UNIVERSITY OF AMSTERDAM

UvA-DARE (Digital Academic Repository)

Reproducing reality. Recreating bonding defects observed in transparent poly(methyl methacrylate) museum objects and assessing defect formation

Laganà, A.; David, M.; Doutre, M.; de Groot, S.; van Keulen, H.; Madden, O.; Schilling, M.; van Bommel, M.

DOI
10.1016/j.culher.2020.11.002

Publication date
2021

Document Version
Final published version

Published in
Journal of Cultural Heritage

License
CC BY-NC-ND

Link to publication

Citation for published version (APA):
Laganà, A., David, M., Doutre, M., de Groot, S., van Keulen, H., Madden, O., Schilling, M., & van Bommel, M. (2021). Reproducing reality. Recreating bonding defects observed in transparent poly(methyl methacrylate) museum objects and assessing defect formation. *Journal of Cultural Heritage*, *48*, 254-268. https://doi.org/10.1016/j.culher.2020.11.002

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)

Download date:11 Feb 2023

Journal of Cultural Heritage 48 (2021) 254–268

Available online at
ScienceDirect
www.sciencedirect.com

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

Original article

Reproducing reality. Recreating bonding defects observed in transparent poly(methyl methacrylate) museum objects and assessing defect formation

Anna Laganà [a,*], Melissa David [a,b], Michael Doutre [a], Suzan de Groot [c], Henk van Keulen [c], Odile Madden [a], Michael Schilling [a], Maarten van Bommel [d]

[a] Getty Conservation Institute (GCI), 1200 Getty Center Drive, Suite 700, Los Angeles, CA 90049, USA
[b] Private Conservation Practice, Turin, Italy
[c] Cultural Heritage Agency of the Netherlands | Rijksdienst voor het Cultureel Erfgoed (RCE), Hobbemastraat 22, NL-1071 ZC, Amsterdam, The Netherlands
[d] University of Amsterdam (UVA), Conservation and Restoration of Cultural Heritage, P.O. Box 94552, 1090 GN, Amsterdam, The Netherlands

INFO ARTICLE

Historique de l'article :
Reçu le 24 juillet 2020
Accepté le 2 novembre 2020
Disponible sur Internet le 29 janvier 2021

Keywords :
Poly(methyl methacrylate)
PMMA
Solvent welding
Adhesives
Bonding
Crazing

ABSTRACT

The most common method chosen by artists, designers, and craftsmen to realize artworks and objects with transparent poly(methyl methacrylate) (PMMA) is to bond pieces from premanufactured sheets using solvents or adhesives. This method is considered relatively easy to use, however achieving bonds that are both transparent and strong can be difficult. Artifacts from museum collections made by bonding transparent PMMA often exhibit a variety of bonding defects and failures not yet addressed in depth in the conservation literature.

Therefore, an international project started with the aims of classifying these bonding issues and understand their causes. This paper presents the results of the first part of this project which included the following research activities: surveys of bonding defects in PMMA artworks and design objects in museum collections, a literature review of the most recommended materials and methods used to bond PMMA over time, the preparation of bonded PMMA mock-ups based on literature review, chemical characterization of the bonding materials, thermal ageing of mock-ups, and finally technical examinations of the PMMA bonded mock-ups. The main defects observed in the museum objects surveyed were successfully recreated in the lab and the causes of their formation were assessed.

© 2020 J. Paul Getty Trust. Publié par Elsevier Masson SAS. Cet article est publié en Open Access sous licence CC BY-NC-ND (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Introduction

Poly(methyl methacrylate) (PMMA) is a transparent polymer commonly known as acrylic or by the trade-names Perspex, Plexiglas, and Lucite. PMMA became available in its solid forms in the 1930′s and since then has been used for innumerable applications [1–3] due to its optical clarity, manufacturing versatility, weathering resistance, toughness and rigidity [4].

Many artists, designers, and craftsmen have found PMMA an ideal medium for the creation of three-dimensional objects and sculptures. A frequent method to create these artifacts is bonding together PMMA pieces, generally prefabricated cast and extruded sheets, blocks, rods, tubes, or 'hand-made' cast pieces [5,6]. Bonding PMMA is known to be challenging because of the difficulties in obtaining a strong, stable, and transparent joint where both the optical clarity and the refractive index of the polymer are matched [7–12]. Nevertheless these challenges did not stop the creation of bonded PMMA artifacts, many of which have entered museum collections.

Conservation surveys carried out by the main author over the years on plastics in art and design collections revealed that most artifacts made by bonding PMMA pieces (>95%) exhibit defects and failures in their joints which compromise the transparency and strength of their construction and seemed to be recurrent. However, most of the bonding issues observed and their causes are not mentioned, let alone classified, in plastics conservation literature currently available to conservators, with the exception of crazing [7,8,10,13–15].

Consequently this study focused on determining the most recurrent defects and failures on bonded PMMA objects in museum collections, to reproduce them in the lab and closely investigate their origin and causes. In this work, the main PMMA bonding issues affecting objects were identified through bonding defects surveys in several museum collections and then an experimental part was carried out. Historical sources on bonding PMMA were reviewed to

* Corresponding author at: Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, CA 90049, USA.
Adresse e-mail : alagana@getty.edu (A. Laganà).

https://doi.org/10.1016/j.culher.2020.11.002
1296-2074/© 2020 J. Paul Getty Trust. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

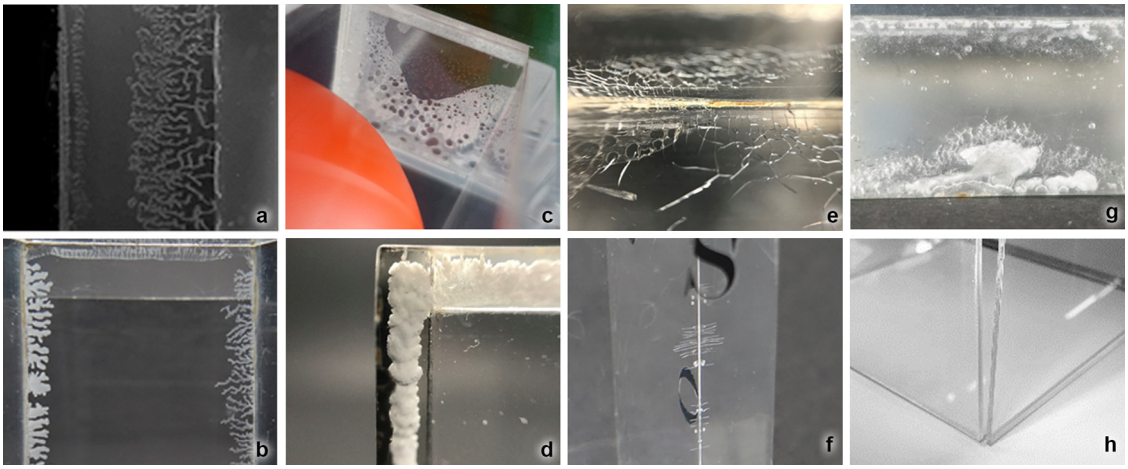

Fig. 1. Bonding defects observed in museum objects: bubbles (a-b), haziness (c-d), crazing (e-f-g), and joint separation (h). Collection Stedelijk Museum Amsterdam (a,b,c,d,f,h) and RCE Collection (e,g).

understand how this plastic has been bonded over time, and PMMA mock-ups were prepared using the main bonding materials and methods mentioned in these sources. The chemical composition of the bonding materials was investigated with Fourier Transform Infrared Spectroscopy (FTIR) and pyrolysis-Gas Chromatography-Mass Spectrometry (py-GC/MS) analysis. The stability of the bonds was studied using thermal aging on some of the mock-ups. Finally aged and un-aged PMMA bonded mock-ups were examined using optical and scanning electron microscopy.

Research aims

Given the lack of information in the plastics conservation literature on PMMA bonding issues and their causes, the primary aim of this research is to fill this gap in knowledge. This study with its extensive review of trade, craft, industrial, physics, and macromolecular literature, and its experimental recreation of bonding techniques intends to provide conservators all the necessary knowledge and understanding to properly assess the condition of PMMA bonded objects in museum collections. Moreover, this work aims to inform artists, designers and conservators on materials and methods that are unsuitable for the creation of transparent and stable bonds on clear PMMA.

Bonding defects surveys

The project started surveying the condition of transparent PMMA bonded artifacts in museum collections in order to identify and describe the most recurring bonding defects to be experimentally reproduced and investigated.

Bonding defects surveys were undertaken at the Stedelijk Museum Amsterdam (SMA) (sculpture and design collections), at the Cultural Heritage Agency of the Netherlands (RCE) in Rijswijk, at the Museo del Novecento in Milan, and at the Galleria Nazionale d'Arte Moderna in Rome. In these collections a total of forty PMMA bonded artifacts, including sculptures, design objects, and an installation dating from 1960′s onwards, were identified and the condition of their bonds were surveyed.

Identification of these works as PMMA was generally based on the documentation provided, in combination with the use of non-analytical methods to recognize plastics, and when sampling was possible with FTIR analysis.

Artifacts' constructions and bonds were examined visually, with magnification, and with ultraviolet light (UV). UV light was used to observe any fluorescence along the bond that may indicate the use of an adhesive. Additionally, at the SMA objects where further examined with a strain viewer to visualize the presence of stresses close to the joints caused by bonding.

Overall and detail images of each artifact were taken with a digital camera, and close-ups of bonding defects were captured using a macro lens equipped smartphone.

The results were collected in a 'bonding defect survey form' designed for this project. The main categories of information collected were: object's data (title, author, and date), description of material and technique, and description of any bond defects/failures.

The majority of the artifacts examined were found to be made by bonding together pieces of transparent or colored transparent sawn cut PMMA sheets (cast and/or extruded) with variable thickness, or by joining thick transparent PMMA cast blocks.

Two main types of joints were observed in these artifacts: butt joint and full lap joint (also known as laminate). It was generally difficult to determine how PMMA was bonded in each artifact. In some objects, observations with both the naked eye and UV light clearly revealed the presence of an adhesive bonding line along the joints. In many others the bonding material was imperceptible, suggesting that the PMMA was bonded to itself using solvents. In few others a bonding line was visible, but it showed the same fluorescence as the PMMA.

All artifacts were found to have bonding issues. Particular types of defects and failures seemed to recur, which suggests they may relate to specific bonding materials and/or methods used. The main issues were: bubbles, haziness, crazing, and joint separation.

Bubbles showed a variety of shapes and were observed in the middle of bonds and/or along their edges (Fig.1a-b).

Haziness was noticed at the joints interface and appeared in two main different forms: as a hazy flat patch/area with undefined outlines (sometime within bubbles) (Fig.1c), and as a hazy three-dimensional spot with a cloud-like pattern (Fig.1d).

Crazing were observed along the bonding line (Fig.1e) as well as at the bond interface (Fig.1f), and in some objects close to the cloud shaped hazy spots (Fig.1g).

And finally joint separation was observed in objects which included butt joints made with very thin PMMA sheets (Fig.1h).

Materials and methods

Review of historical and current sources on bonding PMMA

With the most recurring bonding issues identified, a diversity of sources on bonding PMMA that could have been available over

the years to artists and designers were reviewed. The purpose of this literature review was to determine historically which bonding materials and methods have been recommended in order to select the most representative ones for creating mock-ups of bonded PMMA.

The sources reviewed span from the 1940's to present and comprise primarily trade literature issued by the leading manufacturers and suppliers of PMMA (e.g. Rohm & Haas, Imperial Chemical Industries, Du Pont, Arkema, Evonik), craft manuals, artist's handbooks of plastics, and technology books on plastics joining. Trade literature included in particular catalogues, technical handbooks, operating manuals, and sales brochures.

These publications provided important information on PMMA bonding (joint preparation, bonding materials and methods, curing processes) and also on its defects. It was noticed that all these sources provide similar information. Generally the leading PMMA manufactures were the first to publish information such as lists of materials and bonding instructions, which are then repeated in suppliers' catalogues, craft manuals, artist's handbooks of plastics, technologies books and also in their own yearly issues. Therefore, this section will refer only to the most significant and comprehensive references and not to all the eighty sources reviewed.

Regarding the materials used to bond PMMA, the majority of the sources defined these materials as 'cements', and the action of bonding or joining PMMA to itself as 'cementing'. The cements suggested in literature over the years generally match, while the way of categorizing them and the number of these categories varies; in some sources bonding materials are classified by composition, in some by curing process, and in others by application method. However, crossing all the references the most representative categories of cements were: *Solvent Cements, Monomer-Solvent Cements, Polymer-Solvent Cements* and the *Polymerizable Cements*.

Solvent Cements includes pure solvents or mixtures. Solvents are the most frequently suggested bonding materials since 1940s, as they are considered the easiest, most economical, and convenient cements to use on PMMA. Sources generally recommend the use of glacial acetic acid and chlorinated solvents such as chloroform, methylene dichloride, ethylene dichloride, 1,1,2-trichloroethane and 1,1,2-trichloroethene, or their blends. These solvents soften and swell the PMMA surfaces so that complete fusion can be achieved at the joint's interface, which then hardens into a transparent bond as solvent diffuses and evaporates [16–21]. Therefore, bonding occurs by a physical process. Bonding time and joint strength varies between solvents. Rohm and Haas repeatedly reported that chloroform and 1,1,2-trichloroethane form low strength bonds due to solvent retention, while methylene dichloride and ethylene dichloride produce bonds with medium strength. Methylene dichloride and ethylene dichloride are recommended for quick setting, while glacial acetic acid for joints that require longer working time [18,20,22,23]. Also, there is agreement that solvents should be used in environments above 21 °C, as lower temperatures can slow down their action on the PMMA [24,25].

Monomer-Solvent Cements include solvents (e.g. chlorinated) and small amounts of methyl methacrylate monomer (MMA) which are both able to soften the PMMA. These products, as the Solvents Cements, form bonds by softening and swelling the PMMA surfaces to be joined and fuse them together as the bonding materials dissipate. They allow rapid assembly, medium-strength joints, and have poor to fair outdoor weathering resistance [25–27].

Polymer-Solvent Cements or *Solvent-Polymer Cements* includes solution of PMMA in solvents (e.g. chlorinated), or solution of PMMA in solvents and MMA. The latter are sometime called Monomer-Polymer-Solvent Cements [27]. These cements act as the pure solvents swelling the PMMA surfaces, but also deposit polymer in the joint as solvents evaporate and migrate into the material. Manufactures, as ICI, developed these cements to retard rapid drying occurring with pure solvents. Their bond strength is higher than solvent and monomer-solvent cements but lower than polymerizable cements, and their resistance to weathering and moisture is moderate. These products can also be handmade by dissolving PMMA chips or shavings in any of the pure solvents mentioned above, to produce a syrup-like cement. [21,25,28–31].

Finally, *Polymerizable Cements or Adhesives (*also called *Polymerization Adhesives, Reactive Cements, or Monomer Type Cements* in the earlier references*)* includes one, two, or three components adhesives that cure by chemical reaction (polymerization of MMA). The monomer dissolves the PMMA in the same manner as other solvents, but then polymerizes in the joint instead of evaporating. Polymerization of MMA can be induced by catalyzation, irradiation (visible or UV light) in the presence of a photocatalyst, or by heating [32]. One-component adhesives are generally viscous solutions of PMMA in MMA sometimes with a photocatalyst. Two-component adhesives consist of MMA/PMMA solutions and a catalyst (often benzoyl peroxide or a photocatalyst), or of stabilized monomer and a catalyst. Lastly, three-component adhesives comprise often a solution of MMA/PMMA, a benzoyl peroxide catalyst which can be also combined with a plasticizer, and a promoter (MMA). Polymerizable adhesives give the advantage of fast initial set. They are recommended for bonding large areas and when assemblies require maximum strength and weathering resistance [16,18,20,28,33,34].

Some sources define any category based on solvents, or where solvent action plays a role, as *Solvent Cements* or *Solvent type* [16,18,25]. Moreover, some Monomer-Solvent Cements, as Rohm and Haas Cement II, are provided with catalyst giving them a dual action: the power to dissolve the PMMA surface and simultaneously to polymerize. Solvents and monomer-solvents, being low viscosity, are also called unthickened cements, while polymer-solvents and polymerizable adhesives are thickened cements, with few exceptions [18,28,33].

Sources also reported comprehensive descriptions of the bonding methods that should be used with all cement categories and information regarding bonding preparation. They generally recommend to check if parts to be bonded match well, to use jigs, clamps or weights, and especially to mask areas along the bonds with solvent-resistant tape, gelatin, or glue masking compound [18,35].

Three main bonding methods have been consistently employed from the 1940s onwards and their use depends upon the viscosity of the cement: the capillarity method, the soak or dip method, and the glue method [17,18,33,35].

Capillarity method is recommended for low-viscosity materials (unthickened cements) such as solvents or monomer-solvent cements [33]. Parts to be bonded must be closely fitted with no visible gaps. For butt joints, a jig should be used to secure pieces during the process. Cement can be applied with a needle, hypodermic syringe, eye dropper or similar instrument, along the edges of the joint and allowed to spread throughout by capillarity action [6,17,24,26,33,35–38]. Solvent flow can be facilitated by inserting fine wires in the bond to slightly separate the parts. Wires are then pulled out and light pressure is applied to the joint. Setting time can vary from a few minutes to over an hour depending on the product, and the ambient temperature [33]. Capillarity produces joints with variable strength, lower than those made with soaking method or polymerizable adhesives [18,24,39].

Soak or dip method is also suggested for unthickened cements. In this method, one of the parts is placed in a container holding the cement until the soaked surface softens and swells forming a 'cushion' [18]. While soaking, clamps or blocks can be used to hold the piece upright, and nails or metal wire can be placed underneath to prevent PMMA from adhering to the container. When the cushion is formed, the parts are then rapidly assembled. The cushion from the soaked piece forms a second cushion on the other piece by solvent action [16–18,24,26,33,35,39,40]. Light pressure is

then applied to ensure the intermingling of the two cushions, and the bond is allowed to set. Some leading manufacturers recommend to wait 30 to 60 seconds prior to apply pressure to the bond to avoid the soft cushion being squeezed out of the joints [18,29].

The time required to produce the cushion (soaking time), varies according to the cement used, though discrepancies were found. For instance in 1964, Rohm and Haas [18] reports soaking times of approximately 3 to 10 minutes with methylene dichloride, 3 to 8 minutes with ethylene dichloride and 5 to 10 minutes with 1,1,2-trichloroethane. While ICI, in the same year, states that a soaking time between 1 to 5 minutes will be sufficient to develop an adequate cushion with most solvents [19]. Shorter soaking times (30 seconds-3 minutes) were also found in earlier publications by the same manufacturers and other suppliers [17,29].

The *Glue method* is used with viscous or thickened cements which included the polymer-solvents cements and polymerizable adhesives. In this method the bonding material is applied directly, generally in a cross shape, on one of the parts to be bonded using a spatula, glass rod, brush, or similar tools. Parts are then assembled, applying pressure to spread the adhesive throughout the joint and squeeze air bubbles and excess cement out [19,33,40–42].

Some of the sources also revealed information on PMMA bonding defects, their possible causes, and remedies, sometimes displayed as troubleshooting guides [20,33,34,38,43,44]. The defects mentioned included those most recurrently identified during the survey such as bubbles, haziness, crazing, and joint separation, although the terminology used to classified them varied between sources.

Sources report *haziness* (also called cloudiness, whitening or haze) is caused by excessive moisture in atmosphere [18,34,38]. High humidity and low ambient or material temperature are said to produce cloudy or turbid joints due to moisture condensed from the air by the cooling effect of fast-evaporating cements, such as methylene dichloride. This phenomenon is associated to the use of solvents or the soak method [18,20,35]. According to literature, haziness can be avoided by increasing the ambient temperature, using a slower evaporating bonding material, or adding diacetone alcohol or glacial acetic acid to fast evaporating solvent or mixtures to reduce evaporation rate [20,35,43].

Regarding *bubbles,* sources report that their formation is primarily related to the bonding material properties and bonding process. Bubbles can be formed by entrapment of air either during the preparation of the bonding material (e.g. when mixing components) or during application of a viscous cement. Additionally, uneven surfaces holding small pockets of air or dirt can also form bubbles [34,38]. Bubbles can also occur with the soak/dip method, as solvents evaporate and the cushions shrink forming voids also called 'dry areas'. Dry or de-bonded areas can also be caused by inadequate pressure or poor fit of parts [34,38]. Furthermore, bubbles can be generated by monomer evaporation due to excessive heat during curing of some polymerizable adhesives [34].

Concerning crazing, (also referred as *stress-crazing/cracking*) [45], this phenomenon is the most frequent PMMA failure reported by manufacturers since the 1940′s. Crazing is described as a network of tiny fissures, generally developing in areas of high localized stresses. This phenomenon occurs in PMMA bonds as result of exposure to solvents or monomers able to attack the PMMA and release stresses present in the plastic unequally. It can occur immediately or over time [18,19,46]. Stresses can be introduced to the PMMA by molding or extrusion, machining and finishing (sawing, drilling, sanding, polishing), excessive pressure applied on the joint (e.g. by jig or clamps), or when joints are forced out of shape [20,34,38,46]. Cast PMMA is often mentioned to have better resistance to crazing than extruded [45,47].

Most of the bonding materials suggested by manufactures are said to cause crazing and therefore they always recommend to first anneal PMMA to avoid this defect [19]. The use of benzene, gasoline, acetone, carbon tetrachloride, xylene, toluene, alcohol, glacial acetic acid, and chloroform are sometimes highlighted as causes of crazing [6,18,48].

In addition, it is stated that polymerizable adhesives can cause crazing not only due to their ingredients, but also as a result of stresses caused by their shrinkage upon curing, or when the heat from or for curing softens the PMMA [34,36]. Furthermore, improper environmental conditions such as fluctuating relative humidity and low temperatures (below 18 °C) are also said to cause crazing [18,33,35].

On *joint separation* (de-attachment) sources highlight that this failure often occurs in low strength bonds. Bonds made with solvents are frequently mentioned as the weakest [21]. It is also said that poor joint strength in solvents bonds can be caused by the presence of too many bubbles or dry spots, shrinkage of the cushion, or by a too low ambient temperature that can reduce solvent action. Poor joints in polymerizable adhesives can also be caused by bubbles, low temperature, or improper mixing of their components [18,33]. Publications also report joint separation can be related to the presence of dirt or residues, delays between the application of the cement and bonding, uneven thickness of the cement, or uneven shrinkage [34].

Recreating PMMA bonds – mock-ups

Bonding materials

Bonding materials were chosen based on recommendations in the reviewed sources and products' availability. The following representative categories and products were selected:

- *Solvent Cements/Pure solvents*: Glacial acetic acid (GAA), Chloroform (CHL); Methylene Dichloride (MDC), Ethylene Dichloride (EDC), 1,1,2-Trichloroethane (TCA), 1,1,2-Trichloroethene (TCE);
- *Monomer-Solvent Cements*. One-component, low viscosity product: Weld-On 3;
- *Polymer-Solvent Cements*. One-component, high viscosity product: Weld-On 16;
- *Polymerizable adhesives*. Two-component, high viscosity products: Weld-on 40, Caseway PS-30. The one-component light curing product: Acryfix ® 1R 0192.

The chemical composition of these materials as reported by the manufacture and as analyzed for this study is presented in Table 1.

Although solvent mixtures were often recommended as Solvent cements, it was decided to restrict this study to the impact of individual solvents on PMMA. The physical properties of these solvents, relevant in bonding, are listed in Table 2 [49,50]. Regarding solvent power of these products, it was found that neither Hildebrand or Hansen solubility parameters, or the related Teas chart, correctly predicted their ability to solvate PMMA. Consequently, the data here reported on their solvent power on PMMA were defined based on solubility tests conducted in this study.

Mock-ups and open-face samples preparation

Mock-ups were made by bonding together PMMA pieces sawn from clear cast (Acrycast®, Calsak Co) and extruded (Acrylite® FF, CYRO) sheets, to evaluate the effect of bonding materials on both types of PMMA. Cast sheets were found by Size Exclusion Chromatography [51] to have an average molecular weight (MW) of 749,299 u, while extruded of 102,720 u.

PMMA pieces (each: 6.3 × 6.3 × 0.63 cm) were unannealed and their edges left unpolished as polishing could rounds corners, preventing the necessary fit, and may produce localized stresses [18].

Butt joint and full lap joint mock-ups were created (Fig.2). For assembling butt joints, a L-shaped jig was made as suggested [17].

Table 1
Bonding materials tested. Composition based on datasheet information and chemical characterization.

Type	Bonding Material	Composition (Datasheet Information)	Chemical characterization FTIR(f) Py-GC/MS(p)
Pure solvent	Glacial acetic acid (GAA)	acetic acid (ethanoic acid)	acetic acid (p)
	Chloroform (CHL)	trichloromethane	trichloromethane (p)
	Methylene dichloride (MDC)	dichloromethane	dichloromethane (p)
	Ethylene dichloride (EDC)	1,2-dichloroethane	dichloroethane (p)
	Trichloroethane (TCA)	1,1,2-trichloroethane	trichloroethane (p)
	Trichloroethene (TCE)	1,1,2-trichloroethene	trichloroethene (p)
Monomer Solvent	Weld-On 3	methyl methacrylate monomer (MMA) stabilized + MDC + TCE	MMA (p)
Polymer Solvent	Weld-on 16	acrylic synthetic resin + MMA + MDC + methyl acetate + methyl ethyl ketone (MEK)	PMMA (f) MMA (p) methyl acetate (p)
Polymerizable Adhesive	Weld-On 40	*Part A (90%):* acrylic synthetic resin +MMA *Part B (10%):* 10% benzoyl peroxide (catalyst) in dibutyl phthalate (DBP)	PMMA (f) MMA (p) DBP (p,f) EA (p,f) benzoic acid (benzoyl peroxide?) (p) unknown alkene (p)
	Caseway PS-30	*Part A*: MMA +2,2'-[(4-methylphenyl)imino] bisethanol +2-(2H-benzotriazol-2-yl)-p-cresol *Part B:* DBP (90-99%) +benzoyl peroxide (catalyst)	PMMA (f) MMA (p) DBP (p,f) *Part A:* MMA (p) MA (p) *Part B:* DPB (p) phthalic anhydride (p) unknown akane/alkene (p)
	Acrifix 1R 0192	acrylic copolymer +MMA	PMMA (f) MA (p) MMA (p)

Before bonding, masking tape was applied around bond edges, to confine softening by solvents and easily remove residues.

Mock-ups were prepared as most recommended in literature, using capillarity, soak, and glue methods. Capillarity and soak methods were used with low viscosity products (*Pure Solvents*, *Monomer-Solvent*). While the glue method was used with high viscosity products, also referred to as adhesives (*Polymer-Solvent, Polymerizable adhesives*).

For capillarity, a hypodermic syringe was chosen to dispense bonding materials along the joints. Pieces of wires were placed in the bond of lap joints to facilitate capillarity action and removed after the materials spread. For soaking, petri dishes were used to hold the low viscosity bonding materials and soak PMMA until the cushion was formed. Considering the discrepancy found in literature on soaking times, tests were performed using all different times suggested to find the optimal for each bonding material. Finally, the following soaking times were used: GAA 21 minutes, CHL 1 minute, MDC 30 seconds, EDC 3 minutes, TCA 5 minutes, TCE 41 minutes, Weld-On 3 3 minutes. After soaking, the two pieces were assembled and the joint gently held together for 60 seconds before applying pressure to not squeeze the cushion. However, since the aim of the work was to study defects, in a set of soaked mock-ups pressure was applied immediately to intentionally squeeze out the cushion.

For the glue method, the two-component adhesives were mixed and applied using a Teflon spatula. The two pieces were assembled, and pressure was manually applied to spread the adhesive and push out air bubbles.

Further pressure was applied on all type of mock-ups using lead shot filled plastic bag weights creating a pressure of 18 g/cm^2 as suggested [52]. Bonds were allowed to set for 24 hours before handling.

Mock-ups were made in a fume-hood creating two different environments (36% relative humidity at 23–26 °C; 60–75% relative humidity at 20–22 °C) to investigate if changes in humidity could cause hazy joints, as sources mentioned. Temperature and humidity were monitored using HOBO dataloggers.

Mock-up preparation was video-recorded to document and study any defect formation during bonding.

In addition to mock-ups, a set of open-face samples was made to easily examine changes on the PMMA surface specifically induced by solvents. Samples were prepared by soaking PMMA pieces in the

Table 2
Properties of the Pure Solvents tested.

Solvents	Chemical structure	Molecular Weight gmol^{-1}	Viscosity n(25 °C) mPa·s	Surface tension γ (25 °C)(*20C) mNm^{-1}	Boiling point °C	Vapor pressure at (25 °C) kPa	Evaporation rate g m^{-1} h^{-1}	Cooling rate kJ m^{-1} h^{-1}	Heat of vaporization ΔHv kJ gmol^{-1}	Solvent power on PMMA
Glacial acetic acid $C_2H_4O_2$ CAS # 64–19-7		60.1	1.1	27.1	117.9	2.13	187	130	41.7	Low
Chloroform $CHCl_3$ CAS # 67–66-3		119.4	0.5	26.7	61.2	26.2	4585	1205	31.4	High
Methylene dichloride CH_2Cl_2 CAS # 75–09-2		84.9	0.4	27.2	39.8	57.3	7125	2658	31.7	Very High
1,2-Ethylene dichloride $C_2H_4Cl_2$ CAS # 107–06-2		99.0	0.8	31.9	83.4	10.8	1557	524	33.3	High/Medium
1,1,2-Trichloroethane $C_2H_3Cl_3$ CAS # 79–00-5		133.4	1.2	34.0	113.0	9.2	1797	516	38.3	Medium
Trichloroethylene C_2HCl_3 CAS # 79–01-6		131.4	0.5	28.7*	86.8	9.2	1768	458	34.0	Very low

Evaporation rate calculated based upon vapor pressure [49], and Cooling rate is the product of the Evaporation rate and Heat of vaporization. All properties, except Evaporation rate, Cooling rate and Solvent power, from [50].

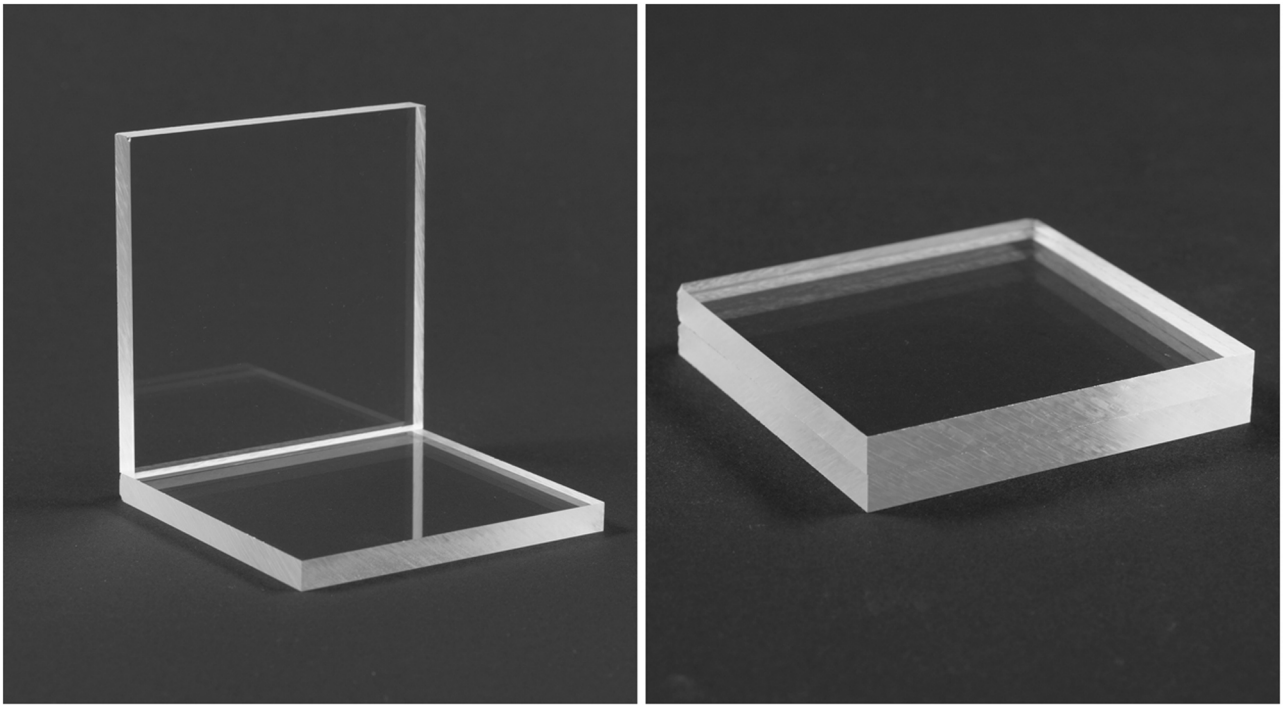

Fig. 2. Butt joint (left) and full lap joint/laminate (right) mock-ups.

low viscosity bonding materials, using the soaking times selected for the mock-ups, and leaving their soaked surfaces to air dry.

Chemical characterization

The composition of the bonding materials as supplied was determined using a 15x Cassegrain objective attached to a Bruker Optics, Inc. Hyperion 3000 FTIR microscope with a MCT detector, and purged with dry air, collecting 64 scans at a resolution of 4 cm^{-1}.

Some bonding materials were further investigated with an Agilent Technologies 5975C inert MSD/7890A GC/MS using an Agilent Thermal Sampling Probe and a Frontier Ultra ALLOY-5 capillary column. Helium carrier gas was flowed at 1.2 mL/minutes. The injector was ramped up from 50 °C to 450 °C at 900 °C/minutes followed by a 3-minute hold, then ramped down 25 °C/minutes to 250 °C and held for 40 minutes. Oven was ramped from 40 °C to 200 °C at 10 °C/minutes, followed by 6 °C/minutes to 300 °C.

Analytical results are reported in Table 1.

Thermal ageing

A set of mock-ups, bonded with each material and method, was thermally aged to investigate if haziness in joints can be induced after bonding by a humid environment, as observed in a previous

study [53]. Based on this study, mock-ups were aged in a Thermotron SM #27−8200 set to 40 °C and 95% humidity for 1000 hours (fluctuating from 88%to 95%). Their condition was examined every 125 hours in the first 500 hours, and at the end.

Optical microscopy

Mock-ups and open-face samples were examined in ring illumination, full and partial coaxial light using a Keyence VHX-6000 digital microscope at 20−500x magnification.

Scanning Electron microscopy (SEM)

SEM was used to closely examine the interaction between the PMMA and bonding materials. This allowed higher magnification than optical microscopy and removed any issue that imaging transparency can cause. Each open-face sample was sputtered with a nanolayer of gold-palladium alloy (Denton Desk II Cold Sputter/Etch), mounted on double-sided carbon tape on an aluminium stub, and further grounded with strips of copper tape. The metal coating was necessary for a crisp image but imparted a rough texture and some cracking visible at higher magnification. Samples were examined in a Zeiss Gemini 300, in secondary electron mode, under high vacuum, with 1−5 kV accelerating voltage, 1000−300,000x magnification, and 3.5–3.8 mm working distance.

Photoelastic stress analysis

Mock-ups were examined using the Sharples General Purpose Strain Viewer to visualize pre-existing stresses in the PMMA and/or caused by bonding, which may be a precondition for crazing and crack formation. Mock-ups were placed between two polarizing filters and a full wave tint plate and viewed in transmitted light. Stressed areas created visually distinct interference patterns, providing information about the distribution and concentrations of stresses.

Results and discussion

The main recurring bonding defects found during the surveys also appeared in the mock-ups, except for 'joint separation' which did not occur in any of the bonds prepared in the lab.

Some of the bonding defects were more recurrent and pronounced in the extruded PMMA mock-ups than the cast. This may be in part due to the lower molecular weight of the extruded PMMA and therefore its lower chemical resistance to the bonding materials used [54]. An overview of the main defects observed in the mock-ups are showed in Table 3.

Unaged bonded mock-ups and open-face samples

The most recurrent defects were voids at the bonding interface, especially bubbles, due to the bonding procedures used and/or to the properties of the bonding materials, as literature suggested. This was also observed in the videos recorded during the bonding process in which bubbles were seen primarily to be formed by inclusion, entrapment, or infiltration of air, and/or by gas generated during the evaporation of solvent or monomer displacing the liquid bonding material.

The soak method produced mock-ups with the most substantial voids. Specifically, type and number of voids were found to be related to solvent evaporation rate and solvent power on the PMMA. Fast evaporating solvents (MDC > CHL > EDC) and bonding materials containing them (Weld-On 3) frequently generated bubbles which remained entrapped at the bond interface. In some cases, the quick evaporation of solvents also left part of the soaked surface/cushion dry, not allowing a complete intermingling of the surfaces, creating unbonded portions called in literature 'dry areas' or spots. During soaking, dry areas were also formed when excess or uneven pressure was applied to the cushion. Moreover, soaking times suggested in literature were often too long for bonding materials with high solvent power (MDC > CHL > EDC), causing dissolution of the PMMA surface, instead of its swelling. This created large depressions in the surfaces by the removal of PMMA.

Mock-ups made with the capillarity method, generally showed fewer or no voids. The formation of voids primarily occurred when the bonding material was not able to spread uniformly, trapping air into the joint (bubbles) or leaving dry spots. Specifically, the bonding materials' flow was impeded by presence of impurities, uneven surfaces, imperfect fit of parts, and in some cases by high solvent power of the bonding material. Regarding the latter, it was observed that bonding materials with higher solvent power tends to immediately interact with the plastics swelling shut the PMMA faces, impeding the flow throughout the rest of the bond, resulting in dry spots when the space between pieces is small and the bond interface large (e.g. lap joints with CHL, MDC). While bonding materials with low solvent power generally tend to form joints free of voids regardless bond interfacial dimension (e.g. GAA, TCA, TCE).

Mock-ups made with the glue method, showed the fewest and smaller voids, except with the solvent based adhesive Weld-On 16 and Acryfix 1R 0192. With polymerizable adhesives, bubbles seemed to be caused by air entrapped during the mixing, during application of the adhesive or, as mentioned in literature, they might have been generated by the evaporation of monomer. Dry spots were also sometimes observed at mock-ups corners due to improper adhesive spreading.

Comparing all mock-ups, it was also noticed that bubbles can show differences in depth depending upon the bonding material used. Bubbles in mock-ups bonded with low solvent power materials generally appeared flat (e.g. GAA), while bubbles from higher solvent power materials were deeper (e.g. CHL). With CHL, bubbles often had characteristic crater-like rings with a depression in the middle, regardless of the bubbles' size (Fig. 3). These structures are generated during solvent evaporation when the dissolved polymer flows out with the solvent and is finally deposited at the rim, as described in macromolecular literature [55]. The shape of the evaporation structures is primarily determined by the dissolution of polymer, solvent evaporation-driven flow, diffusion of dissolved polymer molecules, and polymer swelling. Depending of which of these processes dominates different topologies can be formed. Generally, if the evaporation-driven flow dominates, crater-like structures prevail.

Moreover, regardless of material and method used, very common in each type of bonded mock-ups was the presence of air bubbles entering from the bonds edges, showing a variety of patterns. This bubbles formation, recurrently observed during the surveys, occurred when non-uniform pressure was applied during bond setting. While the formation of different patterns can be attributed to a fluid dynamics phenomenon known as 'Saffman-Taylor instability', 'fingering instability' or 'viscous fingering' which is the unstable displacement of a more viscous fluid by a less viscous fluid. Specifically, when a low-viscosity fluid (air) enters into a space containing a high-viscosity fluid (bonding material), the low-viscosity fluid will begin to form fingers as it moves through the more viscous one. Depending on the contained space and the fluids involved, the finger-like pattern can have different shapes [56,57] (Fig. 4). Over time fingering instability can also develop in the de-bonding of pieces joined by adhesives [58,59].

Another defect recreated in the bonded mock-ups was crazing. This phenomenon, recurrently stated by manufactures' sources as the most frequent PMMA failure, has also been extensively dis-

Table 3
Overview of main defects observed in the PMMA mock-ups (butt and lap joints).

		Capillarity Method		Soaking Method	
		Cast PMMA	Extruded PMMA	Cast PMMA	Extruded PMMA
Pure Solvent	Glacial acetic acid (GAA)	Crazes	**Crazes** *Micro-crazes*	**Crazes**	*Bubbles* **Crazes** *Micro-crazes*
	Chloroform (CHL)	Dry spots Micro-crazes Hazy spots (clouds)	Bubbles **Micro-crazes** **Hazy spots (clouds)**	**Bubbles** **Dry spots** Micro-crazes Hazy spot (clouds) Hazy flat patch	**Bubbles** **Dry spots** Micro-crazes **Hazy spots (clouds)** **Hazy flat patch**
	Methylene dichloride (MDC)	Bubbles *Dry spots* *Crazes* Hazy spots (clouds)	*Bubbles* **Micro-crazes** **Hazy spots (clouds)**	**Bubbles** **Dry Spots** Crazes Micro-crazes **Hazy spots (clouds)** **Hazy flat patch**	**Bubbles** **Dry Spots** Crazes **Micro-crazes** **Hazy spots (clouds)** **Hazy flat patch**
	Ethylene dichloride (EDC)	**Bubbles**	**Bubbles** **Micro-crazes** **Hazy spots (clouds)**	**Bubbles** Dry spots Micro-crazes Hazy spots (clouds)	Bubbles Dry spots **Micro-crazes** **Hazy spots (clouds)** Hazy flat patch
	Trichloroethane (TCA)		**Micro-crazes** **Hazy spots (clouds)**	Bubbles Micro-crazes Hazy spots (clouds) Hazy flat patch (after ageing)	Bubbles Micro-crazes Hazy spots (clouds) *Hazy flat patch*
	Trichloroethene (TCE)	*Crazes*	Micro-crazes Hazy spots (clouds)	*Micro-crazes*	Micro-crazes Hazy spots (clouds)
Monomer Solvent	Weld-On 3		Micro-crazes Hazy spots (clouds)	**Bubbles** **Dry spots** **Crazes** Micro-crazes **Hazy flat patch**	**Bubbles** **Dry spots** **Crazes** **Micro-crazes** **Hazy spots (clouds)** **Hazy flat patch**
		Glue Method			
		Cast PMMA	Extruded PMMA		
Polymer Solvent	Weld-On 16	Bubbles Hazy spots (clouds) Hazy flat patch	**Bubbles** Micro-crazes Hazy spots (clouds)		
Polymerizable Adhesive	Weld-On 40	Bubbles Hazy spots (clouds)	Bubbles		
	PS-30	**Bubbles** Crazes Hazy flat patch (after ageing)	Bubbles Hazy spots (clouds)		
	Acrifix 1R 0192	*Bubbles* Micro-crazes Hazy spots (clouds)	**Bubbles** **Micro-crazes** **Hazy spots (clouds)**		

Bold is for those most extensive and recurrent, Regular is for those that are common, and *Italic* is for uncommon.
The table does not include air bubbles entering from the bonds edges as they are related to the geometry of the sample and the bonding pressure and are not intrinsic to the bonding materials or the methods used to apply them.

cussed in polymer engineering and science literature, even though some of its aspects are still unclear. Crazing is defined as a mode of plastic deformation or an underlying mode of fracture which involves the formation of crazes. Crazes are narrow zones of plastically deformed and highly voided material (40–60%) bridged by fine (5–30 nanometer diameter) polymeric fibrils. In transparent PMMA, crazes appear as fine silvery or white lines, depending on the angle of observation, due to the reflection of light off the voided areas. As a craze grows in width, this fibril structure may break down, leading to a crack [60,61]. Therefore, crazes can be distinguished from cracks when there is no noticeable separation (visible and tactile) of the fracture faces. Crazing can be caused by stresses alone, or by the synergistic action of stresses and contact with specific fluids, commonly referred to as 'Environmental Stress Crazing / Cracking' (ESC) [62] and it is known to occur frequently in PMMA bonds [7,8,63]. Stresses and strain can be internal, introduced during manufacture or external, due to mechanical load during bonding [section 3.1.1]. These areas of localized stresses in PMMA can enhance the absorption of certain fluids (e.g. solvents, monomers, catalysts or plasticizers contained in bonding materials and even water in the atmosphere) which locally plasticises the polymer and reduces its yield strength, allowing the local release of

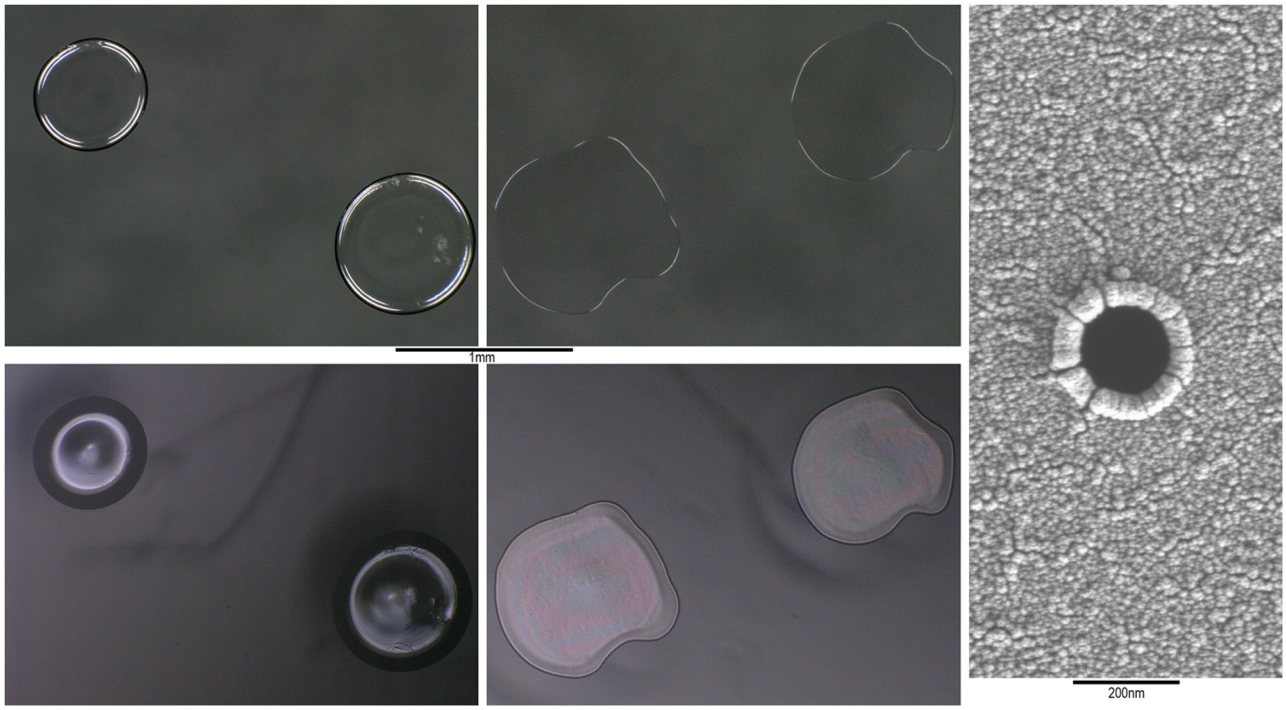

Fig. 3. Flat bubbles in mock-ups bonded with GAA (left column), deeper bubbles with CHL (center column). Bubbles in CHL showing crater-like rings with depression in the middle, visible in coaxial light (bottom center) and in an SEM image of an open-face sample (right column, texture and cracks due to sputtered coating).

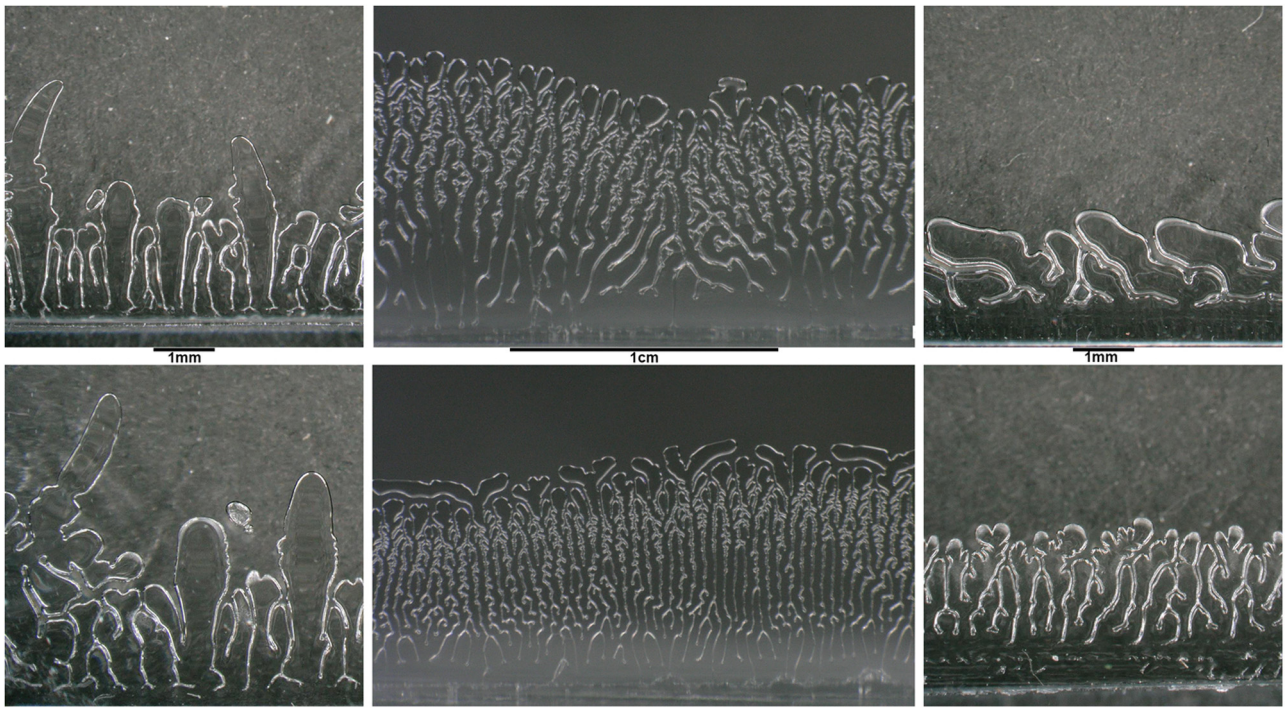

Fig. 4. Air bubbles entering from the edges of bonds made with CHL, GAA, and EDC showing different shapes due to Saffman-Taylor instability.

stresses thought deformation/yielding and craze formation. Type and amount of stresses, the chemical composition of the fluids, their MW, their concentration in which they are absorbed by the polymer, their retention in the bond, and how long the plastic is exposed to them are some of the factors that play a role in the crazing formation and grow [62,64]. Because low molecular weight fluids (e.g. solvent and monomer residues) can stay in cured adhesive joints over long period of time, time-delayed crazing can occur.

In the mock-ups, as in the surveyed objects, two forms of crazing were observed. The first one occurred at the joint interface, along the edges as well as in the middle, and was especially recurrent in mock-ups bonded using glacial acetic acid, which was highlighted in literature as a potential cause of crazing. It occurred particularly when the soak method was used.

This form of crazing consisted of crazes on the order of millimetres, often visible as parallel lines. Additionally, in cast PMMA

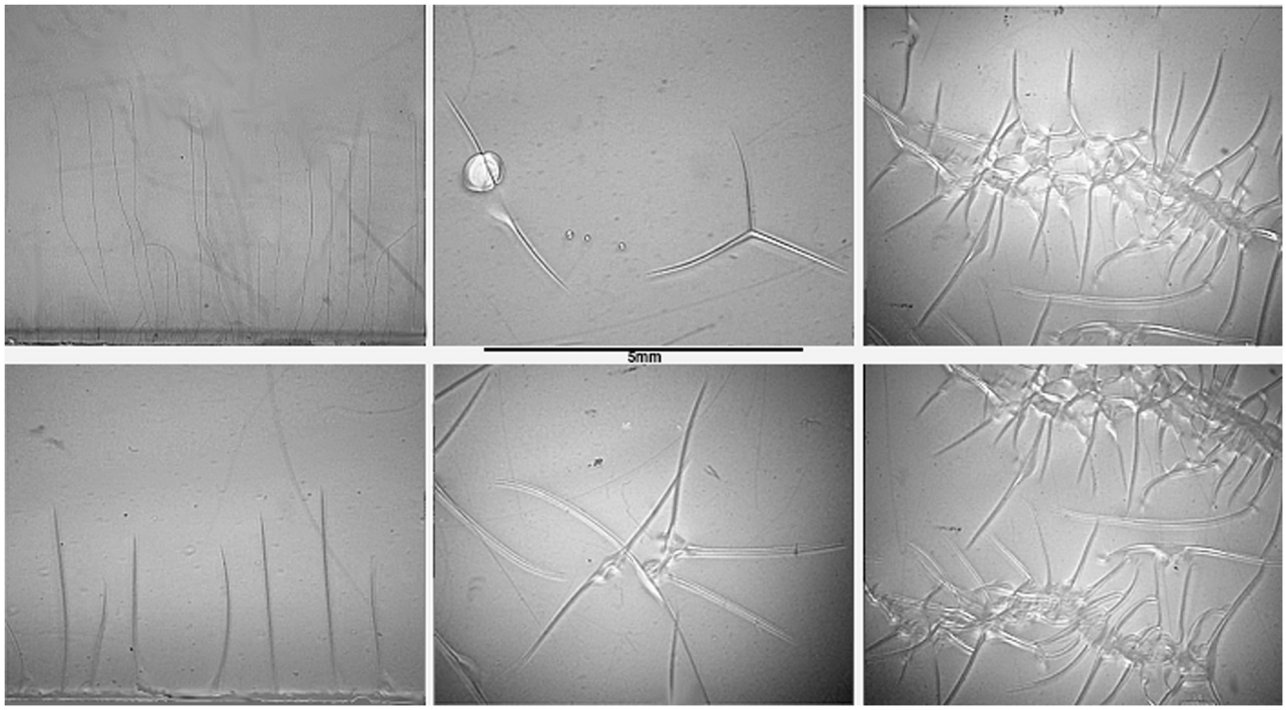

Fig. 5. Mock-ups bonded by soaking with GAA showing crazing: parallel crazes in extruded (top, left column) and cast PMMA (bottom, left column); random crazes developing in star-like patterns (center column) and chain-like structures (right column) in cast PMMA.

mock-ups, more toward the center of the interface, crazes frequently developed with other orientations. These crazes radiated from a single spot forming a star-like pattern (with three or more points) that in some cases further developed over years into a chain-like structures, radiating crazes (Fig.5).

The second form of crazing developed in mock-ups made with all bonding materials months after bonding, except with GAA (solvent with the lowest molecular weight) in which it started to appear only after two years. It occurred more frequently and extensively in extruded PMMA mock-ups than cast. This form of crazing consists of micro-crazes on the order of micrometres which only developed at the joint interface, from bond edges or dry spots. Microscopic observations of mock-ups revealed that this form of crazing may grow and even change patter over time. It initiates as branched micro-crazes with silvery bush-like patterns, which often develop forming a densely packed three-dimensional structure of branched micro-crazes with a white cloud-like pattern (Fig.6). At the naked eye, this latter pattern appears as hazy spots due to scattering of light of the very densely packed micro-crazes. These clouds were observed in the museum objects surveyed and were initially classified as a form of haziness (hazy spot with cloud-like pattern), before microscopic exanimation of the mock-ups revealed that they were in fact a form of crazing.

It is important to mention, that although this particular form of crazing evolving in a cloud pattern seems to be a recurrent defect in museum objects, its morphology, formation and causes are not previously reported in the extensive literature on the subject.

Beyond the cloud-like pattern, the other form of haziness observed in the museum objects consisting in hazy flat patches/areas with undefined outlines were also reproduced in the mock-ups.

This type of haziness occurred primarily on bonded mock-ups and open-face samples made with the soak method, and in a few mock-ups bonded by the glue method with solvent-based adhesive Weld-On 16. In the soaking method this haziness was pronounced and common with MDC and the monomer-solvent containing it (Weld-On 3), less with CHL and EDC, and minimally with TCA. No haziness of this type was observed with GAA and TCE. Haziness appeared on the PMMA surface, immediately after the soaked piece, or the piece covered with the adhesive (Weld-On 16), was exposed to air, before bonding.

Microscopic examinations showed that what to the naked-eye appeared as hazy patches/areas are actually dense agglomerations of micro-voids in the surface. These micro-voids scatter the light so that what the eye perceives is a white surface, rather than transparent.

According to some of the sources reviewed, haziness can be caused by the condensation of water on the plastic surface due to fast evaporating solvents. Condensation of water vapor occurs when the temperature is lowered to the dew point of air. Therefore, to investigate if the evaporation of solvents was cooling the plastic to the dew point, a PMMA piece soaked in MDC was measured at its surface with a thermocouple. The temperature detected while MDC was evaporating and the PMMA surface turning hazy was -2 °C, far below the dew point (7.8 °C), proving that water was condensing on the plastic.

This can explain the presence of micro-voids on the PMMA surface as condensed water droplets are known to be able to sink into solvent swollen PMMA leaving voids on its surface after water droplets and solvent evaporate [65] (Fig.7). This phenomenon is referred to in the coating industry as blushing or solvent blushing.

SEM examination of the soaked PMMA surfaces confirmed that haziness on each sample consisted of micro-voids. Specifically, haziness/micro-voids appeared in soaked samples in proportion with the solvent evaporation and cooling rate. However, this examination showed that solvent power also plays a role. Voids formation is a combination of the number of water droplets condensed on the surface and how deeply water can penetrate the plastic due to the power of the solvent to soften the PMMA.

As evaporation and cooling rates as well as solvent power increase (e.g. MDC, EDC, CHL) more numerous, deeper, and larger voids were observed in the PMMA surface, whereas when these properties are sufficiently low (eg. TCE, GAA) no micro-voids (haziness) were detected (Fig. 8).

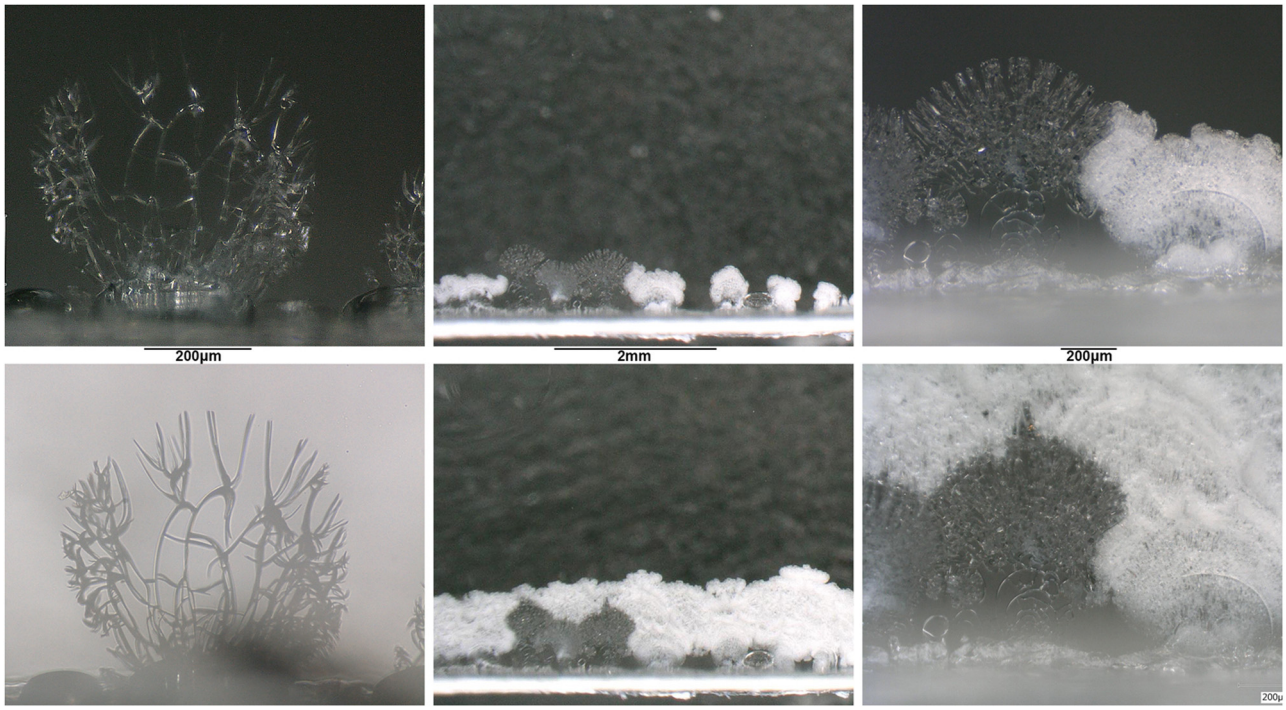

Fig. 6. Bush-like micro-crazes in normal (top, left column) and coaxial light (bottom, left column) in extruded mock-ups bonded with Weld-On 16. Bush-like micro-crazes developing to a cloud-like pattern over time in extruded mock-up bonded by soaking with CHL: four months after bonding (center column), and two years after bonding (right column).

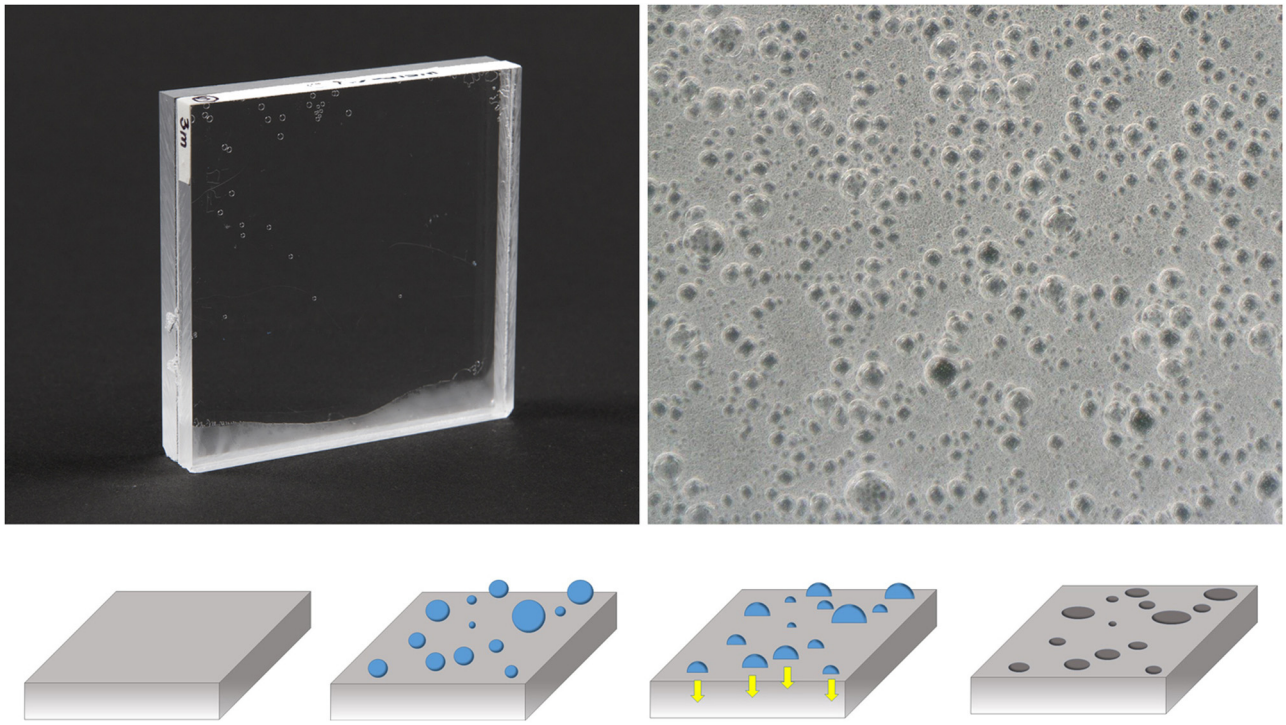

Fig. 7. Haziness in extruded PMMA mock-up bonded with soaking method using MDC (upper left) and detail showing dense agglomeration of micro-voids (upper right). Diagram showing void formation during "solvent blushing" (bottom row, left to right): PMMA soaked sample, condensed water droplets on PMMA surface, water droplets sinking into swollen PMMA, voids on PMMA surface after water droplets and solvent evaporate.

Mock-ups bonded in higher humidity did not display any additional defects compared to those bonded at lower RH. However the humidity ranges used were quite narrow, therefore it cannot be excluded that higher relative or absolute humidity values will cause haziness during bonding.

Photoelastic stress analysis revealed tiny interference patterns in all mock-ups indicating the presence of stress areas along and inside the PMMA bonds carried with all materials.

Generally, the highest level of stresses were noticed in bonds made with solvents, or bonding materials containing them (Weld-

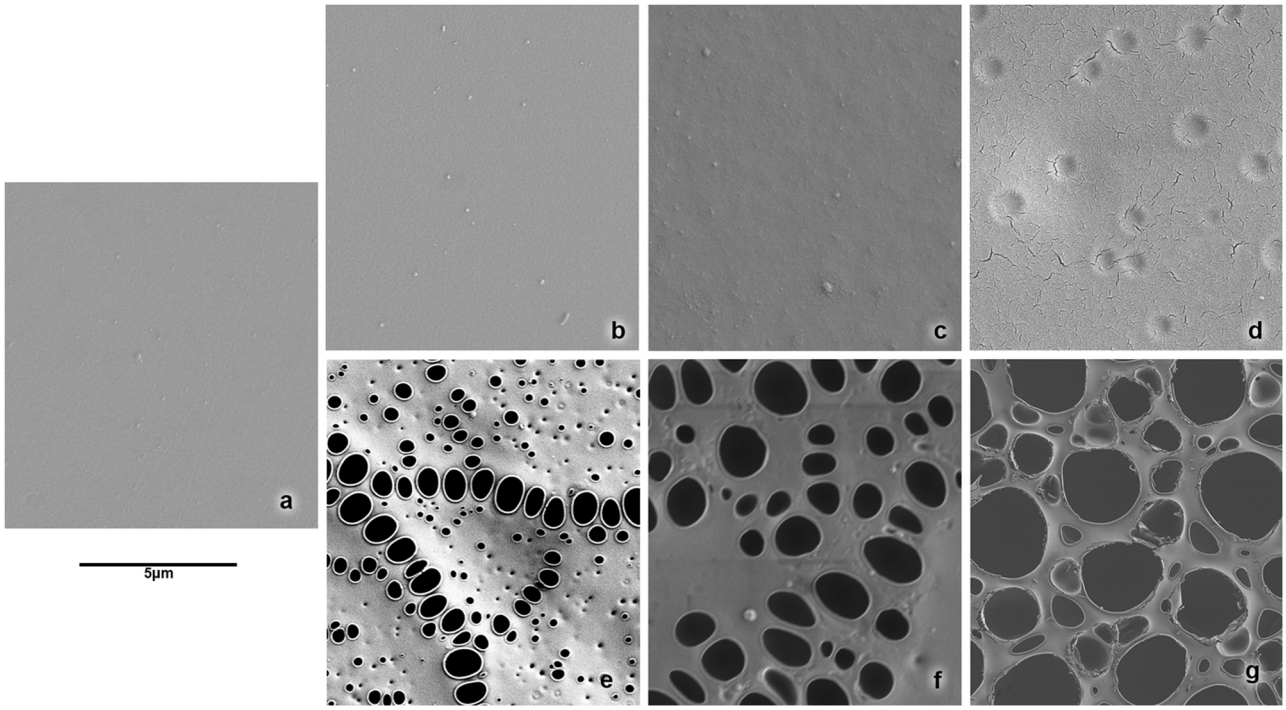

Fig. 8. SEM images of cast PMMA open-face samples: untreated (a), and soaked in TCE (b), GAA (c), TCA (d), CHL (e), EDC (f), MDC(g). (Cracks on d-g are in the sputtered coating).

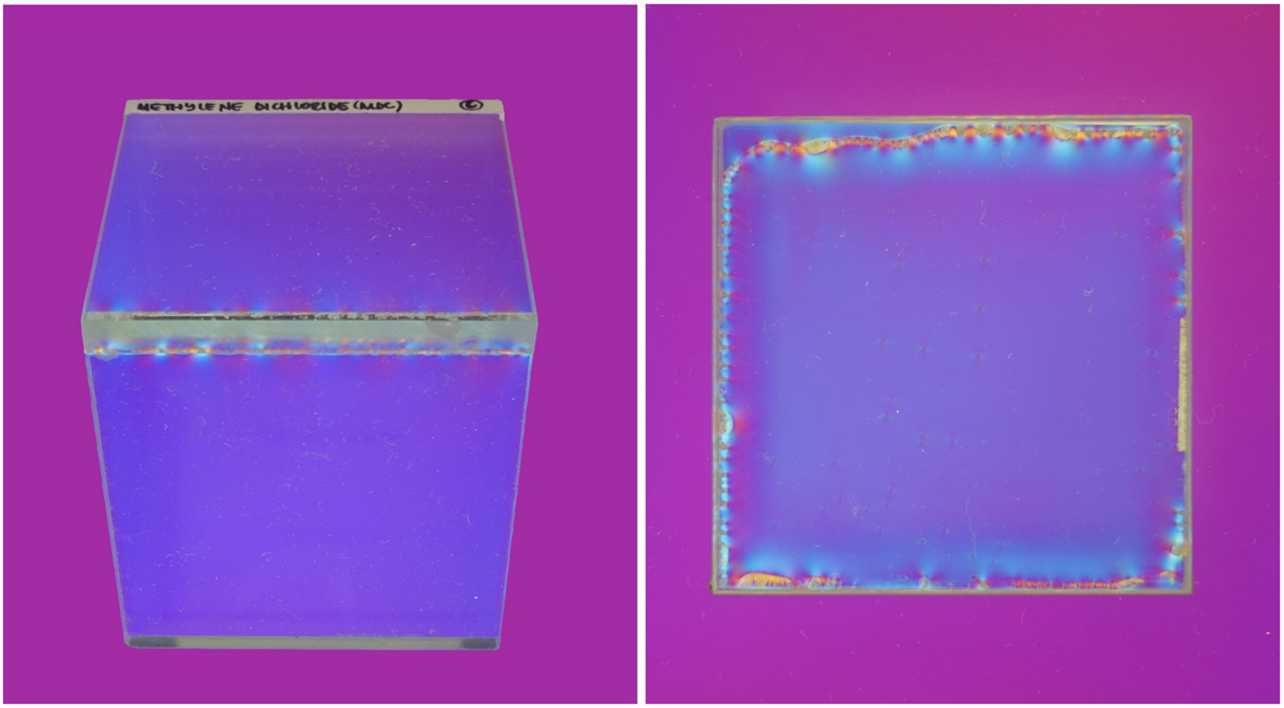

Fig. 9. Extruded PMMA mock-ups made with MDC examined with Sharpless Strain viewer, showing interference patterns (stresses) along white clouds (micro-crazing). Butt (left) and lap joint (right).

On 3 and 16). Within the pure solvents, MDC, CHL, EDC, and GAA generated the most pronounced interference patterns; CHL and MDC particularly in the extruded PMMA, and GAA and TCE in the cast. Stresses were often greater in bonds made with capillarity. Moreover, stresses were particularly pronounced in proximity to white clouds (micro-crazing), especially in the extruded mock-ups (Fig. 9).

Thermally aged bonded mock-ups

Thermal ageing confirmed that haziness can also develop in bonds over time due to an improper environment. Hazy flat patches/areas were observed to develop at the de-bonded corners of mock-ups made with TCA and the adhesives Caseway PS-30. In previous studies it was observed that in bonds made

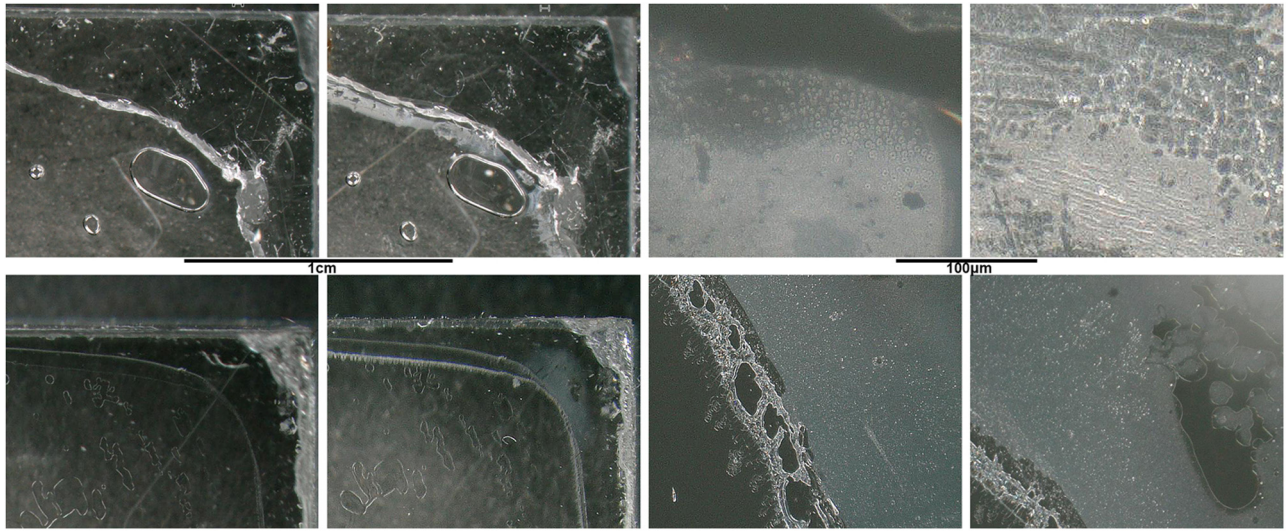

Fig. 10. Corners of mock-ups bonded with Caseway PS-30 (upper row) and TCA (lower row). From left to right: corner before ageing, after ageing showing the developing haziness along de-bonded areas, and details of micro-structures in hazy areas.

with polymerizable acrylic adhesives, high humidity can cause micro-cracks in the adhesive layer by water absorption and desorption which result in hazy areas [53]. In this experiment we could observe some rounded features (bubbles-like) in mock-ups made with both bonding materials, and few micro-cracks in the adhesives ones (Fig.10). However, the nature of the haziness reproduced in the mock-ups was difficult to assess based on optical microscopy and not possible to investigate with SEM as it occurred in between the bonded PMMA pieces rather than on an exposed surface.

Conclusions

Through this study, the main recurrent defects in bonded PMMA museum objects were identified: bubbles, haziness, crazing, and joint separation. These defects, with the exception of joint separation, were successfully recreated in the lab. The majority of those occurred during bonding, with the exception of the cloud-like micro-crazing which was found to slowly developing over time, and the haziness caused by high humidity.

Literature review of trade, craft, and industrial sources provided a comprehensive overview of the main techniques and materials suggested over time for the bonding of transparent PMMA. The review was key to the historical accuracy of the PMMA bonded mock-ups, which led to the recreation of the same defects of those observed in museum objects, indicating that the bonding materials and techniques used were most likely the same.

Additionally, the information provided in these sources directed this study towards the investigation of specific materials and methods as the cause of bonding defects which led to further research into physics and macromolecular literature, allowing a better understanding of each defect formation mechanism. Often these mechanisms cannot be identified by eye as the defects are the result of micro-voids or micro-crazing and therefore it was found that microscopy and SEM are fundamental to understanding the true morphology and causes of these defects' formations.

Finally, although all the bonding materials examined here are frequently recommended to artists, craftsmen, and designers by manufactures and plastics bonding literature, this work demonstrated that every one of these materials can cause defects and damages immediately or over time.

Further research

The second part of this study will focus on the examination, analysis and comparison of the bonding defects reproduced in the reconstructed mock-ups and those of the most representative objects surveyed in museum collections. This will also include the development of a PMMA Bonding Defects Atlas to provide conservators a tool to easily recognize and classify bonding issues in PMMA museum objects.

Additional research to further assess the specific physical and chemical mechanisms of cloud-like micro-crazing and the haziness caused by thermal ageing would be needed to fully understand these novel phenomena, however they are beyond the scope of this research project.

Acknowledgements

Authors thank Ella Hendriks (UVA), Thea van Oosten, Tom Learner (GCI), Anna Flavin (GCI) and David Carson (GCI) for their precious support. Our gratitude goes to Ron Kievits (RCE), Netta Krumperman (SMA), Denise van der Vegt (SMA), Sandra Weernderburg (SMA), Rebecca Timmermans (SMA), Iolanda Ratti (Museo Novecento), Luciana Tozzi (GNAM) for making the condition survey possible and for their wonderful collaboration. Many thanks also to Joy Mazurek (GCI) for molecular weight analysis, providing valuable help to this study.

Références

[1] S. Katz, Plastics, in: Designs and Materials, Studio Vista, London, 1978, pp. 91–99.
[2] S. Katz, Classic plastics, in: From Bakelite to High-Tech, Thames and Hudson, London, 1984, pp. 98–114.
[3] S. Mossman, Early plastics, in: Perspectives: 1850-1950, Leicester University Press, London, 1997, pp. 59–60.
[4] J.A. Brydson, Plastics materials, in: Butterworth-Heinemann, Oxford, 1999, pp. 398–424.
[5] C. Bunch, Acrylic for Sculpture and Design, Van Nostrand Reinhold Company, New York, 1972.
[6] T.R. Newman, Plastics As Design Form, first ed., Chilton Book Co., Philadelphia, 1972, pp. 161–211.
[7] D. Sale, An evaluation of eleven adhesives for repairing poly(methyl methacrylate) objects and sculpture, in: Saving the Twentieth Century: The Conservation of Modern Materials: Proceedings of a Conference Symposium 91, Ottawa: Canadian Conservation Institute, 1993, pp. 325–340.
[8] Y. Shashoua, Conservation of Plastics: Materials Science, Degradation and Preservation, Butterworth-Heinemann, Oxford, 2008, pp. 151–190, 213-219, 271-274.
[9] A. Laganà, T. Van Oosten, Back to transparency, Back to life. Research into the restoration of broken transparent unsaturated polyester and poly(methyl methacrylate) works of art, in: ICOM-CC 16th Triennial Conference Preprints, Lisbon, 19–23 September 2011, Lisbon, 2011, pp. 1–9.
[10] D. Sale, Yellowing and appearance of conservation adhesives for poly(methyl methacrylate): a reappraisal of 20-year-old samples and test methods, in: Proceedings of Symposium 2011 – Adhesives and Consolidants for Conservation: Research and Applications, Ottawa: Canadian Conservation Institute, 2011, pp. 1–19.
[11] J.L. Down, Adhesive Compendium for Conservation, Canadian Conservation Institute, Ottawa, 2015, pp. 24.
[12] A. Laganà, M. Doutre, M. David, M. Lukomski, E. Hendriks, M. van Bommel, In search of a perfect bond: An evaluation of potential adhesives to repair transparent poly(methyl methacrylate) objects, in: J. Bridgland (Ed.), Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, Paris: International Council of Museums, 2021.
[13] A. Quye, C. Williamson, Plastics, in: Collecting and Conserving, NMS Publishing Limited, 1999, pp. 111–135.
[14] F. Waentig, Plastics in art, in: A Study from the Conservation Point of View, Michael Imhof Verlag, Petersberg, 2009, pp. 271–278.
[15] Preservation Of Plastic ARTefacts in Museum Collection, n.d., Collection Survey. Damage Atlas, 2020, accessed October 12 2020, <http://popart-highlights.mnhn.fr/collection-survey/damage-atlas/index.html>.
[16] E. I. du Pont de Nemours & Company, 'Lucite' Aicraft Manual, N.J: E.I. du Pont de Nemours & Co., Plastics Dept., Arlington, 1942, pp. L1–L8.
[17] Rohm and Haas Company, Working with Plexiglas, in: A Manual for the School Shop, Home Craftsman, Occupational Therapist, Rohm and Haas Company (distributed by Studio Publications), New York, 1947, pp. 28–30.
[18] Rohm and Haas Company, Plexiglas, in: Design and Fabrication Data, Rohm and Haas Company, Philadelphia, 1964, pp. 2–15.
[19] Imperial Chemical Industries, 'Perspex' Acrylic Materials. Cementing, Imperial Chemical Industries Limited, Plastics Division, Hertz, 1964, pp. 2–13.
[20] Rohm and Haas Company, Plexiglas® design, and fabrication data, in: PL-7L, Cementing Plexiglas, Rohm and Haas Company, Philadelphia, 1976, pp. 3–30.
[21] Imperial Chemical Industries, 'Perspex' Acrylic Materials Part 3 Cementing, Imperial Chemical Industries Limited, Plastics Division, Hertz, n.d., pp. 5-23.
[22] E. I. du Pont de Nemours & Company, 'Lucite' Acrylic Resin Manual, N.J: E.I. du Pont de Nemours & Co., Plastics Dept., Arlington, 1948, pp. 47–54.
[23] Imperial Chemical Industries, 'Perspex' Acrylic Materials, Imperial Chemical Industries Limited, Plastics Division, Hertz, 1959, pp. 22–24.
[24] Craftics Inc, Fabrication Manual for Working with Acrylic, Plexiglas, Lucite Acrylite, Craftics Inc., Chicago, 1979, pp. 22–26.
[25] Lucite International Inc., Lucitelux. Fabrication Guide, Lucite International Inc., n.d., pp. 16-19.
[26] M. Zahn, Millicent Zahn Book of Plastics Craft, Van Nostrand Reinhold Co, New York, 1973, pp. 9–23.
[27] M.J. Troughton, Handbook of Plastics Joining: A Practical Guide, William Andrew Inc., Norwich, NY, 2008, pp. 215–223.
[28] Rohm and Haas Company, Plexiglas: Fabricating Manual for Plexiglas Sheets and Rods, 9th ed., Rohm and Haas Company, Philadelphia, 1943, pp. 23–29.
[29] Cadillac Plastic and Chemical Company, How to Work With Plexiglas, Cadillac Plastic and Chemical Company, Detroit, 1961, pp. 14–16.
[30] Imperial Chemical Industries, 'Perspex' acrylic sheet, in: A Workshop Handbook. PX 132, 2nd ed., Imperial Chemical Industries PLC, 1986, pp. 27–32.
[31] Imperial Chemical Industries, Perspex' acrylic sheet, in: "Tensol"Cements for "Perspex" Acrylic Sheets. Description, Techniques and Safety Information. PX 128, 6th ed., Imperial Chemical Industries PLC, 1987, pp. 5–17.

[32] Imperial Chemical Industries, 'Perspex' acrylic materials, in: Cementing, Imperial Chemical Industries Limited, Plastics Division, Hertz, 1966, pp. 4–13.
[33] Rohm and Haas Company, Plexiglas Design and Fabrication Data PL-7j, Rohm and Haas Company, Philadelphia, 1973, pp. 3–29.
[34] Evonik Industries, Joining Plexiglas, in: Guidelines for Workshop Practice, Evonik Rohm GmbH, 2019, pp. 4–23.
[35] Altuglas International Arkema, Plexiglas by Arkema, in: Acrylic Sheet Fabrication Manual, Altuglas International Arkema, 2006, pp. 19–28.
[36] E.I. du Pont de Nemours & Company, Du Pont 'Lucite' Acrylic Resin, N.J: E.I. du Pont de Nemours & Co., Plastics Dept., 1949, pp. 37–40.
[37] Rohm and Haas Company, Do It Yourself With Plexiglas Acrylic Sheet, Rohm and Haas Company, Philadelphia, 1971, pp. 12–13.
[38] Quinn-Plastics, Technische Information, n.d., pp. 1-16.
[39] Rohm and Haas Company, Fabrication of Plexiglas, Rohm and Haas Company, Philadelphia, 1959, pp. 13–15.
[40] Rohm and Haas Company, Plexiglas. Craftsman's Handbook, Rohm and Haas Company, Philadelphia, 1953, pp. 1–33.
[41] A. Harness, The Story of Perspex, Loughborough University of Technology, Loughborough, 1986, pp. 16.
[42] Evonik Industries, Fabricating tips for Plexiglas solid sheets, in: Guideline for Workshop Practice, 2010, pp. 10–11.
[43] The Plastic Distributor & Fabricator, Solvent Cementing, The Plastic Distributor & Fabricator, 2017.
[44] Altuglas International Arkema, *Plexiglas Sheet: Cementing and Troubleshooting*, Altuglas International Arkema, n.d.
[45] Lucite International, Perspex, in: Workshop Handbook, Lucite International UK LTD, 2005, pp. 4–24.
[46] Altuglas International Arkema Group, Altuglas, in: Cast and Extruded Sheet. Technical Brochure, Altuglas International Arkema Group, 2006, pp. 9.
[47] Rohm and Haas Company, Plexiglas: Methods of Installation, Rohm and Haas Company, Philadelphia, 1944, pp. 7–8.
[48] Rohm and Haas Company, Plexiglas, in: Acrylic Plastic. Instruction for Handling, Storage, Fabricating, Polishing, Cleaning. PL-80a, Rohm and Haas Company, Philadelphia, 1952, pp. 8.
[49] D. MacKay, I. van Wesenbeeck, Correlation of chemical evaporation rate with vapor pressure, in: Environmental Science and Technology, Washington Dc., 2014, pp. 10259–10263, <https://doi.org/10.1021/es5029074>.48, 17.
[50] J. Rumble (Ed.), CRC Handbook of Chemistry and Physics, 98th ed, CRC Press LLC, Boca Raton, 2017.
[51] J. Mazurek, A. Laganà, V. Dion, S. Etyemez, C. Carta, M.R. Schilling, Investigation of cellulose nitrate and cellulose acetate plastics in museum collections using ion chromatography and size exclusion chromatography, J. Cult. Herit. 35 (2019) 263–270.
[52] Perspex®, in: Creatively Inspired. Solution Driven. Cementing' Perspex' And Extruded Acrylic, 2014, pp. 7.
[53] R.S. Court, M.P. Sutcliffe, S.M. Tavakoli, Ageing of Adhesively Bonded Joints-Fracture and Failure Analysis Using Video Imaging Techniques, Int. J. Adhes. Adhes. 21 (2001) 455–463.
[54] B.A. Miller-Chou, J.L. Koenig, A review of polymer dissolution, Prog. Polym. Sci. 28 (8) (2003) 1223–1270.
[55] L. Guanfen, K. Graf, E. Bonaccurso, D.S. Golovko, A. Best, H.-J. Butt, Evaporation structures of solvent drops evaporating from polymer surfaces: influence of molar mass, Macromolecular Journals, Macromol. Chem. Phys. 208 (2007) 2134–2144.
[56] D. Bonn, H. Kellay, M. Bräunlich, M. Ben Amar, J. Meunier, Viscous fingering in complex fluids, Phys. A Stat. Mech. Its Appl. 220 (1995) 60–73.
[57] J.R. Fanchi, Fluid properties and model initialization, in: Principles of Applies Reservoir Simulation, 4th ed., 2018, pp. 108, chapter 6.
[58] J. Nase, C. Creton, O. Ramos, L. Sonnenberg, T. Yamaguchi, A. Lindner, Measurements of the receding contact angle at the interface between a viscoelastic material and a rigid surface, in: *the royal society of chemistry* 2010, Soft Matter 6 (2010) 2685–2691.
[59] J. Nase, D. Derks, A. Lindner, Dynamic evolution of fingering patterns in a lifted hele-shall cell, Physic of Fluids 23 (2011), <https://doi.org/10.1063/1.3659140>.
[60] E.J. Kramer, L.L. Berger, Fundamental processes of craze growth and fracture, Crazing in Polymers vol. 2 (1990) 5, Advances in Polymer Science, vol 91/92, H.H. Kausch (eds).
[61] D.W. van Krevelen, Properties of Polymers. Their Correlation With Chemical Structure: Their Numerical Estimation and Prediction From Additive Group Contributions, Elsevier B.V., Amsterdam, 1997, pp. 415.
[62] D. Wright, Environmental Stress Cracking of Plastics, Shrewsbury Rapra Technlogy Limited, 1996, pp. 3–105.
[63] A. Comiotto, Naum Gabo's sculpture 'Construction in Space: Crystal' (1937): evaluating a suitable bonding strategy for stress loaded poly(methyl methacrylate), in: Future Talks 009. The Conservation of Modern Materials in Applied Arts and Design. 22-23 October 2009, Die Neue Sammlung. The International Design Museum Munich, 2009, pp. 61–69.
[64] H. Warburton Hall, E.W. Russell, Polymethyl Methacrylate (Perspex Type) Plastics: Crazing, Thermal and Mechanical Properties, Aeronautical Research Council Reports and Memoranda, 2764, London: H.M.S.O, 1949, pp. 2–27.
[65] E. Bormashenko, Breath-figure self assembly, a versatile method of manufacturing membranes and porous structures: physical, chemical and technological aspects, Membranes 7 (3) (2017) 45, <https://doi.org/10.3390/membranes7030045>.