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Effects of selected solvents on PMMA after prolonged exposure: unilateral NMR and ATR-FTIR investigations

Stefani Kavda^{1*}, Stavroula Golfomitsou² and Emma Richardson³

Abstract

Exposure of heritage plastics to solvents can cause several changes to their surface layers and bulk. The amorphous nature of certain plastics, particularly polymethyl methacrylate (PMMA), allows penetration and diffusion of low-molecular liquids, which can lead to swelling, cracking, plasticisation or stiffening, extraction and dissolution of polymer and additive components. Such phenomena compromise the visual characteristics, chemical and physical structure of heritage collections and remain, for the most part, unexplored. Research studies present contradicting evidence concerning the use of solvents and their safe application on PMMA. The main discrepancy is about PMMA being permeable to water or not. Alcohols have also triggered debates about whether they cause leaching and/or depolymerisation. This paper investigates the potential effects that selected free polar and non-polar solvents—employed in different media as cleaning systems—can have on PMMA after prolonged contact. The Hildebrand solubility theory was used to select solvents based on PMMA's miscibility. The effects of deionised water, ethanol, isopropanol and petroleum ether are examined through a 30-day immersion study of PMMA via microscopic examination, weight change measurements, ATR-FTIR, peak height ratios, and NMR MOUSE. All four solvents extracted soluble components, i.e. unreacted residual monomer, and increased PMMA's surface sensitivity to abrasions. Water and petroleum ether did not cause any measurable chemical or physical changes. Alcohols caused surface crystallisation and crazing, with isopropanol leading to stiffening and ethanol to plasticisation of the material. These effects, although extreme and absent in most routine cleaning timeframes, demonstrate the cumulative damage these solvents can potentially induce to PMMA.

Keywords Conservation of plastics, Polymethyl methacrylate (PMMA), Solvent diffusion, Polymer dissolution, Crazing, Crystallisation, Plasticisation, Hildebrand solubility parameter, ATR-FTIR, Unilateral NMR

Introduction

The use of solvents in heritage conservation is widespread. However, concerns have been raised over the last decade regarding their impact on the environment and the users' health. An additional concern when it comes to the conservation of plastics is that organic solvents, as well as water, chemically and physically interact with plastics, potentially damaging sensitive surfaces [1, 2]. Penetration and diffusion of a liquid into a plastic can cause extraction of additive and polymer components, dissolution, swelling [3, 4], softening/plasticisation, resulting in a localised reduction in yield strength that

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leads to the formation of crazes and, finally, fracture [5]. All these types of damaging phenomena render cleaning plastics one of the most delicate and complex operations in conservation. In the last decade there has been increasing research into alternative cleaning systems such as gels [6] and supercritical carbon dioxide [7]. Still, to the authors' knowledge and with the exception of a study from 1989 [8], the effect of solvents on treated plastic substrates has not yet been systematically studied.

Due to acrylics' high sensitivity to solvent damage (i.e., cracking, crazing), some conservators reject solvent use [9]. As an amorphous material, PMMA has the potential for penetration of low-molecular-weight liquids. This is dependent on various factors, including solvent miscibility and similarity between the Hildebrand solubility parameters of PMMA and solvents, which almost certainly leads to irreversible stress cracking and embrittlement [5, 10]. Such phenomena compromise not only the visual characteristics of heritage objects and artworks but their physical structure too, and remain for the most part unexplored.

Solvents used for the cleaning of heritage PMMA

There is contradicting information in the literature concerning the use of solvents and their safe application on PMMA [6]. Regarding water, some scholars verify its safe use [11–13], while others state it is detrimental [14, 15], unsuccessful and ineffective [16]. The discrepancy lies in the fact that PMMA is occasionally stated to be permeable to water. PMMA's ester side group is polar, thus inherently susceptible to water [17, 18]. Studies in orthopaedics demonstrated that when immersed in water for 24 h, PMMA absorbed up to ~2% w/w [19, 20], whereas after 14 days it showed environmental stress cracking (ESC) caused by the propagation of a single craze that proliferated rapidly across the sample [21]. However, this is arguable since the bulk PMMA is largely hydrophobic due to its non-polar hydrocarbon backbone that renders it hard for water—due to low viscosity and high surface tension, to access the hydrophilic ester group.

A polymer's dissolution behaviour is a complex process profoundly influenced by polymer tacticity and sample preparation (processing conditions) [22]. In this study, the Hildebrand solubility parameters¹ were used to provide a systematic description of the miscibility behaviour of solvents [23]. According to this solubility theory, solvents with less than two units difference from PMMA's solubility parameter (18.7 MPa^{1/2}) are likely to dissolve the

Table 1 Hildebrand solubility parameters of selected solvents

Solvent	MPa ^{1/2}	PMMA dissolution
Hexane	14.9	no
Petroleum ether	16.1	no
Acetone	19.7	yes
Isopropanol	24.2	no
Ethanol	26.2	no
Water	48.0	no

Hildebrand solubility parameters (δ) of selected solvents commonly employed in conservation cleaning

material (Table 1) [24]. Based on the largely hydrophobic PMMA and the fact that deionised water presents a solubility unit of 48.0 MPa^{1/2} (Table 1), water is not expected to solubilise PMMA [25].

According to Waentig [26], PMMA at room temperature is resistant to aliphatic hydrocarbons. Petroleum ether is recommended for PMMA museum objects for its degreasing effect [11, 26, 27]. Balcar et al. [16] found it to be the least effective in removing oil-based soil, but also the least damaging. Its low craze and crack-promoting action has also been highlighted by Comiotto and Egger [28]. By contrast, hexane presented a reduced effect in removing oil [29] and increased scratching [16]. Although good solubility is expected between amorphous non-polar PMMA and non-polar petroleum ether (16.1 MPa^{1/2}) [28], non-polar solvents have been demonstrated to moisten PMMA without dissolving it [30].

More recent studies agree that aliphatic, non-aromatic hydrocarbons are safe on PMMA [13, 31, 32]. Aliphatic alcohols, in particular ethanol and isopropanol, have been found to be the most effective in cleaning PMMA [16, 26, 33]. Additionally, ethanol has been documented to induce the least surface abrasion [16]. Although it is considered safe for use with objects, it can cause a crazing effect after prolonged exposure [11, 31].

Ethanol (26.2 MPa^{1/2}) and isopropanol (24.2 MPa^{1/2}) with Hildebrand solubility units larger than 2 MPa^{1/2} are expected to be safe for use on PMMA. Contrary to this, some studies have indicated that the two alcohols diffuse into the polymer causing disentanglement of its chains and increased leaching of MMA monomer [34], plasticisation, shape change and swelling after ethanol [35], and rapid dissolution of PMMA with no noticeable swelling after isopropanol [36]. Alcohol molecules can easily penetrate the PMMA matrix and chemical adsorption may take place between the hydroxyl hydrogen alcohol atom and the carbonyl oxygen atom of the ester group of PMMA side chain through hydrogen bonding [37].

¹ It provides a systemic description of the relative solvency/miscibility behaviour of solvents. The solubility parameter is a numerical value derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporisation divided by the molar volume.

It is noteworthy that a water:isopropanol solution (50:50) was recommended as safe for cleaning PMMA in the conservation science literature [9]. However, attention is needed when mixing water with alcohols. Many scholars confirmed that water:alcohol co-solvency increases the solvating power of each other [38, 39] causing swelling [40] and increasing PMMA's dissolution rate [25, 41]. A possible explanation is that alcohols act as carriers of water molecules in the PMMA, giving water access to the polar pendant ester group and allowing it to interact favourably with the hydrophilic carbonyl groups once near them [42].

Research aims

This paper focuses on the effect of neat/free solvents on PMMA to better understand the interactions taking place during prolonged contact. For this purpose, a 30-day immersion study of samples in deionised water, ethanol, isopropanol and petroleum ether environments was undertaken. The samples' behaviour and monitoring of potential change was investigated through microscopic observation, weight change measurements, Attenuated Total Reflectance Fourier-transform Infrared spectroscopy (ATR-FTIR) analysis and peak height ratios, and unilateral Nuclear Magnetic Resonance Mobile Universal Surface Explorer (NMR MOUSE). Although no direct correlation can be established between our solvent immersion study and real-life solvent treatments, this paper intends to assess the potential cumulative visual, chemical and physical alterations that prolonged contact with solvents—employed in various media as cleaning systems, can cause to PMMA.

Methods/experimental

Materials

PMMA samples

Commercially available transparent syndiotactic PMMA square coupons (Goodfellow Inc., cast, $25 \times 25 \times 1.0$ mm) were used for the 30-day immersion study in four solvent environments. Coupons were UV-aged for comparative purposes and used as references against which the treated samples were correlated. A Ci3000 Atlas Weather-Ometer with xenon arc lamps and an inner Right Light and outer Quartz daylight filter combination (UV wavelength: 280–400 nm) were employed to produce accelerated artificially aged samples. Test method A Cycle No.1 [43] was followed for 'artificial weathering' mimicking outdoor conditions. The exposure period lasted 32 days and included an initial dry phase of 102 min (irradiance: 60 ± 2 W/m², chamber temperature: 38 ± 3 °C, relative humidity: $50 \pm 10\%$) and a wet phase (water spray) of 18 min (irradiance: 60 ± 2 W/m²).

The exposure resulted in chemical and physical change similar to collections displayed outdoors, experiencing illumination levels containing damaging UV radiation. This study addresses everyday objects with a user life, design objects, public art and sculptures designed to be displayed outdoors, in addition to collections found in indoor museum conditions.

Solvents

Based on the literature, deionised water, ethanol ($\geq 99.5\%$, VWR Chemicals), isopropanol ($\geq 99.5\%$, VWR Chemicals), and petroleum ether ($> 99\%$, VWR Chemicals) appeared likely candidates for the safe cleaning of PMMA. Water's conflicting results about its effect, its unique properties of being highly dielectric, a good medium for chemical reactions (i.e., chelation, emulsification or detergency) [44], the least hazardous, most accessible and commonly used solvent among conservators in removing surface dirt, supported the decision to include it in this study. The selection of ethanol and isopropanol is justified by their reported cleaning efficiency and lubricating behaviour that reduces scratching. Lastly, examining a nonpolar, lipophilic solvent was considered necessary for cases where dissolution of greasy dirt, commonly encountered in heritage objects and artworks, is required. Apart from offering an additional chemical type of cleaning agent next to polar water and alcohols, petroleum ether was added by virtue of its purported degreasing effect.

Immersion study

New coupons were immersed in 10 mL of deionised water, ethanol, isopropanol and petroleum ether in airtight vials for 30 days and kept at constant laboratory conditions (21 °C, $60\% \pm 5\%$ RH) throughout immersion. The length of exposure aims for the 'worst case scenario' effects and is an arbitrary decision based on orthopedics and dentistry studies investigating immersion of PMMA in solvents for 24 h, 1 week, 14 days and 1 month. Once removed from their baths they were air-dried for 24 h in lab environment to allow excess solvent evaporation for observation and analysis. Two controls, a new/unaged and a 32-day UV-aged, were kept in airtight vials with no liquid to determine whether the changes were solvent-induced alterations and independent of external factors (i.e. environment). The controls were imperative in evaluating potential changes in the immersed samples.

Evaluation methods of solvent effects

Microscopy

Microscopic observation offered descriptive data to evaluate visual change and phenomena taking place on the immersed surfaces. A Leica DM 2500P optical microscope and a Leica M205 A 3D stereomicroscope were used at different time intervals throughout the 30-day period.

Weight change measurements

Weight measurements were performed using a Sartorius MSE225S-000-DU Cubis Semi-Micro Balance (accuracy: 0.01 mg). Percentage change was calculated from measurements before immersion (initial weight) and every 24 h for a period of 1 month. Samples were arbitrarily weighed 5 hrs after standing in laboratory conditions allowing solvent evaporation. Values were calculated from three replicate samples.

Although gravimetric studies comprise one of the most popular methods of monitoring polymer degradation [17, 43], caution is needed when interpreting changes influenced by competing processes related to chemical reactions, possibly occurring concurrently. Gravimetric studies overlook the possibility of simultaneous extraction and diffusion of components. Weight loss may denote depolymerisation during degradation, but also dissolution, extraction and subsequent evaporation of (volatile) additive and polymer components, such as unreacted residual methyl methacrylate (MMA) monomer from incomplete free radical polymerisation reactions [44, 45]. Weight gain may result from solvent absorption and diffusion in the sample. In turn, the absorbed liquid interferes with the polymer chains affecting the physical properties and causing swelling [46]. It is therefore important to combine gravimetry with other techniques, and in this case weight change was examined alongside relaxation data acquired from unilateral NMR [47, 48].

ATR-FTIR and peak height ratios

ATR-FTIR detected potential chemical changes induced by the immersion of PMMA in the four solvents. Analysis was performed with 32 scan accumulation at ambient temperature and pressure with a zinc selenide (ZnSe)/diamond Universal ATR Sampling Accessory (Perkin Elmer FT-IR/NIR Frontier) between 4000 and 600 cm^{-1} (mid-IR region), with a resolution of 4 cm^{-1} and a maximum penetration depth of the IR beam into the samples between 0.5 and 5 μm . The spectra of unaged and UV-aged PMMA were averaged from three replicates, whereas that of immersed samples were averaged from three spot analyses. Perkin Elmer Spectrum version

10.5.1 (2015) software was used to obtain the ATR spectra and calculate peak height ratios, while softwares *Spectragryph* and *Essential FTIR* were used for processing and manipulation of data.

Ratios of peak heights allowed for semi-quantitative detection of relative surface chemical change. To account for intensity variations in sampling depths across the sample set and ensure that any changes present relate to chemical change (due to depletion) and not differences in path length, the peak height of the 1723 cm^{-1} vibration was normalised to an internal standard vibration at 750 cm^{-1} . Height ratio absorption bands were plotted manually and compared against the unaged and 32-day UV-aged controls as reference points for relative chemical change. A linear baseline correction was applied between the beginning and end of each peak of interest on all spectra. The peak height was the maximum absorbance between the baseline and the apex of the peak (a vertical line showing the maximum height measured relative to the linear baseline).

The internal standard peak at 750 cm^{-1} corresponds to vibrations of C–H bonds in the methylene group (CH_2) of the main chain [49]. It remains chemically constant during analysis, it is not known to alter in the presence of solvents and its intensity remained invariant during UV ageing, providing a reference spectral band for the assessment of photo-oxidation in PMMA [50]. The prominent carbonyl vibration at 1723 cm^{-1} was chosen as it showed extensive changes in intensity.

NMR Mouse

Experimental set up

NMR relaxation studies were carried out using a PM-5 Profile ^1H NMR MOUSE (Magritek, Aachen, Germany) with a field strength of approximately 0.5 T (ca. 19 MHz proton frequency). Scanning was set to 16 echoes, the number of scans to 1536 acquisitions at each depth to reduce noise with repetition time 250 ms, echo time 50.2 μs and pulse length 3.8 μs . The magnet was mounted on a precision lift controlling its horizontal position. Profile scans were recorded by collecting Carr–Purcell–Meiboom–Gill (CPMG) echo radiofrequency pulse sequences [51], obtained at 50 μm depth increments. A 2.0 mm spacer adjusted the sampling depth (working distance) from an initial 5250 μm to 3250 μm . For the $T_{2\text{eff}}$ values to be calculated, the resulting CPMG echo decay curve is fitted with a single exponential model decay function [52].

Data processing

NMR data were acquired using Prospa software (Magritek Aachen, Germany) and processed with OriginPro 2016 Software. The data is visualised as 2D

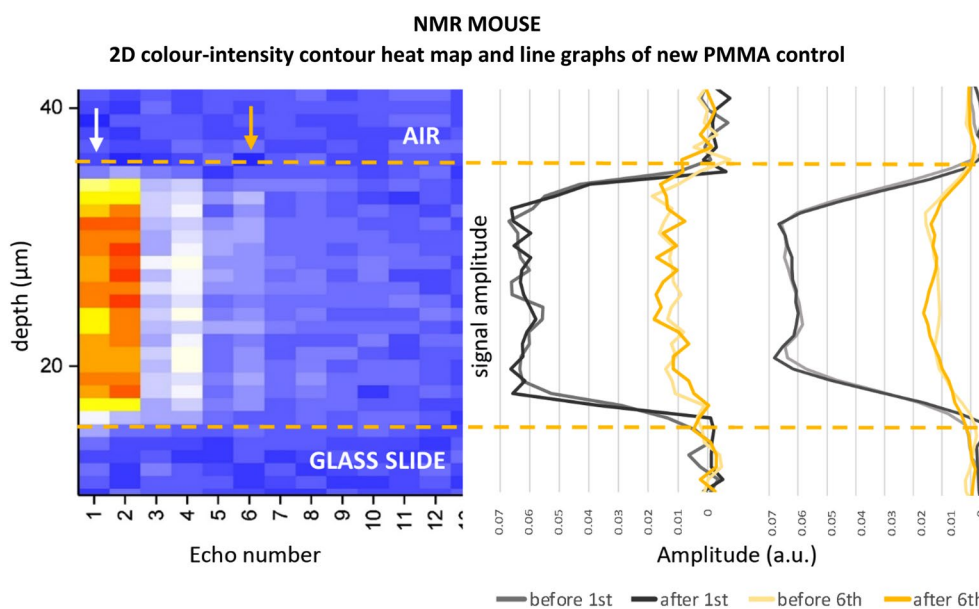


Fig. 1 An example of the 2D colour-intensity contour heat map (left) obtained for the new PMMA control. A vertical slice through the 2D data at the 1st (white arrow) and 6th (yellow arrow) echo yields a profile of the proton density through the scan depth (1st echo: black line, 6th echo: yellow line). The central line graph is before smoothing and the one on the right is after smoothing using Savitzky-Golay filtering with a nine-point convolute

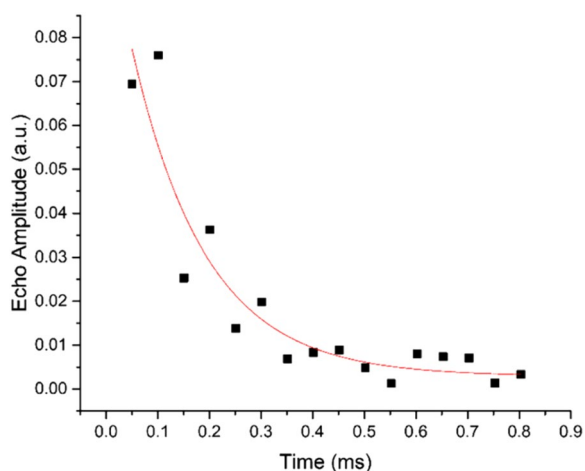


Fig. 2 Relaxation curve of new PMMA sample from Fig. 1 depicting the signal intensity (echo amplitude) and relaxation time at a specific sample depth. PMMA as a rigid material has low mobility atoms and a fast relaxation. The harder the material, the shorter the relaxation

colour-intensity contour heat maps created for each sample before and after immersion. An example is shown in Fig. 1 with a 2D map (left) obtained for a new PMMA sample. The x-axis represents the CPMG echo decay and the y-axis the sample depth (step number in microns). Each horizontal segment ‘slice’ through the thickness of the sample represents a step of 50 μm , while each vertical

segment ‘slice’ (from echo 1 to 16) represents the signal decay at each depth. This can be better understood from Fig. 2: the relaxation curve depicts the signal intensity (echo amplitude) and relaxation time of a specific sample depth [53], offering information on the molecular mobility [54] and material stiffness at this depth [47]. The profile scan localises the boundaries of the air-sample and sample-glass slide interface (yellow dotted lines).

To aid visualisation, the sum of the signal amplitude of the 1st (Fig. 1 – white arrow) and 6th (Fig. 1 – yellow arrow) echoes before and after immersion are presented against depth as line graphs. The data were smoothed (Fig. 1 – right) using a Savitzky-Golay filter with a 9-point convolute (window) [55] and normalised to the back (bottom surface) of the samples.

Results and discussion

Microscopy: visual effects of solvents

Macroscopically, samples removed from all four solvents display fine surface deposits that resemble dust under the stereomicroscope. These deposits were successfully removed with a moistened cotton swab in deionised water (see Fig. 3 for PMMA after 2 and 15 days in petroleum ether). It was ruled out that these deposits are solvent impurities due to solvents being 99% pure. However, they may be the result of some degree of environmental contamination. Deposits may also indicate leaching of soluble non-volatile components or/and dissolution of

Stereomicroscope images of PMMA before and after 2 and 15 days in petroleum ether

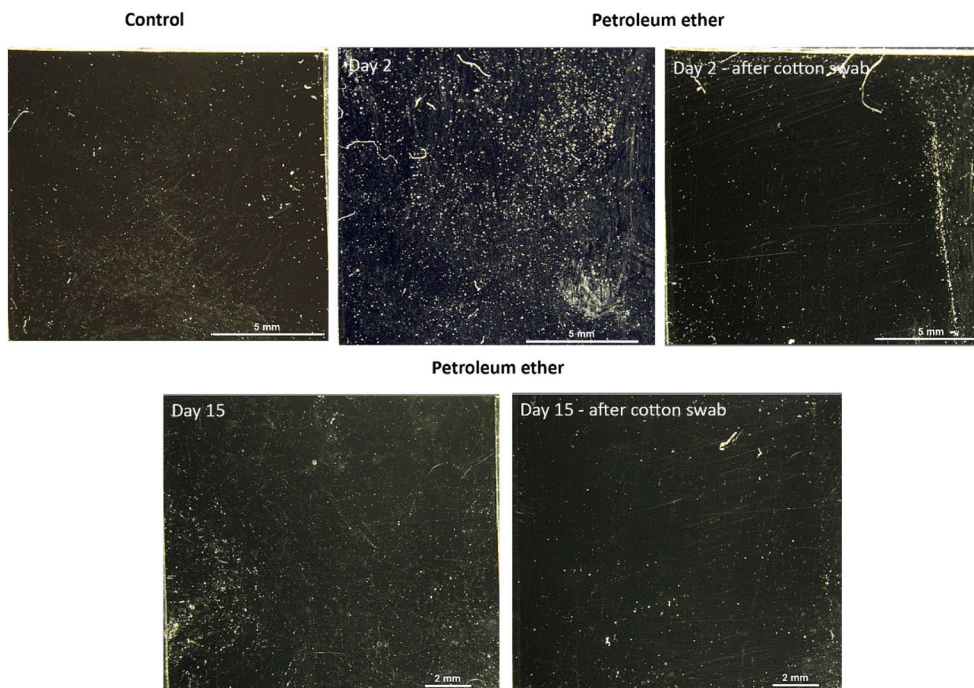


Fig. 3 Stereomicroscope images under Leica M205 A 3D ($\times 78.1$) of the unaged PMMA before and after 2 and 15 days of immersion in petroleum ether: before and after surface clearance with moistened cotton swab. After immersion surfaces show dust-like residues, removed with swab use

PMMA redeposited after solvent evaporation. This effect is intensified after the first few days of immersion in all solvents, up until day 15 when residues are significantly reduced and only visible under magnification. After all immersions, surfaces are rendered more sensitive to formation of abrasions compared to the control. This became discernible upon removal of surface deposits with cotton swabs, which left scratches particularly visible after immersion in alcohols (Fig. 4), and less in deionised water.

Ethanol caused the greatest deformation to the PMMA matrix possibly due to plasticisation. After 7 days of immersion, samples start to form a network of crazes visible under the microscope. By day 15, the crazes are fully formed across the whole sample surface and visible to the naked eye. Detailed images under several magnifications clearly show fine fibrils illustrating the formation of an organised crazing network (Fig. 5). According to Ouano et al. [22], PMMA samples have occasionally displayed extensive cracking on dissolution. This depends on tacticity and shape, factors which influence the dissolution behaviour. Crazing seen here always precedes cracking (taking place on dissolution) [56] leading us to believe that dissolution of PMMA may be taking place. Based on visual examination, ethanol is the most aggressive amongst the studied solvents in terms of physical

damage resulting from the prolonged exposures used in the experiments.

Weight measurements: quantitative indication of material changes

Gravimetric measurements before and after immersion in the solvents monitored simultaneous weight changes due to material leaching/dissolution and solvent absorption. The unaged control sample (average weight: 0.813 g) remained unaltered throughout the 30 days (Fig. 6). Samples were not swab cleaned after immersion and before weighing. The material behaviour displayed during the first 24 h is potentially of most interest here, and the most representative, given that cleaning treatments commonly last up to a few hours. Changes are not dramatic and mostly close to the limit of accuracy of the balance but they are statistically significant. Therefore, conclusions about PMMA's behaviour in contact with the four solvents can be drawn.

Deionised water caused a steady weight increase ($+0.004\%$) in the first 24 h. Following a 1-month immersion, PMMA showed a pattern of weight increase (average weight: $+0.007 \pm 0.001\%$) (Fig. 6) with a consistent daily absorption rate. These results indicate water's tendency to fill the overall PMMA free volume, as anticipated based on the literature [17–20]. PMMA in

Stereomicroscope images of PMMA before and after 13, 22 and 30 days in alcohols

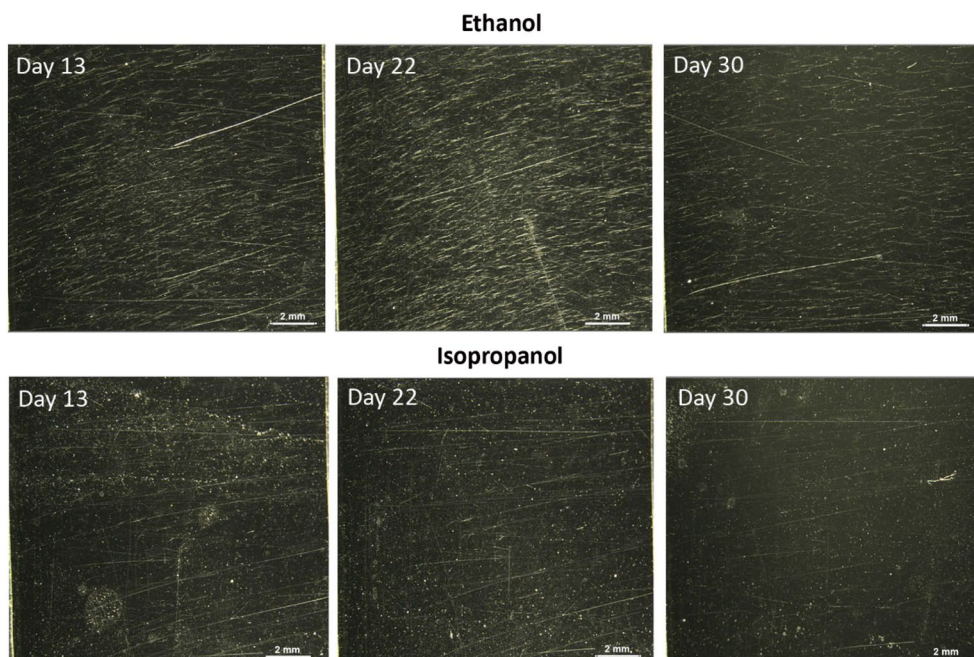


Fig. 4 Stereomicroscope images under Leica M205 A 3D ($\times 78.1$) of the scratches induced to the unaged PMMA after 13, 22 and 30 days of immersion in ethanol and isopropanol. Samples were surface cleared with moistened cotton swabs. The longer PMMA remained in the solvents, the less the residues

petroleum ether behaved similarly to the control (Fig. 6) indicating a high degree of stability in the solvent. Alternatively, it could mean loss of components in the solvent or evaporated during air-drying (dissolution/leaching) and a concurrent mass increase (solvent absorption, or/and redeposition of non-volatile precipitates as seen in Fig. 3). These possibilities are further explored using NMR MOUSE.

The most interesting behaviour is displayed by samples immersed in the alcohols. Although the two solvents are relatively chemically similar and PMMA would have been expected to show a comparable behaviour in both, the solvents induced opposite effects to PMMA in the long-term (Fig. 6). During the first 24 h both caused similar weight losses (-0.002% and -0.003% , respectively). Ethanol caused the most erratic behaviour: after 10 days, the sample started gaining weight, which in the last 4 days, increased exponentially reaching an average of $0.004 \pm 0.006\%$. PMMA in isopropanol maintained its initial behaviour throughout the month with negligible weight fluctuations and an average loss of $0.003 \pm 0.001\%$.

The initial loss of material is interpreted as alcohol diffusion and extraction of various soluble components, such as initiators, plasticisers and unreacted residual monomers [20, 57]. A diffusant liquid and voids left

from extracted components may cause an increase in the free volume, which can lead to weakening or breaking of polymer bonds [58]. This mechanism is potentially responsible for further weight loss in isopropanol. However, an increase in free volume can also cause swelling of the material, which can allow further absorption of liquids. This would lead to weight gain displayed in samples after ethanol [3, 59]. Swelling is directly connected to the nature of the solvent and solubility of PMMA [45]. These results are further discussed conjointly with the relaxation data.

ATR FTIR & peak height ratios: chemical changes

New control

In the new PMMA spectrum (Fig. 7), absorption bands in the region between 3000 and 2800 cm^{-1} are fundamental stretching vibrations of the methyl (CH_3) in the ester side group [49]. Two distinct peaks at 2995 and 2950 cm^{-1} are characteristic of the stretching vibration of $\text{O}-\text{CH}_3$ in the ester side group, while peaks 2920 and 2850 cm^{-1} are attributed to combination bands also associated with the ester methyl (CH_3) [49, 60, 61]. The strong absorption of peak 1723 cm^{-1} is characteristic of carbonyl ($\text{C}=\text{O}$) stretching vibration in the ester side group. Bands 1483 cm^{-1} , 1387 cm^{-1} and 965 cm^{-1} are attributed to the α -methyl group ($\alpha\text{-CH}_3$) in the main chain [49],

Optical microscope images of PMMA sample after 30 days in ethanol

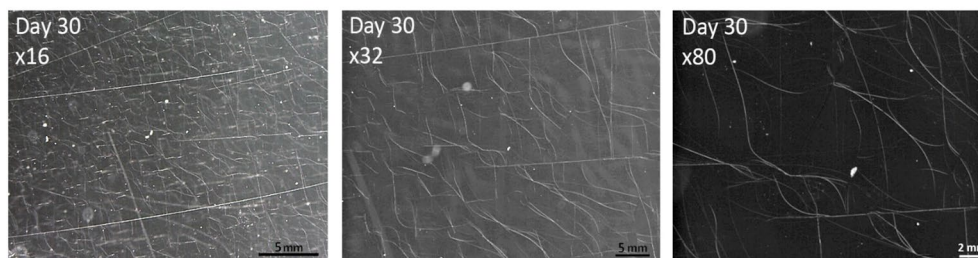


Fig. 5 Leica DM 2500P optical microscope images of the PMMA sample immersed in ethanol for a month at different magnifications. The sample was surface cleared with moistened cotton swab. The organised network of crazes shows fine fibrils

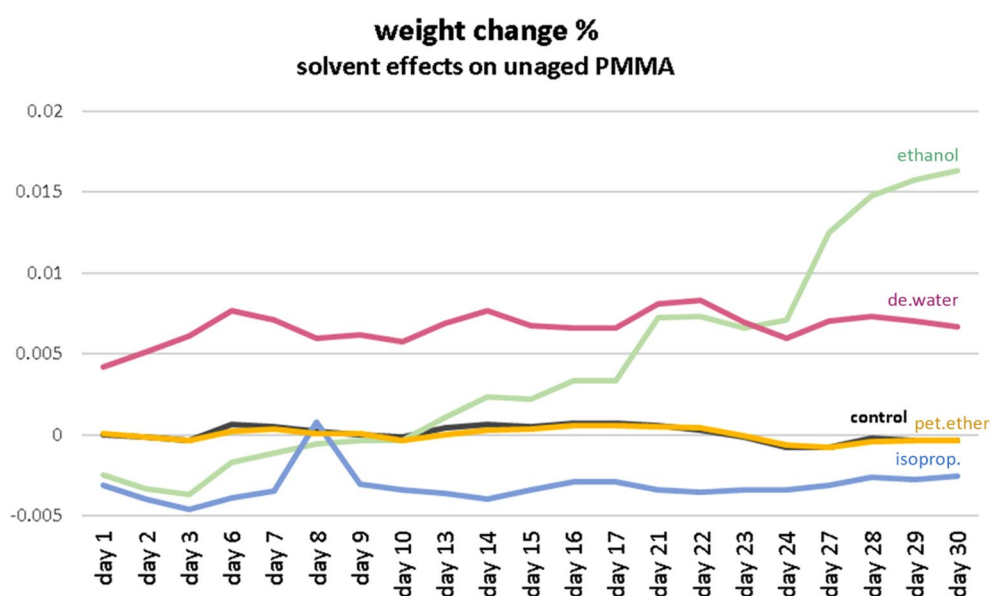


Fig. 6 Weight change % of control PMMA (black) and samples in ethanol (green), deionised water (pink), isopropanol (blue) and petroleum ether (yellow) for 30 days. Changes % are relative to the initial weight (pre-immersion) set at zero

whereas band 1447 cm^{-1} to the methylene group (CH_2) in the main chain. Absorption at 1435 cm^{-1} is assigned to the stretching vibration of $\text{O}-\text{CH}_3$ in the ester side group [49, 61, 65]. The weak band at 1369 cm^{-1} may correspond to the amorphous band associated with vibrations of the main chain methyl ($\alpha\text{-CH}_3$) [50]. Bands between 1300 and 1000 cm^{-1} are attributed to $\text{C}-\text{C}-\text{O}$ between the main chain and the ester side group [49, 61]. Strong absorptions at 1190 cm^{-1} , 1144 cm^{-1} and 986 cm^{-1} are assigned to $\text{C}-\text{O}-\text{C}$ stretching in the ester side group [49, 61, 66]. Peaks between 1000 and 800 cm^{-1} are generally associated with main chain $\text{C}-\text{C}$ stretching vibrations (vinyl absorption) of PMMA [64]. Band 965 cm^{-1} is associated with vibrations of the α -methyl ($\alpha\text{-CH}_3$) in the main chain [49] and peaks located at 840 cm^{-1} [61] and 749 cm^{-1} with vibrations of the methylene group

(CH_2), also in the main chain [49]. For a detailed list of all absorption peaks of unaged PMMA refer to Table 2.

Aged control

Photo-oxidative degradation is reported to cause a number of competitive reactions and phenomena, expected to take place simultaneously [60, 65, 66]. These reactions include main chain scission of $\text{C}-\text{C}$ bonds, side group cleavage of the pendent ester (methoxycarbonyl) (COOCH_3) or the methyl (CH_3) in the ester group, formation of new oxidised products and free radicals, crosslinking, and direct UV-depolymerisation [61, 65, 67].

Following UV exposure for 32 days, the IR spectrum (Fig. 7) shows the following distinct changes (see Table 2): An increase of shoulder peak absorbance at 2920 cm^{-1} along with an increase in the absorption and amplitude of

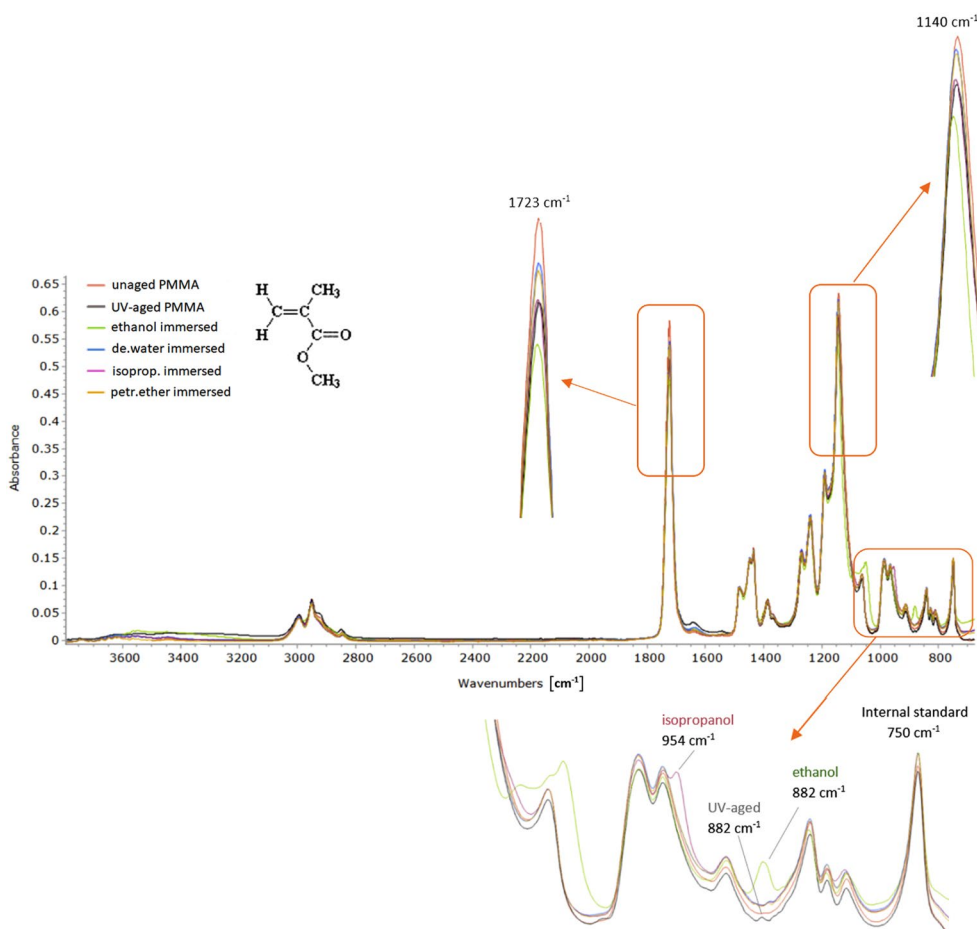


Fig. 7 Spectra of PMMA samples: unaged control (orange), 32-days UV-aged control (grey) and 30-days immersed samples in ethanol (green), deionised water (blue), isopropanol (pink) and petroleum ether (yellow). Regions 1750–1700 cm^{-1} , 1200–1100 cm^{-1} and 1000–700 cm^{-1} are enlarged and presented in detail. MMA monomer chemical structure inset

2850 cm^{-1} confirm chain scission reactions in the methyl (CH_3) in the ester side group. The decrease in intensity of peaks 1270 cm^{-1} and 1240 cm^{-1} evidences complete side group elimination from the main chain upon UV radiation [60]. A decrease in the carbonyl absorption (reduction of peak 1723 cm^{-1}) is attributed to loss of the $\text{C}=\text{O}$ bond [67], seen as a result of scission of the pendant ester group from the main chain [69]. A decrease in intensity of the peaks at 1190 cm^{-1} and 1140 cm^{-1} confirms ester group chain scissions [69].

The increase of absorption at 1640 cm^{-1} is attributed to the generation of carbon double bonding ($\text{C}=\text{C}$ bonds/vinyl unsaturation), resulting from several, often conflicting, processes. 1. *Complete or incomplete ester side group cleavage*, earlier confirmed by an increase of peaks 1270/1240 cm^{-1} and decrease of 1723 cm^{-1} , known to lead to carbon double bonding ($\text{C}=\text{C}$) in the main chain [69–71]. 2. *Main chain radicals* formed after complete ester side group cleavage [72] may have formed crosslinks

between them, leading to the generation of unsaturated $\text{C}=\text{C}$ bonds [73]. 3. *Incorporation of oxygen* ($\text{O}=\text{O}$) in the main polymer chain may have caused random chain scission generating a terminal vinyl group, which would act as a weak link from which depolymerisation could initiate [74, 75]. Oxygen is also capable of causing hydrogen-abstraction, leading to the formation of hydroxyl groups (oxidised structures). In both cases, carbon double bonds arise as a result of oxygen incorporation [71].

The appearance of a new, small band at 882 cm^{-1} (Fig. 7) is assigned to the $\text{C}=\text{CH}_2$ [76] between the α -carbon and the α -methylene (CH_2) comprising the polymer backbone. This double bond, absent in the new material, is a clear indication of UV ageing of PMMA, during which several processes, including side group eliminations and oxidation gave rise to vinyl unsaturation. Absorption at 882 cm^{-1} is characteristic of PMMA's crystalline phase [63], and is typically weak or barely visible as a shoulder [68]. Existence of crystalline structures

Table 2 Diagnostic IR absorptions/wavenumbers (cm^{-1}) and tentative band assignments of unaged PMMA, UV-aged PMMA and solvent-immersed PMMA

unaged PMMA	UV-aged PMMA	solvent-immersed PMMA	Tentative band assignment
2995, 2950			O-CH ₃ (ester group)
2920, 2850			CH ₃ (ester group)
1723			C=O (ester group)
1640			C=C (main chain)
1483, 1387			α -CH ₃ (main chain)
1447			CH ₂ (main chain)
1435			O-CH ₃ (ester group)
		1341 *isopropanol	unknown
1270, 1240			C-C-O (ester group)
1190, 1144, 986			C-O-C (ester group)
		1086 *ethanol	unknown
1063			C-C skeletal (main chain)
965			α -CH ₃ (main chain)
		954 *isopropanol	α -CH ₃
	882	882 *ethanol	C=CH ₂
840, 749			CH ₂ skeletal (main chain)

Assignments of diagnostic IR absorptions of the unaged PMMA reference analysed with ATR-FTIR. The new bands formed with UV-ageing and upon immersion in ethanol and isopropanol are also presented

at 882 cm^{-1} is evidence of annealing [77]. Industrially annealed PMMA is carried out at temperatures around $70\text{--}90\text{ }^\circ\text{C}$ [28], near, but sufficiently below the polymer's T_g at $114\text{ }^\circ\text{C}$. Grohens et al. [78] have shown that any controlled thermal treatment, even conditioning at room temperature for 3 months, could cause a more highly PMMA organised structure. Here annealing is interpreted as the thermal/heating process the samples underwent during UV exposure.

Overall, increased absorption of certain peaks in the PMMA spectrum after UV radiation indicates formation of crosslinking structures [73] or double bonds [69–71, 73]. It has not been possible to confirm crosslinks based on the FTIR data obtained here.

Samples in deionised water and petroleum ether

PMMA immersed in deionised water and petroleum ether for 30 days present similar spectra (Fig. 7—blue and yellow) to the new control (Fig. 7—orange) suggesting no measurable surface chemical changes.

Samples in ethanol

PMMA's spectrum in ethanol exhibits the formation of a new band at 882 cm^{-1} (Fig. 7), which as previously seen, is characteristic of the crystalline phase of isotactic PMMA [68]. The same absorption was observed on the surface of UV-aged PMMA samples (Fig. 7) and attributed to the thermal/heating process they underwent in the weathering chamber [62, 68]. The syndiotactic PMMA under

study has a strong tendency to form ordered aggregated structure (crystalline phase) via solvent treatment [68]. Therefore, the intensity increase of peak 882 cm^{-1} after exposure to ethanol is attributed to crystallisation due to prolonged contact of PMMA with a free organic solvent.

The 1723 cm^{-1} band visible in the ethanol sample is distinct and slightly less pronounced than in the aged spectrum (Fig. 7). In the aged PMMA, this peak reduction is due to photoirradiation causing the reduction of carbonyl (C=O) (scission of the pendant ester group from the main chain). The degradation pathway of this solvent-induced chemical change has not yet been determined and requires further study. A new band also formed at 1086 cm^{-1} in ethanol could not be attributed to a specific absorption or phenomenon in the literature.

Samples in isopropanol

Changes in the absorption spectrum of PMMA in isopropanol include the formation of a minor peak at 1341 cm^{-1} , and a new, distinct shoulder peak at 954 cm^{-1} (Fig. 8). Band 1341 cm^{-1} is characteristic of the crystalline phase of stereoregular PMMA, mostly in reference to isotactic forms [63]. Regrettably, no reference to the band assignment was found. It is reported that PMMA polymers with different tacticities (i.e. isotactic and syndiotactic) often show similar, slightly shifted absorptions [62]. Therefore, even though the PMMA here is syndiotactic, appearance of a peak at 1341 cm^{-1} is potentially due to the transition from amorphous to partially

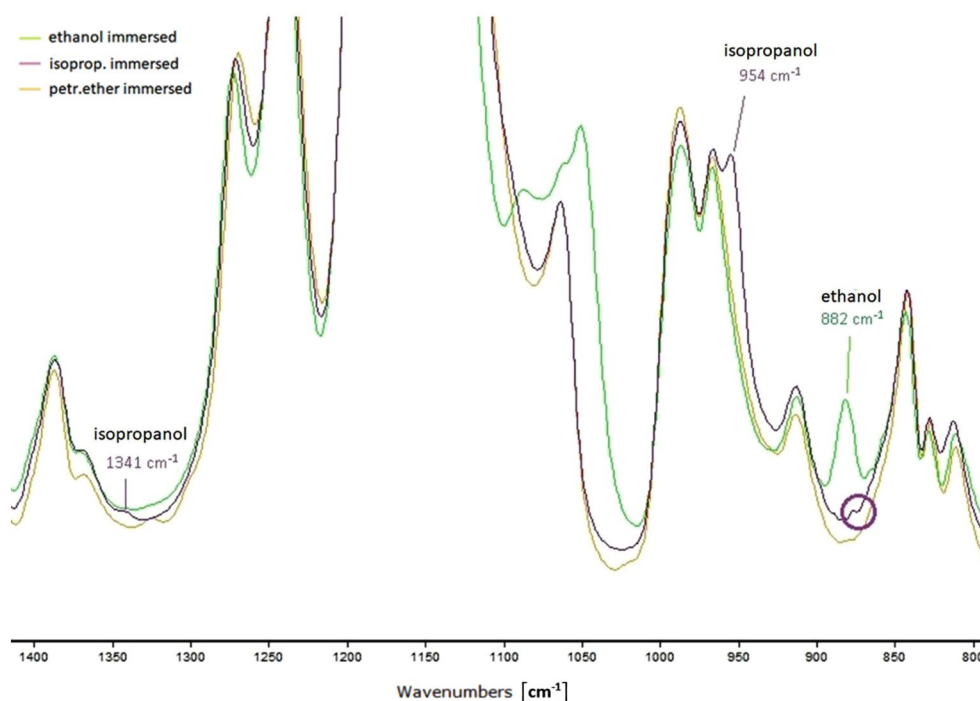


Fig. 8 Detail of spectra of PMMA samples with the new peaks formed after immersion in ethanol (green) and isopropanol (purple) for 30 days

crystalline states and from unordered to ordered [62]. Crystallisation of amorphous PMMA of any tacticity is extremely slow, rendering the study of its progress hard, but also indicating the negligible, yet clear, initial formation.

Band 954 cm^{-1} is a doublet with 965 cm^{-1} and is assigned to the α -methyl ($\alpha\text{-CH}_3$) attached to the main chain [49, 72]. The two peaks, both assigned to PMMA's backbone conformation, are also reported to relate to polymer crystallinity. Specifically, 954 cm^{-1} has been shown to increase, while 965 cm^{-1} to decrease during crystallisation [62]. Simultaneous occurrence of the two new bands at 1341 cm^{-1} and 954 cm^{-1} after prolonged contact of PMMA with a free organic solvent presents sufficient evidence to support that isopropanol induced crystallisation of PMMA. This is also supported by the negligible, yet clear, initial formation of peak 882 cm^{-1} in the isopropanol spectrum (Fig. 8—circled in purple), similarly to PMMA after ethanol.

Peak height ratios

Referring to the ratios (Fig. 9), samples immersed in all four solvent environments show loss of carbonyls relative to the new control PMMA (the smaller the ratio the greater the change). The progression of relative changes is based on the decrease of peak 1723 cm^{-1} , indicating chain scission from the loss of carbonyl $\text{C}=\text{O}$ and subsequent shortening of polymer chains evidenced as

detachment/loss of the ester side group. Deionised water caused the least surface chemical change, followed by petroleum ether. PMMA immersed in isopropanol and ethanol for 30 days exhibits a comparable carbonyl degradation to the aged PMMA (Fig. 9).

NMR Mouse: diffusion of solvents and relaxation behaviour New and aged controls

PMMA controls do not show significant changes between the new and aged conditions. The edges of both samples show an increased signal (over 0.07 a.u.) compared to their bulk (ca. 0.065 a.u.) (Fig. 10). This is clearly the case for the 1st echo that represents the highest intensity throughout the whole sample depth, less visible for the 6th. The controls have almost fully relaxed by the 6th echo with signal ca. 0.015 a.u. for the bulk and ca. 0.02 a.u. for the edges.

PMMA samples immersed in solvents

The smoothed line graphs were normalised to the samples' constant back (bottom surface of scanned samples), so that any real change in the front of the samples could be established regardless sample thickness or solvent treatment. To visualise this, in Fig. 11, vertical slices through the 2D data at the 1st and 6th echoes yield profiles of the proton density of samples submerged in solvents through the scan depth.

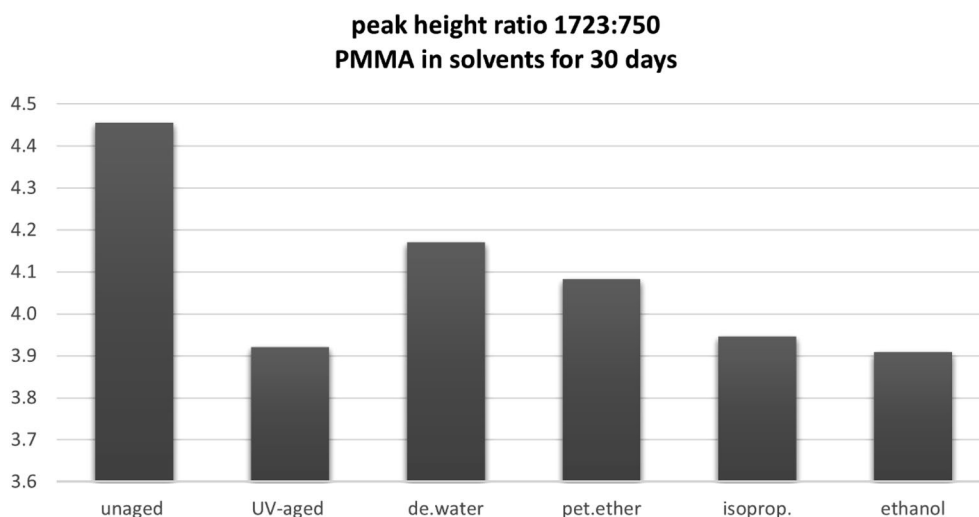


Fig. 9 Ratios between the peak heights at 1723 cm^{-1} and 750 cm^{-1} of new and 32-day UV-aged controls and PMMA samples in deionised water, petroleum ether, isopropanol and ethanol for 30 days. Ratios were based on the loss of carbonyl bands ($\text{C}=\text{O}$) in relation to a constant peak

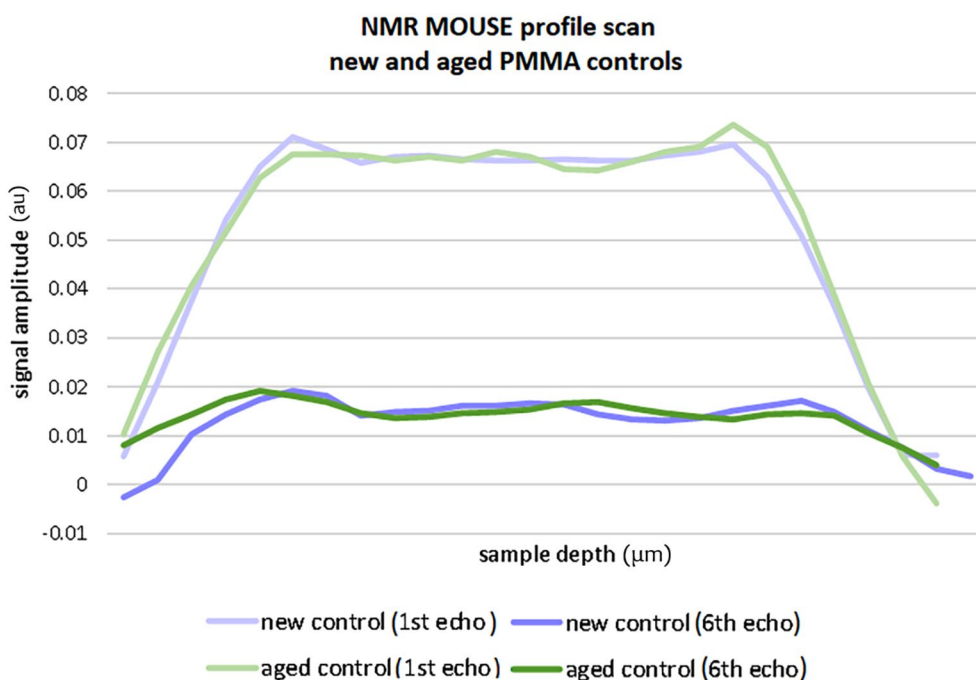


Fig. 10 Smoothed line graphs of NMR profile scans of 1st and 6th echoes: unaged PMMA control (purple tones) and aged PMMA control (green tones)

Samples immersed in deionised water and petroleum ether display profile scans similar to the controls, suggesting no physical change to the material. Ethanol and isopropanol caused measurable change. The behaviour of PMMA is different in the two solvents. The signal of the 1st echo of isopropanol-immersed PMMA is reduced to almost half (ca. 0.03 a.u.) compared to ca. 0.07 a.u. seen in controls (Fig. 11—green). By the 6th echo the signal is

almost zero. This suggests a faster relaxation time, therefore, a harder material compared to the control samples. Rigid materials have low mobility atoms which translate in fast relaxation [48, 79] and reduced $T_{2\text{eff}}$ relaxation times [80]. Stiffening of PMMA in isopropanol can be the result of crosslinking [81], which could not be confirmed here, or crystallisation [5] as indicated by FTIR.

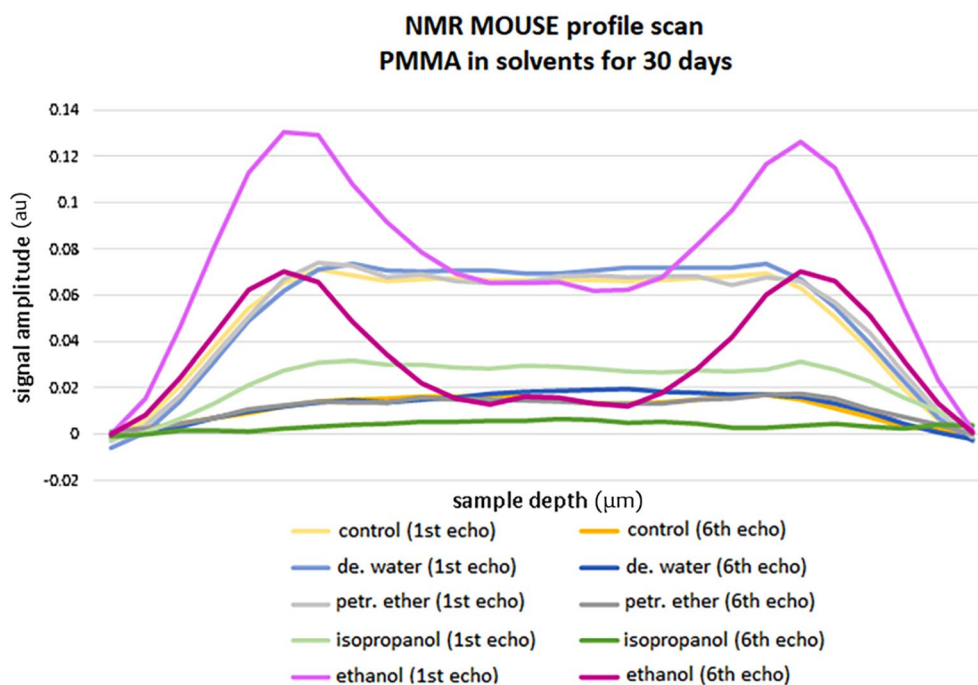


Fig. 11 Smoothed line graphs of NMR profile scans of PMMA samples immersed in deionised water, ethanol, isopropanol or petroleum ether for 30 days. Samples were scanned 24 h after removal from solvents to allow liquid evaporation. The scans represent the extreme physical damage these solvents are capable of inducing—when applied free-standing

A very interesting phenomenon is encountered after 1 month in ethanol (Fig. 11—pink): the two edges of the sample appear to have an increased signal—almost double that of the controls—for both 1st and 6th echoes. However, the centre of the material and its bulk behave differently, showing relaxation similar to the controls with no change at all. This surface effect of PMMA in ethanol, while magnified, is consistent in different magnitudes in all immersed and control samples. Their surface pattern exhibits edges with an increased signal compared to their bulk. This may be the result of industrial surface treatment of the specific manufactured PMMA sheet or cutting it into coupons, which may have increased sensitivity of the upper surface layers. The augmented signal amplitude of the ethanol sample corresponds to an increase of $T_{2\text{eff}}$ relaxation times, translating to a slower relaxation [81]. This can be attributed to the plasticising effect of the solvent present in the upper surface material layers or to changes in the polymer's molecular packing. Leaching of soluble components, i.e. plasticiser or unreacted MMA polymer, causes an increase in free volume and, in turn, an increase in plasticisation (softening) [35].

To better understand this effect, the sample was left in the lab environment for another 72 h to allow any remaining solvent residues to evaporate and was rescanned to understand how that influenced the

relaxation behaviour. Results show the same pattern after 24 and 96 h upon removal from ethanol, with the latter showing a negligible decrease in signal (ca. 0.02 a.u.) within error (± 0.03). This rules out the possibility of solvent trapped in the upper layers of the surface edges and confirms that ethanol plasticises the material. Hence, it could be confirmed that with time, some sort of plastic deformation (possibly swelling) is taking place and that PMMA cannot recover its initial shape/size.

Discussion of the solvent effects on PMMA

Solvents investigated here for their effect on PMMA were expected to cause immediate chemical and physical changes. Weight change measurements were interpreted in conjunction with the other methods used to show chemical and physical processes possibly occurring concurrently. Our results agreed that water did not solubilise PMMA, as per the Hildebrand solubility parameters. However, water was consistently absorbed for all 30 days of immersion. Several accounts confirm water's tendency to fill PMMA's free volume [17–19]. Water molecules are small enough that although chemically incompatible, are able to diffuse between PMMA molecules [15, 20]. These studies also suggest swelling [17–19] which was not observed here. On the contrary, unilateral NMR showed no change in PMMA's relaxation behaviour and no

measurable plastic deformation after long-term immersion in water.

Petroleum ether was the only solvent in this study not to show any observable chemical and physical effects on PMMA. The close proximity of the solvent's solubility unit ($16.1 \text{ MPa}^{1/2}$) to PMMA's ($18.7 \text{ MPa}^{1/2}$), a little over the two units difference required to dissolve the material, led to contradictory opinions. According to Comiotto and Egger [28], good solubility was expected between the non-polar solvent and amorphous non-polar PMMA. Another report states that petroleum ether moistens PMMA without dissolving it [30]. In this study, samples showed no detectable mass changes and surface chemistry similar to the control. Assumptions about concurrent material loss, solvent absorption, or/and redeposition of non-volatile precipitates were negated by the relaxation data showing that no mechanical, structural change occurred in the material after prolonged contact. This was in fact sustained by certain scholars affirming PMMA's resistance to aliphatic hydrocarbons [26] and recommending its use for cleaning heritage PMMA objects [27, 79].

Direct contact with isopropanol and ethanol caused measurable changes to PMMA. Samples exposed to alcohols were the only ones to show mass loss amongst the immersed samples. This is in agreement with studies indicating the increased, rapid leaching of MMA monomer after contact with both alcohols [34, 37]. Microscopic observation revealed the presence of fine particulate matter, supporting the idea of leaching. This phenomenon has not been documented or discussed in previous studies examining solvents in relation to the conservation of plastics. In our opinion, presence of particulate matter can be linked to liquid droplets forming on PMMA during treatment and causing the local loss of soluble components. During solvent evaporation, a mechanism of fluid flow from the interior of the droplets allows extracted and precipitated non-volatile PMMA components to be carried along and be deposited at the droplets' edges [80]. Simple cotton swab cleaning removed these solutes without mechanical damage.

Ethanol was the most aggressive environment, followed by isopropanol. Alcohols are known to aggravate the mechanical behaviour of the polymer they are in contact with [81]. This was confirmed by NMR MOUSE analysis indicating that prolonged contact with isopropanol caused hardening, whereas free ethanol caused softening of PMMA and mechanical deformation manifested as swelling of the sample edges. Although this opposing behaviour of PMMA is surprising given the relative chemical similarity of the two alcohols, these effects have been consistently observed throughout this study. ATR-FTIR indicated that the surface layers of samples

in isopropanol have started to crystallise. This information can be better understood when studying it in parallel with the relaxation data indicating hardening of the material, because an increase in the degree of crystallinity translates in an increase in the polymer's hardness [5].

The NMR MOUSE data of ethanol are better understood when interpreted along with microscopic images and weight changes. The initial loss of material is attributed to ethanol diffusion and component leaching that creates voids in the PMMA [58]. This increase of free volume enables additional solvent to be absorbed and diffused in the polymer. The effects of this lead to two phenomena: plasticisation and swelling [35, 46]. In the former, ethanol diffusion lowers PMMA's glass transition temperature resulting in plasticisation [82]. This effect, in turn, causes a reduction in yield strength that leads to crazing [5], observable under the microscope as a fully formed network of crazes – sometimes even visible to the naked eye. Swelling, confirmed by NMR MOUSE, has commonly been linked with weight gain [3, 59], observed in the samples after several days of immersion in ethanol.

At this point, it is worth mentioning that an increase in free volume could also lead to depolymerisation [58], that is, dissolution of PMMA. This could not be verified here, but the formation of crazing sustains this hypothesis: PMMA has occasionally displayed cracking on dissolution, and crazing seen here always precedes cracking [22, 56]. If that is indeed the case, then a concurrent weight gain and loss take place with softening and swelling having a larger effect on the polymer. This polymer dissolution that causes an increase in free volume for further ethanol diffusion and subsequent weight gain could even explain the diverse behaviour of PMMA in the two alcohols. Polymer dissolution could be taking place in samples exposed to ethanol, and this perhaps is suggested from the more aggressive effect of ethanol on PMMA's surface layers, witnessed as a fully formed network of crazes and as surface swelling—not encountered after immersion in isopropanol.

Conclusion

A 30-day immersion study systematically evaluated the potential visual, chemical and physical alterations of PMMA resulting from prolonged exposure to free solvents commonly employed in plastics conservation cleaning. Based on our results, we proposed that all four solvents, namely deionised water, ethanol, isopropanol and petroleum ether, caused extraction of soluble components (leaching): the volatiles evaporated while the non-volatiles re-deposited on the surface after solvent evaporation. Water and petroleum ether did not cause any measurable chemical or physical changes to the material, although water was systematically absorbed

soon after immersion for the whole period of the study. FTIR data suggested the initial formation of crystalline phases after prolonged contact with both alcohols. Crystallisation may have been responsible for the hardening of PMMA in isopropanol, whereas ethanol induced softening. This is possibly due to competing processes that occur concurrently, including leaching, swelling and depolymerisation. The pathways responsible for the opposing behaviour of PMMA in the chemically similar alcohols need to be further elucidated. Prolonged exposure to all solvents increased surface sensitivity to abrasions, whereas ethanol, being more aggressive, also caused a macroscopically visible organised network of crazes. These effects, although extreme and absent in most routine cleaning timeframes, demonstrate the cumulative damage that these solvents are capable of inducing to PMMA. The various methods and analytical techniques used here complemented one another and offered a holistic understanding of solvent-induced changes in PMMA. When planning a conservation cleaning campaign for heritage plastics, it is advised to consult solubility theories with caution and to take into consideration all polymer material and solvent aspects involved.

Abbreviations

PMMA	Polymethyl methacrylate
ATR-FTIR	Attenuated Total Reflectance Fourier-transform Infrared spectroscopy
NMR MOUSE	Nuclear Magnetic Resonance Mobile Universal Surface Explorer
CPMG	Carr-Purcell-Meiboom-Gill Echo

Acknowledgements

The authors are grateful to Prof. Thilo Rehren for his continuous support. They would also like to acknowledge the following institutions: UCL Qatar in Doha and UCL Department of History of Art in London. Special thanks go to the Journal reviewers for their constructive comments.

Author contributions

All authors contributed to the study conception and design. Material preparation, experiments, analysis, and data collection were performed by SK. NMR MOUSE analysis was performed by SK and ER. All authors contributed to the interpretation of the data. The first draft of the manuscript was written by SK. SG and ER commented on and revised all versions of the manuscript. All authors read and approved the final manuscript.

Funding

This research project received funding in the framework of a 3-year PhD programme from Qatar Foundation. Additional financial support was provided by the Henry Moore Foundation under the Research and Travel Grant Agreement No 2023009. Open access was made possible by the kind support of The Getty Conservation Institute (GCI).

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

Received: 28 October 2022 Accepted: 12 February 2023
Published online: 29 March 2023

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