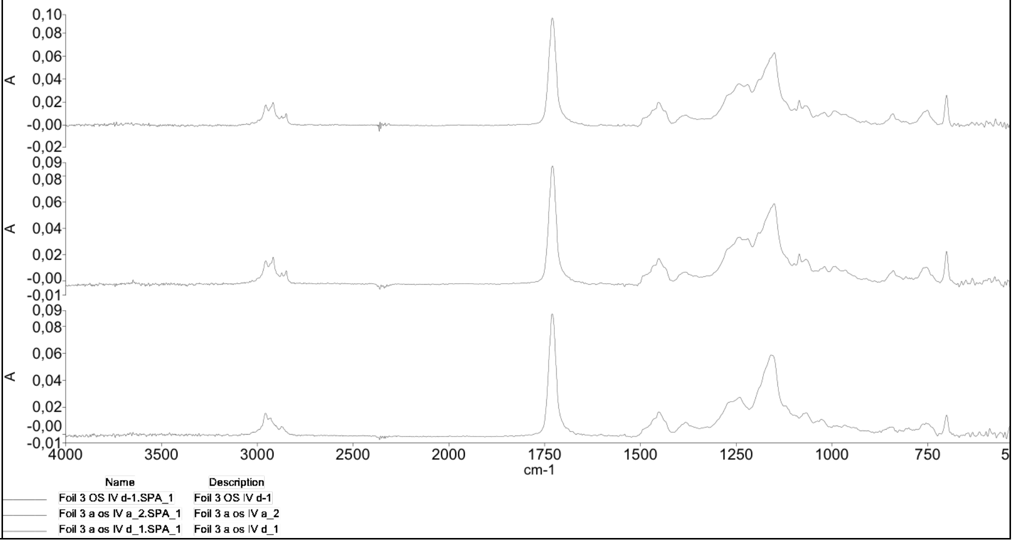
Medium for consolidation

Before ageing

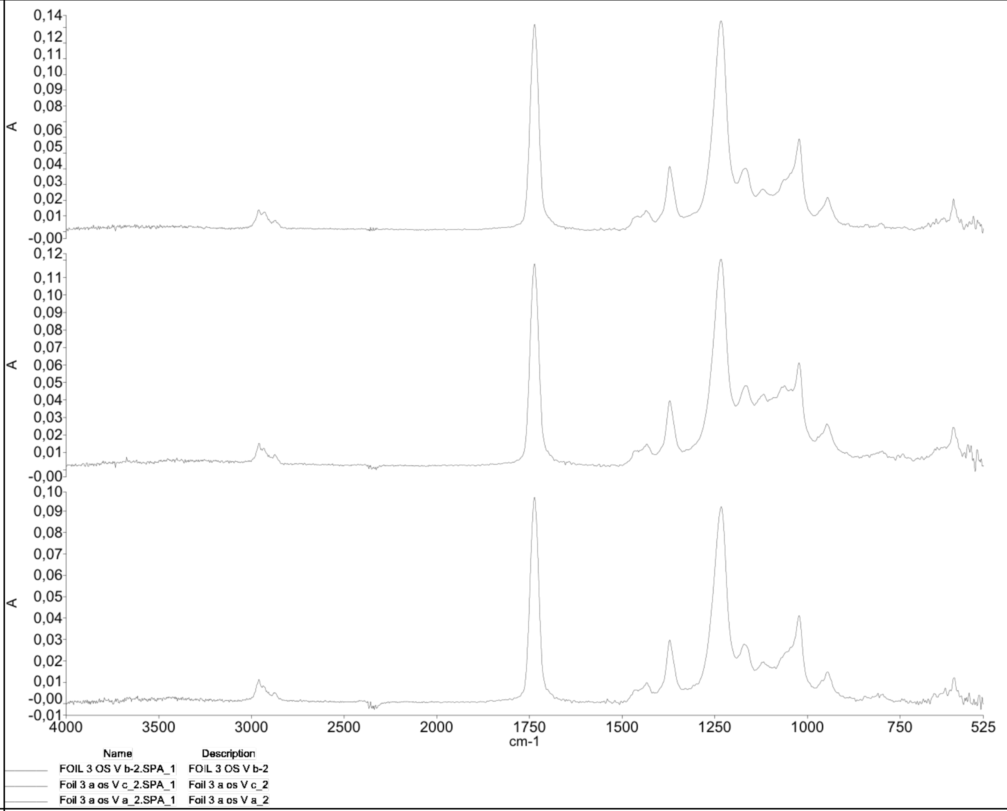
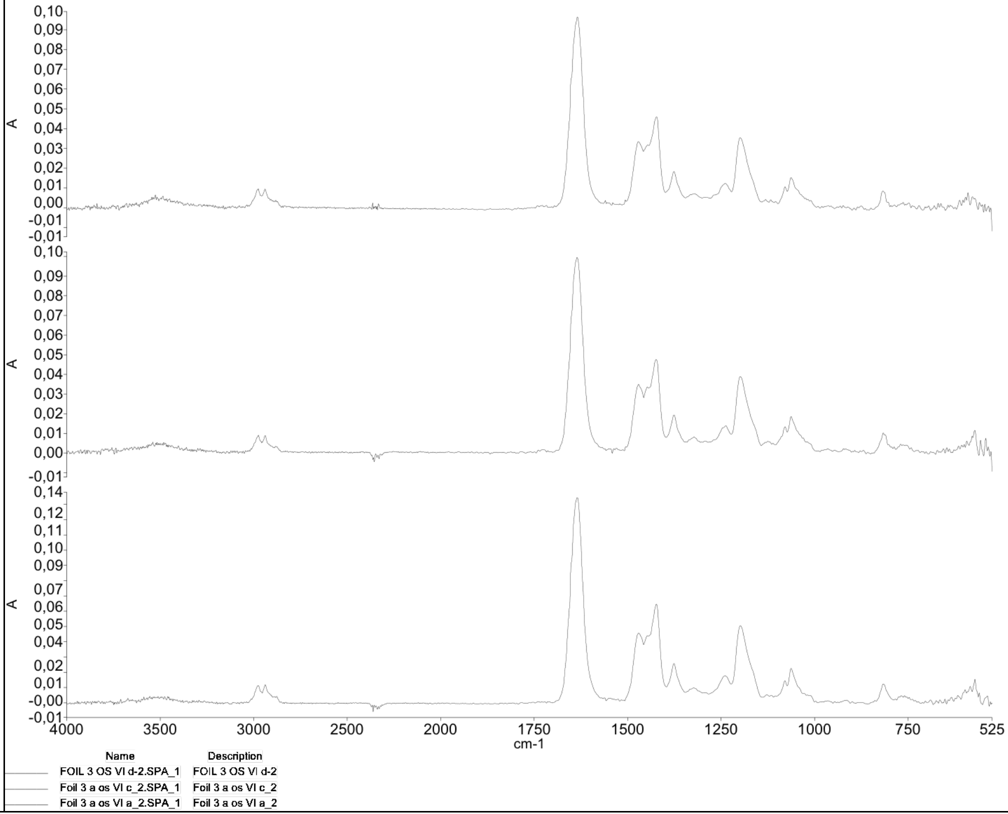
Natural ageing in the dark

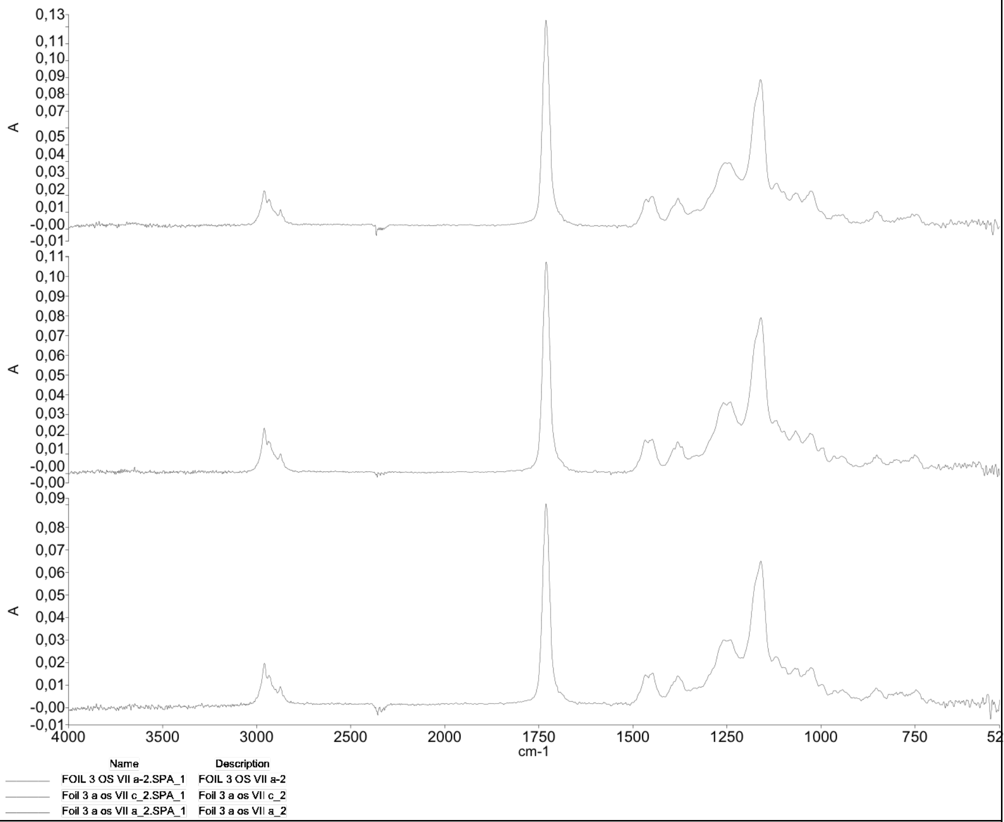
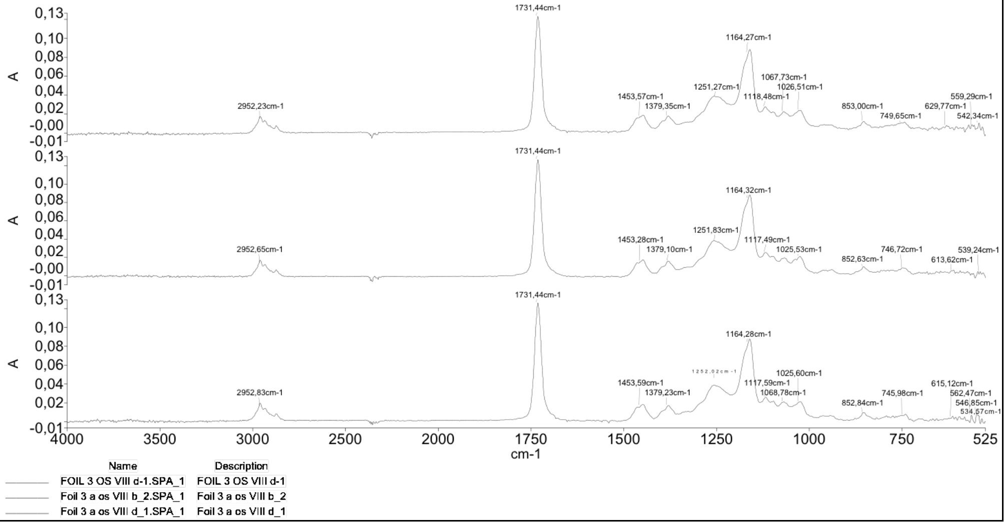
Light ageing

</td>
<td>

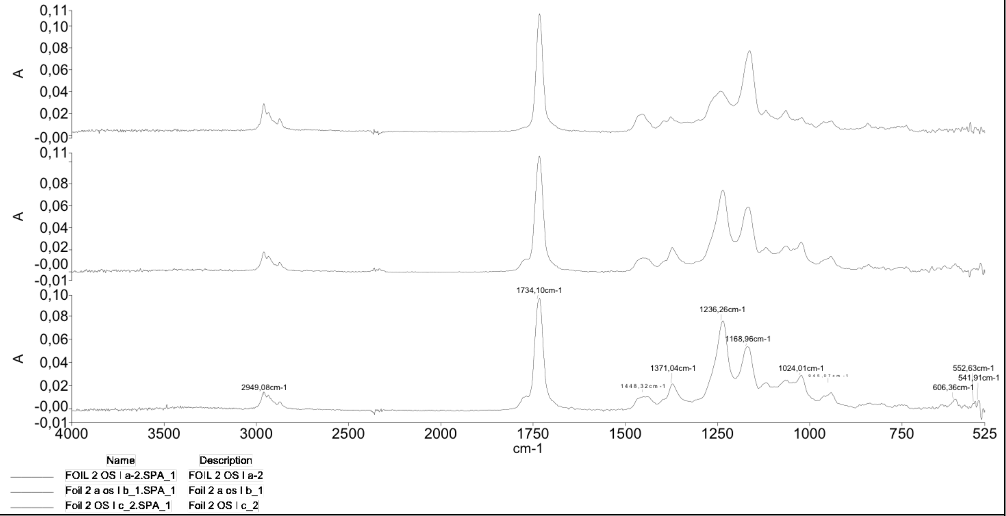
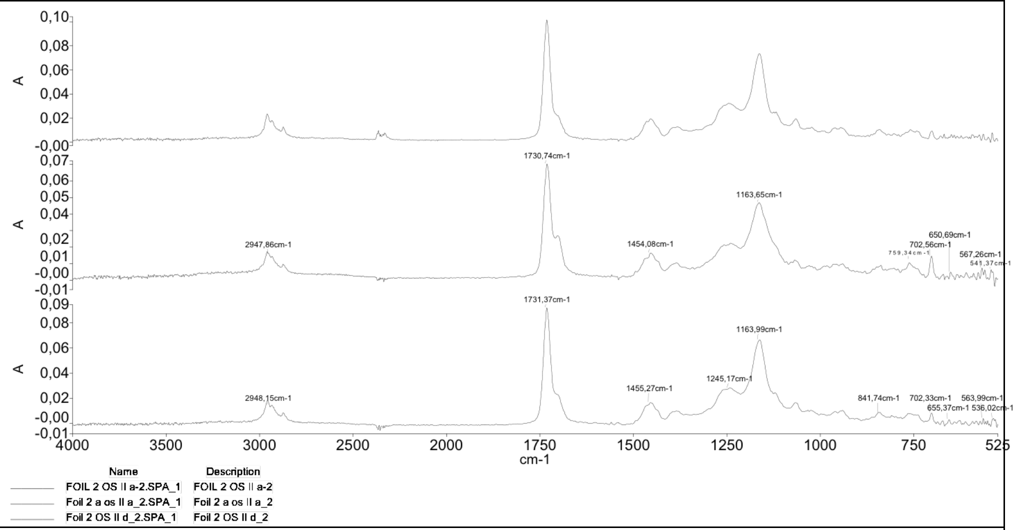
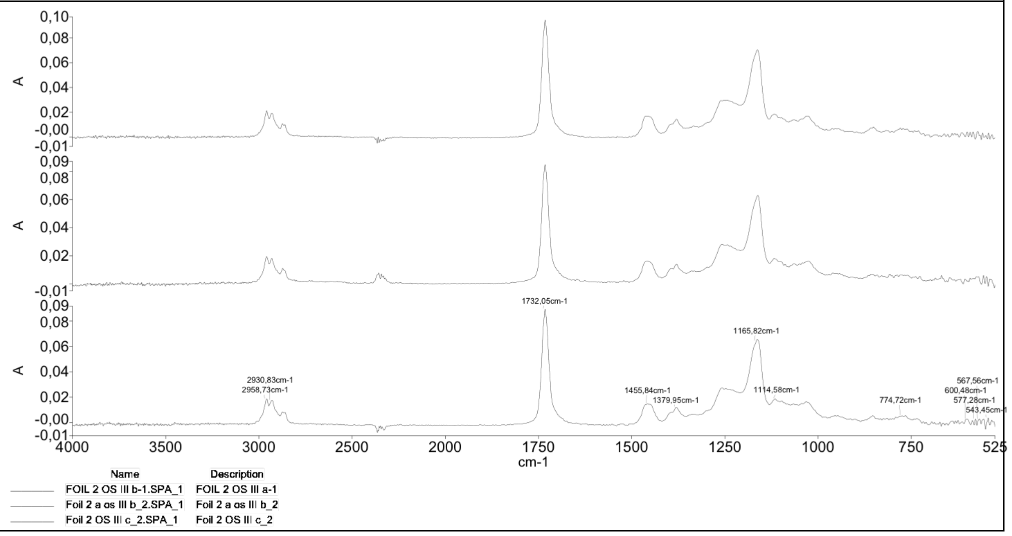


</td>
</tr>
</table>

Mowilith DMC2 Before ageing Natural ageing in the dark Light ageing	
Aquazol 200 Before ageing Natural ageing in the dark Light ageing	

1:1 Plexigum PQ611/ Paraloid B67 Before ageing Natural ageing in the dark Light ageing	
PSA Before ageing Natural ageing in the dark Light ageing	

9.5 Appendix 5. FTIR results. Adhesive side of PP carrier

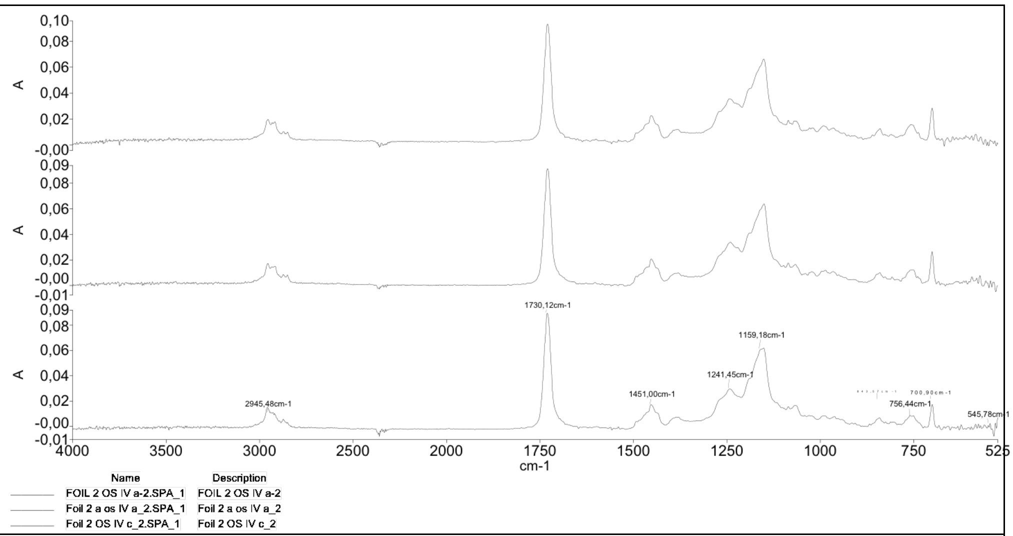
Acronal D500 Before ageing Natural ageing in the dark Light ageing	
Primal WS24 Before ageing Natural ageing in the dark Light ageing	
Dispersion K360 Before ageing Natural ageing in the dark Light ageing	

Lascaux Medium for Consolidation

Before ageing

Natural ageing in the dark

Light ageing

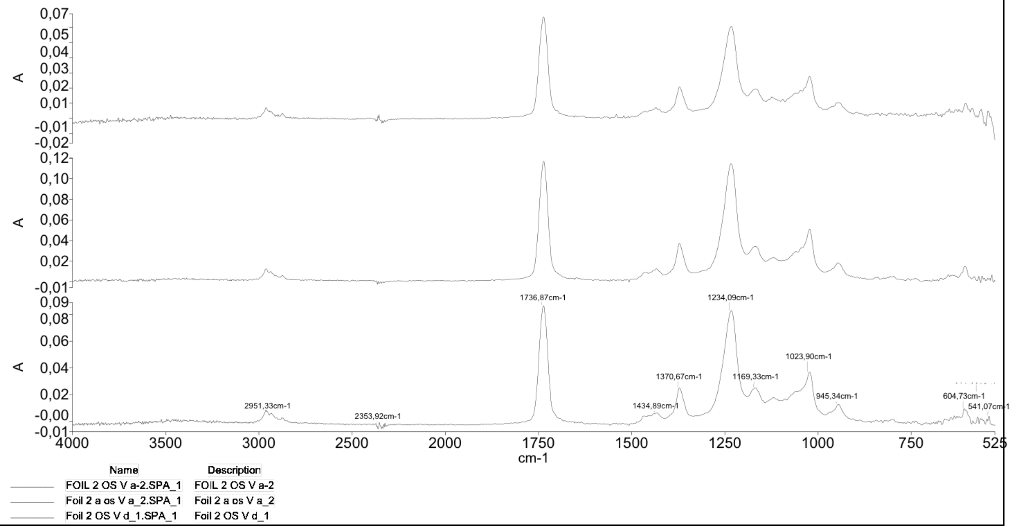


Mowilith DMC2

Before ageing

Natural ageing in the dark

Light ageing

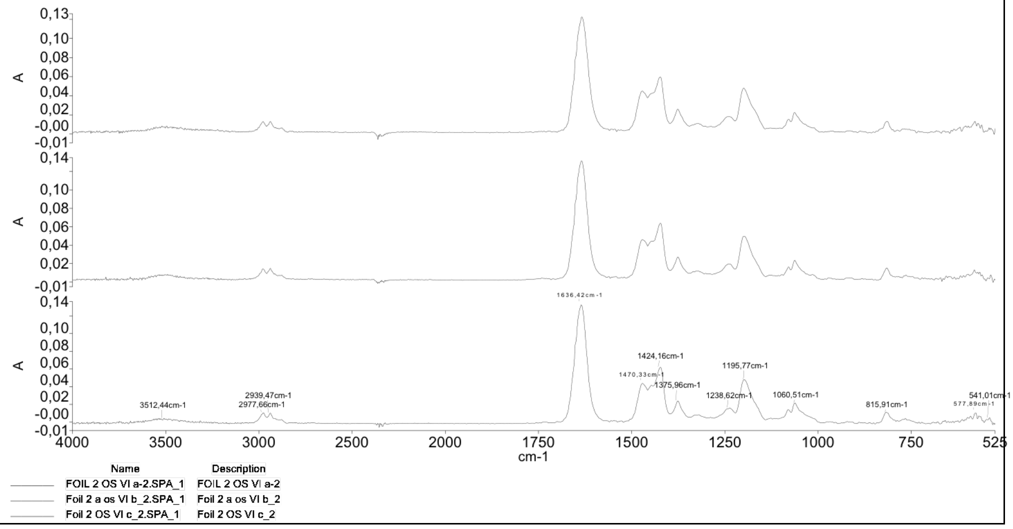


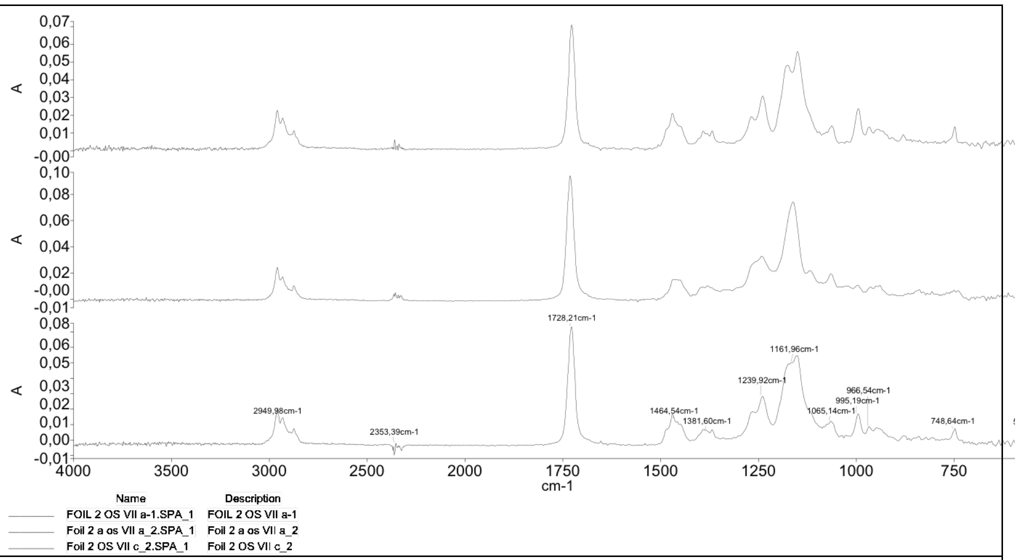
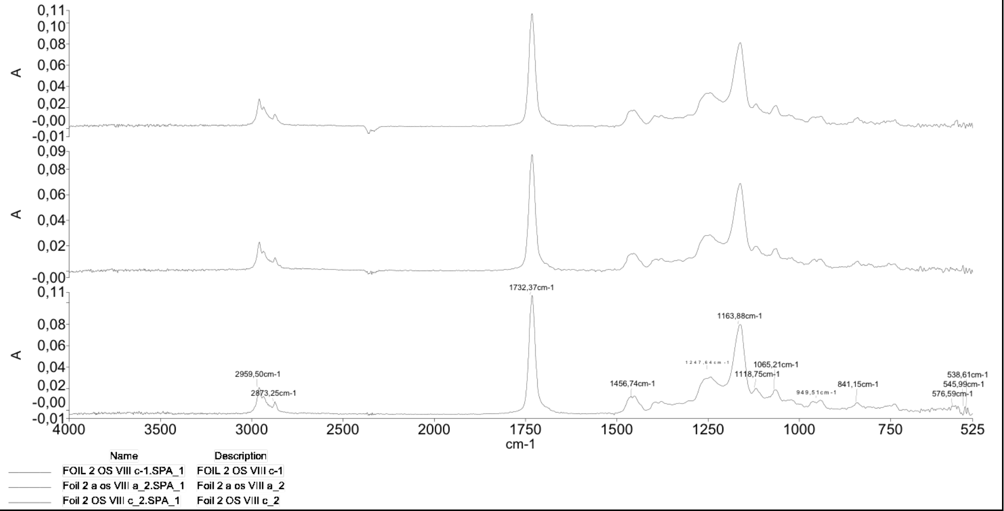
Aquazol 200

Before ageing

Natural ageing in the dark

Light ageing



1:1 Plexigum PQ611/Paraloid B67 Before ageing Natural ageing in the dark Light ageing	
PSA Before ageing Natural ageing in the dark Light ageing	

9.6 Appendix 6. FTIR summary results. Adhesive side of PVC carrier film

	Acronal D500	**Primal WS24**	**Dispersion K360**	**Lascaux MFC**	**Mowilith DMC2**	**Aquazol 200**	**Plexigum PQ611/Paraloid B67**	**PSA**
Polymer	nBA/VAC/VC, acrylic acid ester copolymer	nBMA (nbutyl methacrylate)	Aqueous emulsion of a thermoplastic acrylic polymer BA/MMA (butyl acrylate/methyl methacrylate)	Finely dispersed aqueous dispersion of acrylic copolymers based on acrylate ester, styrene and methacrylic ester	Aqueous dispersion of a copolymer based on vinyl acetate and maleic acid di-n-butyl ester. 35% dibutylmaleate with a celluloce ether stabiliser	Poly (2-ethyl-2-oxazoline)	butyl methacrylate solution of an acrylic polymer / Isobutyl methacrylate	Butyl acrylate
Hydrocarbons C-H 3100 – 2850 cm^{-1}	No significant change	No significant change	No significant change	Change in absorption intensity and band distribution after light ageing	Minor change in absorption intensity	No significant change	Possibly formation of shoulder after light ageing	No significant change
Hydroxyl (-OH)	No change	No change	No change	Peak appearing (light)	Broadening (light)	Tendency to stronger absorption (light)	Less prominent peaks (light)	No change
Carbonyl (-C=O) 1690 – 1760 cm^{-1}	No change	Prominent peak forming at – 1700 cm^{-1} (dark)	Splitting at – 1700 cm^{-1} (light).	Shift in shoulder (light)	No change	Flattening/broadening of band and shoulder (dark). Less prominent peaks (dark and light)	Tendency to negative peak. Shoulder forming at -1800 cm^{-1} (light)	No change
Acid salts (-CO_2)	Shift in peaks (dark and light)	Several peaks appearing (light)	Loss of absorption at -1600 and 1500 cm^{-1} (dark and light)	Disappearance of peaks (dark)	Shifts in peaks (dark and light).	Negative peaks (dark and light)	Stronger peaks at 1600/ 1650 cm^{-1} (light)	No change
Carbon-oxygen (-C-O-) 1260-1050 cm^{-1}	Disappearing of shoulder	Splitting at – 1250 cm^{-1} (dark and light)	Splitting at – 1100 and 1000 cm^{-1} (light)	Shift in peak at 1160 cm^{-1} (light). Disappearance of peak at 1085 (light)	No change	Tendency to splitting at -1230 cm^{-1}, and broadening of band and shoulder (light)	Disappearance of peak at -1100 cm^{-1} (light)	Rounding of peaks at 1117 cm^{-1} (dark) Splitting in the 1025 cm^{-1} region (dark)
Phthalates 1620 – 1560 cm^{-1}	No change	Possibly appearance of phthalates after ageing in the dark	Possibly less absorbance in the phthalate region after ageing	No change	Possibly stronger presence of phthalates after ageing in dark and light	Less absorbance in the phthalate region after ageing	Slightly stronger absorbance in the phthalate region after ageing in dark and light	Less absorbance in the phthalate region after light ageing
Other		Splitting at -900 cm^{-1} (dark and light). Strong increase in bond strength at -600 cm^{-1} (dark and light)	Flattening/broadening at -600 cm^{-1} (dark)	Disappearance of peak at 990 cm^{-1} (light). Broadening at -750 cm^{-1} (light)	Shift in broadening (C-H rock) (dark) Shoulder building at – 900 cm^{-1} (dark and light) Shift at – 600 cm^{-1} (light)	Broadening of peaks at -690 cm^{-1}	Peak splitting at -1400 (crystalline region. Splitting at -900 (dark and light). Peak forming at -690.	Broadening of shoulder at 746 cm^{-1}

* Note that all results are from the composite of test adhesive, PSA and PVC, and not from test adhesive alone.

9.7 Appendix 7. FTIR summary results. Adhesive side of PP carrier film.

	Acronal D500	**Primal WS24**	**Dispersion K360**	**Lascaux MFC**	**Mowilith DMC2**	**Aquazol 200**	**Plexigum PQ611/Paraloid B67**	**PSA**
	nBA/VAC/VC, acrylic acid ester copolymer	nBMA (nbutyl methacrylate)	Aqueous emulsion of a thermoplastic acrylic polymer BA/MMA (butyl acrylate/methyl methacrylate)	Finely dispersed aqueous dispersion of acrylic copolymers based on acrylate ester, styrene and methacrylic ester	Aqueous dispersion of a copolymer based on vinyl acetate and maleic acid di-n-butyl ester. 35% dibutylmaleate with a celluloce ether stabiliser	Poly (2-ethyl-2-oxazoline)	butyl methacrylate solution of an acrylic polymer / Isobutyl methacrylate	Butyl acrylate
Hydrocarbons C-H 3100 – 2850 cm^{-1}	Decrease of absorbance	No significant change	No significant change	Disappearance of bands after light ageing	No significant change	Minor change after ageing in the dark	Slight decrease in absorbance	No significant change
Hydroxyl (-OH) 1700 – 1600 cm^{-1} (and 3700 – 3100 cm^{-1}9	Minor change after light ageing	No significant change	No significant change	No significant change	No significant change	Minor changes after ageing	No significant change	No significant change
Carbonyl (-C=O) 1690 – 1760 cm^{-1} (and 1350 – 1150 cm^{-1})	Appearance of shoulder at ≈ 1760 cm^{-1} after ageing.	Stronger absorbance of shoulder at ≈ 1710 cm^{-1} after natural ageing in the dark.	No significant change	No significant change	No significant change	No significant change	Slight increase in absorbance.	No significant change. Decrease in absorption after ageing in the dark
Carbon-oxygen (-C-O-) 1260-1050 cm^{-1}	Stronger absorption at 1236 cm^{-1} after ageing.	Disappearance of shoulder and broadening of peak at 1163 cm^{-1}after natural ageing in the dark.	Slight flattening of band at approx.. 1100 cm^{-1}	Sight change after ageing in the dark	Flattening of band after light ageing	Minor change after light ageing	Flattening of bands after ageing in the dark. Broadening of bands after light ageing	Minor changes after light ageing
Phthalates 1620 – 1560 cm^{-1}	No change	Appearance of bands at approx.. 1600 cm^{-1} after light ageing	No significant change	Flattening of bands after ageing in the dark				
Other	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}	Changes in absorbance intensity between 800 – 600 cm^{-1}	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1} after ageing in the dark	Several minor changes in absorbance intensity beween 800 – 600 cm^{-1}

* Note that all results are from the composite of test adhesive, PSA and PP, and not from test adhesive alone.

9.8 Appendix 8. Colour measurements. Adhesive side of PVC carrier film

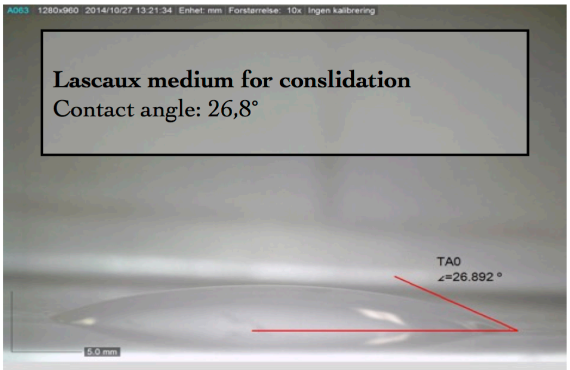
			Before aging							After aging						
ADHESIVES	**Film number**	**Aging**	**L*(D65)**	**a*(D65)**	**b*(D65)**	**dL*(D65)**	**da*(D65)**	**db*(D65)**	**dE*ab (D65)**	**L*(D65)**	**a*(D65)**	**b*(D65)**	**dL*(D65)**	**da*(D65)**	**db*(D65)**	**dE*ab (D65)**
Acronal D500	**Foil 3 Os Ia**	**Dark**	**94,68**	**−0,51**	**2,31**	**−2,6**	**−0,43**	**2,28**	**3,5**	**111,1**	**−0,67**	**3,59**	**16,42**	**−0,16**	**1,28**	**16,5**
	Foil 3 OS 1 b	**Dark**	**94,38**	**−0,79**	**0,98**	**−2,9**	**−0,72**	**0,97**	**3,1**	**111,26**	**−0,7**	**3,83**	**16,88**	**0,09**	**2,85**	**17,1**
	Foil 3 OS I c	Light	95,07	−0,58	2,25	−2,21	−0,49	2,24	3,2	111,58	−0,67	2,76	22,67	−0,67	2,59	22,8
	Foil 3 OS I d	Light	94,32	−0,77	1,03	−2,96	−0,67	0,99	3,2	111,45	−0,7	2,79	22,55	−0,70	2,61	22,7
Primal WS24	**Foil 3 OS II a**	**Dark**	**94,02**	**−0,64**	**1,74**	**−3,29**	**−0,56**	**1,71**	**3,7**	**110,97**	**−0,65**	**3,9**	**16,95**	**−0,01**	**2,16**	**17,1**
	Foil 3 OS II b	**Dark**	**94,72**	**−0,59**	**1,95**	**−2,61**	**−0,52**	**1,94**	**3,3**	**111,32**	**−0,68**	**3,81**	**16,60**	**−0,09**	**1,86**	**16,7**
	Foil 3 OS II c	Light	94,3	−0,54	2,45	−3,01	−0,46	2,45	3,9	111,44	−0,61	2,62	22,54	−0,61	2,44	22,7
	Foil 3 OS II d	Light	94,24	−0,6	2,17	−3,06	−0,5	2,19	3,8	111,25	−0,68	2,56	22,34	−0,68	2,39	22,5
Dispersion K360	**Foil 3 OS III a**	**Dark**	**95,11**	**−0,61**	**2,3**	**−2,23**	**−0,51**	**2,29**	**3,2**	**110,45**	**−0,84**	**3,76**	**15,34**	**−0,23**	**1,46**	**15,4**
	Foil 3 OS III b	**Dark**	**94,83**	**−0,74**	**1,55**	**−2,5**	**−0,65**	**1,56**	**3,0**	**111,07**	**−0,72**	**3,71**	**16,24**	**0,02**	**2,16**	**16,4**
	Foil 3 OS III c	Light	94,57	−0,75	1,63	−2,76	−0,67	1,65	3,3	111,35	−0,72	2,75	22,44	−0,72	2,57	22,6
	Foil 3 OS III d	Light	94,29	−0,74	1,74	−3,03	−0,65	1,75	3,6	111,08	−0,72	2,85	22,18	−0,72	2,68	22,4
Lascaux Medium for consolidation	**Foil 3 OS VI a**	**Dark**	**94,62**	**−0,75**	**1,33**	**−2,72**	**−0,66**	**1,33**	**3,1**	**111,36**	**−0,68**	**3,55**	**16,74**	**0,07**	**2,22**	**16,9**
	Foil 3 OS VI b	**Dark**	**95,02**	**−0,59**	**2,43**	**−2,33**	**−0,52**	**2,46**	**3,4**	**109,71**	**−0,76**	**3,08**	**14,69**	**−0,17**	**0,65**	**14,7**
	Foil 3 OS VI c	Light	95,34	−0,62	2,27	−2,01	−0,53	2,27	3,1	111,66	−0,7	2,59	22,75	−0,70	2,42	22,9
	Foil 3 OS VI d	Light	95,29	−0,66	1,98	−2,07	−0,57	1,99	2,9	111,52	−0,74	2,85	22,61	−0,73	2,67	22,8
Mowilith DMC2	**Foil 3 OS V a**	**Dark**	**94,67**	**−0,64**	**1,85**	**−2,69**	**−0,56**	**1,88**	**3,3**	**111,48**	**−0,72**	**4,1**	**16,81**	**−0,08**	**2,25**	**17,0**
	Foil 3 OS V c	Light	measurements missing							111,63	−0,64	2,61	22,72	−0,64	2,43	22,9
Aquazol 200	**Foil 3 OS VI a**	**Dark**	**95,57**	**−0,54**	**1,83**	**−1,83**	**−0,46**	**1,86**	**2,6**	**111,15**	**−0,62**	**2,85**	**15,58**	**−0,08**	**1,02**	**15,6**
	Foil 3 OS VI b	**Dark**	**95,14**	**−0,63**	**2,38**	**−2,26**	**−0,54**	**2,41**	**3,3**	**110,75**	**−0,71**	**3,76**	**15,61**	**−0,08**	**1,38**	**15,7**
	Foil 3 OS VI c	Light	95,36	−0,62	2,69	−2,03	−0,54	2,72	3,4	111,66	−0,7	2,59	22,75	−0,70	2,42	22,9
	Foil 3 OS VI d	Light	94,35	−0,66	2,33	−3,03	−0,57	2,35	3,9	111,52	−0,74	2,85	22,61	−0,73	2,67	22,8
PlexigumPQ611/ ParaloidB67	**Foil 3 OS VII a**	**Dark**	**95,47**	**−0,53**	**2,09**	**−1,94**	**−0,45**	**2,15**	**2,9**	**110,66**	**−0,7**	**3,36**	**15,19**	**−0,17**	**1,27**	**15,24**
	Foil 3 OS VII b	**Dark**	**94,12**	**−0,62**	**1,82**	**−3,29**	**−0,52**	**1,86**	**3,8**	**110,06**	**−0,82**	**3,07**	**15,94**	**−0,20**	**1,25**	**15,99**
	Foil 3 OS VII c	Light	95,65	−0,57	2	−1,76	−0,49	2,03	2,7	111,64	−0,64	2,68	22,73	−0,64	2,50	22,88
	Foil 3 OS VII d	Light	95,88	−0,55	2,21	−1,54	−0,46	2,25	2,8	111,14	−0,69	2,59	22,23	−0,68	2,42	22,37
Acrylic PSA only	**Foil 3 OS VIII a**	**Dark**	**95,24**	**−0,58**	**2,09**	**−2,21**	**−0,51**	**2,13**	**3,1**	**111,38**	**−0,67**	**3,88**	**16,14**	**−0,09**	**1,79**	**16,24**
	Foil 3 OS VIII b	**Dark**	**95,79**	**−0,52**	**2,65**	**−1,65**	**−0,43**	**2,71**	**3,2**	**110,44**	**−0,69**	**3,8**	**14,65**	**−0,17**	**1,15**	**14,70**
	Foil 3 OS VIII c	Light	95,84	−0,59	2,33	−1,61	−0,49	2,36	2,9	111,09	−0,76	2,37	22,19	−0,76	2,19	22,31
	Foil 3 OS VIII d	Light	96,33	−0,53	2,45	−1,11	−0,45	2,49	2,8	111,73	−0,69	2,8	22,82	−0,69	2,63	22,99

SCI Excluded
CIELab 1967 colour space

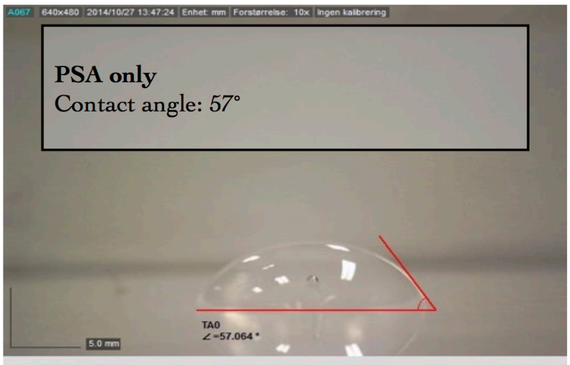
9.9 Appendix 9. Colour measurements. Adhesive side of PP film carrier

			Before ageing				**After ageing**			
		Data Name	**dL*(D65)**	**da*(D65)**	**db*(D65)**	**dE*ab(D65)**	**dL*(D65)**	**da*(D65)**	**db*(D65)**	**dE*ab(D65)**
Acronal D500	Dark #1	**Foil 2 OS 1 a**	20,41	−0,02	0,23	20,40	12,49	−0,18	0,32	12,49
	Dark #2	**Foil 2 OS I b**	−4,99	−0,14	0,08	5,00	20,93	0,00	0,09	20,90
	Light #1	**Film2 OS I c**	−4,58	−0,13	0,13	4,60	21,09	−0,09	0,06	21,10
	Light #2	**Foil 2 OS I d**	−2,57	−0,17	0,04	2,60	20,74	−0,03	0,11	20,70
Primal WS24	Dark #1	**Foil 2 OS II a**	−2,28	−0,17	−0,01	2,30	14,50	−0,05	0,39	14,50
	Dark #2	**Foil 2 OS II b**	−2,56	−0,20	0,04	2,60	14,81	−0,03	0,32	14,80
	Light #1	**Foil 2 OS II c**	−2,64	−0,21	0,13	2,70	20,82	0,00	0,01	20,80
	Light #2	**Foil 2 OS II d**	−2,65	−0,19	0,05	2,70	20,78	−0,02	0,06	20,80
Dispersion K	Dark #1	**Foil 2 OS III a**	−2,07	−0,21	0,04	2,10	14,42	−0,03	0,40	14,40
	Dark #2	**Foil 2 OS III b**	−2,47	−0,19	0,06	2,50	15,10	−0,03	0,36	15,10
	Light #1	**Foil 2 OS III c**	−2,46	−0,15	0,09	2,50	20,74	−0,08	0,18	20,80
	Light #2	**Foil 2 OS III d**	−2,81	−0,20	0,14	2,80	20,87	0,00	0,15	20,90
Lascaux MFC	Dark #1	**Foil 2 OS IV a**	−2,44	−0,17	−0,04	2,40	14,74	−0,04	0,36	14,70
	Dark #2	**Foil 2 OS IV b**	−2,49	−0,18	−0,06	2,50	14,81	−0,03	0,29	14,80
	Light #1	**Foil 2 OS IV c**	−2,52	−0,17	−0,02	2,50	20,99	−0,03	−0,06	21,00
	Light #2	**Foil 2 OS IV d**	−2,49	−0,20	−0,02	2,50	21,02	−0,03	−0,01	21,00
Mowilith DMC2	Dark #1	**Foil 2 OS V a**	−2,06	−0,20	−0,06	2,10	14,80	−0,05	0,23	14,80
	Dark #2	**Foil 2 OS V b**	−2,60	−0,21	0,23	2,60	14,79	−0,05	0,40	14,80
	Light #1	**Foil 2 OS V c**	−2,54	−0,21	0,15	2,60	21,02	0,00	0,00	21,00
	Light #2	**Foil 2 OS V d**	−2,55	−0,22	0,17	2,60	20,92	0,04	0,06	20,90
Aquazol 200	Dark #1	**Foil 2 OS VI a**	−2,70	−0,15	−0,05	2,70	14,68	−0,05	0,38	14,70
	Dark #2	**Foil 2 OS VI b**	−2,87	−0,20	0,14	2,90	14,77	−0,01	0,36	14,80
	Light #1	**Foil 2 OS IV c**	−2,80	−0,17	0,11	2,80	20,38	0,01	0,14	20,40
	Light #2	**Foil 2 OS VI d**	−2,83	−0,18	0,05	2,80	20,37	0,02	0,10	20,40
Plexigum/B67	Dark #1	**Foil 2 OS VII a**	−5,22	−0,14	0,03	5,20	17,99	−0,07	0,27	18,00
	Dark #2	**Foil 2 OS VII b**	−2,00	−0,17	−0,06	2,00	14,58	−0,04	0,38	14,59
	Light #1	**Foil 2 OS VII c**	−2,02	−0,16	−0,08	2,00	21,36	−0,03	−0,01	21,36
	Light #2	**Foil 2 OS VII d**	−1,89	−0,21	−0,01	1,90	21,22	−0,01	−0,05	21,23
PSA	Dark #1	**Foil 2 OS VIII a**	−2,13	−0,18	−0,02	2,10	14,51	−0,02	0,42	14,52
	Dark #2	**Foil 2 OS VIII b**	−2,08	−0,17	0,00	2,10	14,56	−0,06	0,36	14,56
	Light #1	**Foil 2 OS VIII c**	−2,18	−0,17	−0,03	2,20	21,05	−0,02	0,04	21,05
	Light #2	**Foil 2 OS VIII d**	6,95	−0,20	−0,19	7,00	20,87	−0,04	0,10	20,87

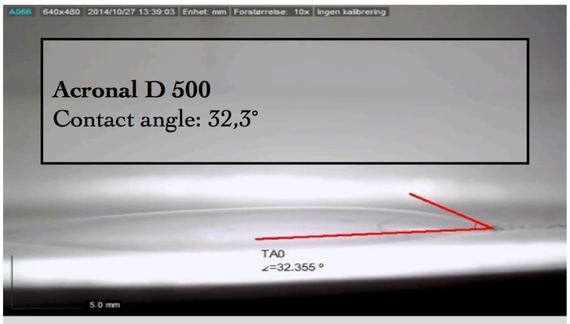
9.10 Appendix 10. Contact angle measurements



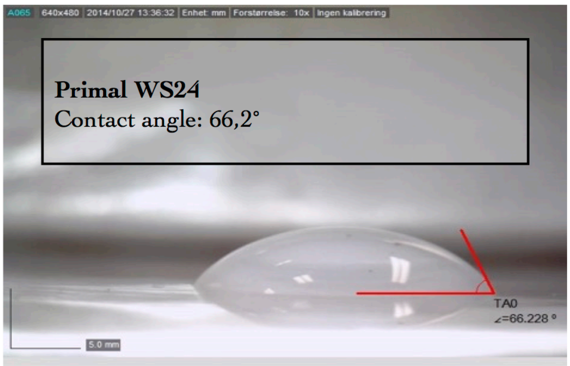
Lascaux medium for conslidation
Contact angle: 26,8°



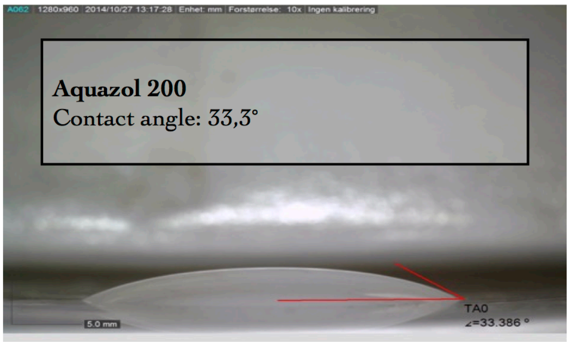
PSA only
Contact angle: 57°



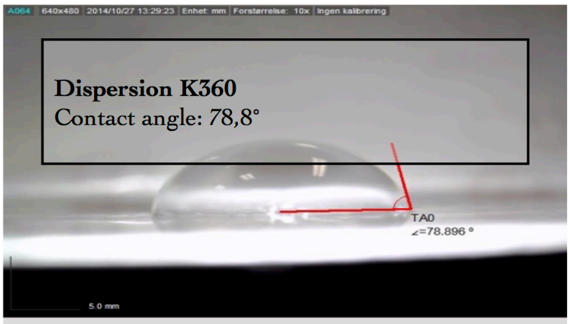
Acronal D 500
Contact angle: 32,3°



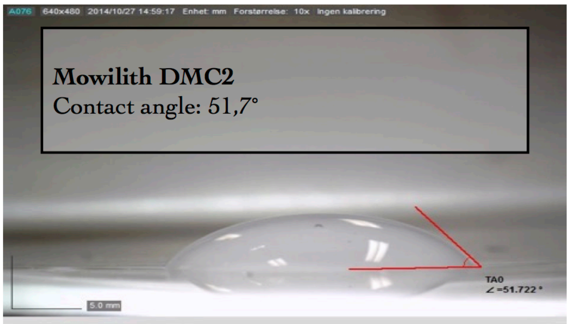
Primal WS24
Contact angle: 66,2°



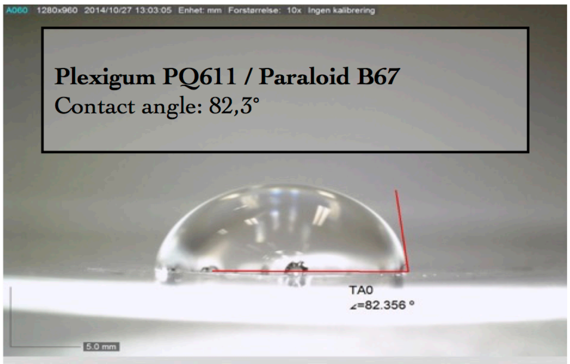
Aquazol 200
Contact angle: 33,3°



Dispersion K360
Contact angle: 78,8°



Mowilith DMC2
Contact angle: 51,7°



Plexigum PQ611 / Paraloid B67
Contact angle: 82,3°

9.11 Appendix 11 pH measurements

Adhesive	**pH before aging 1**	**pH after aging 1**
Acronal D 500	5.963	5.371
Acronal D 500	5.568	4.688
Aquazol 200	5.280	5.053
Aquazol 200	5.274	5.563
Dispersion K360	5.298	4.400
Dispersion K360	5.797	4.449
Lascaux medium for conslidation	5.201	4.781
Lascaux medium for conslidation	4.933	4.389
Mowilith DMC2	4.877	4.788
Mowilith DMC2	5.836	4.797
Plexigum PQ611 / Paraloid B67	6.138	5.286
Plexigum PQ611 / Paraloid B67	6.588	4.600
Primal WS24		4.565
Primal WS24	5.919	5.973
PSA only	5.293	4.618
PSA only	6.079	4.423

9.12 Appendix 12 T-peel test. PVC film carrier

Test adhesive	Aging	T-peel test N	Pull	Cohesive failure	Adhesive failure	Bond failure
Acronal D 500	Dark aging	20	Even pull	x		Cohesive failure. Even pull
Acronal D 500	Light aging	20	Even pull	x		Cohesive failure. Even pull
Acronal D 500	Reference	20	Clamps failed once	x		Cohesive failure. Clamps failed once
Primal WS24	Dark aging	20	Even pull	x		Cohesive failure. Even pull
Primal WS24	Dark aging	20	Slightly uneven pull	x		Cohesive failure. Slightly uneven pull
Primal WS24	Light aging	20	Even pull	x		Cohesive failure. Even pull
Primal WS24	Light aging	20		x		Cohesive failure. Even but uneven pull
Primal WS24	Reference	20	Fairly even pull	x		Cohesive failure. Fairly even pull
Dispersion K360	Dark aging	20	Even pull	x		Cohesive failure. Even pull
Dispersion K360	Dark aging	20	Even pull	x		Cohesive failure. Even pull
Dispersion K360	Light aging	20	Even pull	x		Cohesive failure. Even pull
Dispersion K360	Reference	19		x		Cohesive failure
Lascaux medium for conslidation	Dark aging	20	Slightly uneven pull	x		Cohesive failure. Even distribution of adhesive. Slightly uneven pull
Lascaux medium for conslidation	Dark aging	20		x	x	Cohesive and adhesive failure. Very strong force to pull. Areas of strong adhesive pull-off
Lascaux medium for conslidation	Light aging	20	Clamps failed once	x	x	Cohesive and adhesive failure. Very strong pull force. Pull failed once due to clamp failure. Areas of strong adhesive pull-off in the beginning of pull
Lascaux medium for conslidation	Light aging	20	Clamps failed twice	x	x	Cohesive and adhesive failure. High force to pull. clamps failed twice. Areas of strong pull-off of adhesive at the start of pull
Lascaux medium for conslidation	Reference	20	Even pull	x		Cohesive failure. Even pull and distribution of adhesive
Mowilith DMC2	Dark aging	20	Even pull. Clamps failed once	x		Cohesive failure. Even pull and distribution of adhesive. Clamp jaws failed on first pull.
Mowilith DMC2	Dark aging	20	Even pull	x		Cohesive failure. Even pull and distribution of adhesive on both films.
Mowilith DMC2	Light aging	20	Even pull	x		Cohesive failure. Even pull and distribution of adhesive.
Mowilith DMC2	Light aging	20		x	x	Cohesive and adhesive failure. Strong pull off of adhesive in the start. Even distribution the remaining 2/3
Mowilith DMC2	Reference	20	Clamps failed twice	x	x	Cohesive and adhesive failure. Strong pull-off of adhesive. Test failed twice due to slip of clamps.
Aquazol 200	Dark aging	20	Even pull. Clamps failed twice	x	x	Cohesive and adhesive failure. Even pull. Clamps failed twice during pull
Aquazol 200	Dark aging	20	Even pull	x	x	Cohesive and adhesive failure. Even pull
Aquazol 200	Light aging	20	Clamps failed once	x	x	Cohesive and adhesive failure. Strong pull-off of adhesive to one film. Clamps failed once during pull
Aquazol 200	Light aging	20	Even pull	x	x	cohesive and adhesive failure. even pull
Aquazol 200	Reference	20		x	x	Cohesive and adhesive failure
Plexigum PQ611 / Paraloid B67	Dark aging	20		x	x	Cohesive failure. Adhesive failure:Strong pull-off on both films at the start of the pull
Plexigum PQ611 / Paraloid B67	Dark aging	20		x	x	Cohesive failure. Adhesive failure: Strong pull-off at the start of the pull
Plexigum PQ611 / Paraloid B67	Light aging	20		x		Cohesive failure. Sample slightly more tacky than dark aged.
Plexigum PQ611 / Paraloid B67	Light aging	20		x		Cohesive failure. Slightly more soft than dark aged samples
Plexigum PQ611 / Paraloid B67	Reference	20		x	x	Cohesive and adhesive failure. Strong pull-off on both foils at the start of the pull
PSA only	Dark aging	20	Even pull	x		Cohesive failure
PSA only	Dark aging	20	Even pull	x		Cohesive failure
PSA only	Light aging	20	Even pull	x		Cohesive failure
PSA only	Light aging	20	Even pull	x		Cohesive failure
PSA only	Reference	20		x	x	Cohesive failure. Some pull-off on both films

9.13 Appendix 13 T-peel test. PP film carrier

Test adhesive	Cohesive failure	Adhesive failure	Film failure
Acronal D 500 (Reference)	x	x	
Acronal D 500 (Dark)	x	x	
Acronal D 500 (Dark)	x	x	x
Acronal D 500 (Light)	x	x	x
Acronal D 500 (Light)	x	x	
Primal WS24 (Reference)	x	x	
Primal WS24 (Dark)	x	x	
Primal WS24 (Dark)	x	x	
Primal WS24 (Light)	x	x	
Primal WS24 (Light)	x	x	
Dispersion K360 (Reference)	x	x	
Dispersion K360 (Dark)	x	x	
Dispersion K360 (Dark)	x		x
Dispersion K360 (Light)	x		
Dispersion K360 (Light)	x	x	x
Lascaux MFC (Reference)	x	x	
Lascaux MFC (Dark)	x	x	x
Lascaux MFC (Dark)		x	x
Lascaux MFC (Light)		x	x
Lascaux MFC (Light)		x	
Mowilith DMC2 (Reference)	x	x	
Mowilith DMC2 (Dark)	x	x	
Mowilith DMC2 (Dark)	x	x	
Mowilith DMC2 (Light)	x	x	
Mowilith DMC2 (Light)	x	x	
Plexigum / B67 (Reference)	x	x	
Plexigum / B67 (Dark)	x	x	
Plexigum / B67 (Light)	x	x	
Plexigum/ B67 (Dark)	x	x	
Plexigum/ B67 (Light)	x	x	
Aquazol 200 (Reference)	x	x	
Aquazol 200 (Dark)	x	x	
Aquazol 200 (Dark)	x	x	
Aquazol 200 (Light)	x	x	
Aquazol 200 (Light)	x	x	
PSA (Dark)		x	
PSA (Dark)		x	x
PSA (Light)		x	x
PSA (Light)		x	x
PSA (Reference)	x	x	