

The effect of gelling agents and solvents on poly(methyl methacrylate) surfaces: a comparative study

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Introduction

Gels were introduced to the field of conservation to optimize cleaning treatments through their assumed ability to control solvent diffusion and limit mechanical stresses. We are currently undertaking a systematic study into the impact of solvent gel combinations to increase our understanding of their effect on poly(methyl methacrylate) (PMMA) artefacts. The isotropic, amorphous nature of PMMA renders it vulnerable to low molecular weight liquid penetration (Shashoua 2008). Their diffusion into PMMA results in changes to mechanical behaviour; a localized reduction in yield strength renders the material highly susceptible to scratches, crazes and brittle fracture (Michler 1989: 378). Based on the hypothesis that solvent-based gels permit solvent penetration into the PMMA surface, while minimizing the risk of material dissolution (Khandekar 2004), this study assesses the damage potential of the individual materials employed in gel systems. Experimental work examined the effect, safety and time-dependent action of solvents, hydrogel matrices and solvent-gel mixtures.

Experimental details

Mechanically cut transparent, colourless PMMA samples (Goodfellow UK, ME303001, 0.38 × 25 × 25 mm) were used. Agar (Sigma-Aldrich) was dissolved in deionized water (conductivity 1 µS) and heated twice to boiling conditions (c.90 °C) to form a 2% (all by weight) solution (pH 7.0). Carbopol EZ2/Ethomeen C-25 and Pemulen TR-2 gels (1% Pemulen:5% triethanolamine (TEA)) were prepared according to Stavroudis and Blank (1989) and Stavroudis (2012), and 80PVAc-borax (5%:1%) was prepared according to Angelova *et al.* (2016). All gels, except agar, were left to stand overnight to fully disperse. The same procedures were followed for the

solvent gels, loaded with 20:80% solvent:deionized water mixtures, with deionized (DI) water, ethanol (EtOH), isopropanol (IPA) or petroleum ether (PET).

General full-factorial experiments examined the effect of four hydrogels and four free solvents, at two application times (5 and 60 minutes) to understand their interaction with PMMA. Treatments, carried out in triplicate for hydrogels and free solvents, and duplicate for solvent gels, were assigned to samples in a randomized order, to eliminate systematic errors. The solvents were applied as three drops via micropipette directly on the sample surface. All gels were placed on samples with a Teflon spatula. Agar and PVAc-borax gel required a glass weight to increase the contact with the PMMA surface. Gels weighed approximately 2 g and were applied as 2 mm thick layers. During treatment, samples were protected with a cover to limit the evaporation of solvents. Rigid agar and elastic PVAc gels were easily removed from the samples, while gel pastes made from Carbopol/Ethomeen and Pemulen were wiped with a Teflon spatula. Treatments were followed by three separate cotton swabs moistened with DI water, linearly rolled towards one direction.

Methods

Evaluation of treatment outcome was carried out using a Leica M205A stereomicroscope with raking light. Elimination of the scattering effect of light under the stereomicroscope was achieved in a darkroom, against a black background, resulting in images appearing as though grey-scaled. A JEOL JSM-6610LV scanning electron microscope (SEM) was used for imaging gold-coated samples (10 kV accelerating voltage in high vacuum mode). Melinex was employed as masking to standardize the documentation process of a surface area before and after treatment. Treated samples were left at ambient temperature for 24 hours prior to weighing with a Sartorius MSE225S-000-DU Cubis Semi-Micro Balance

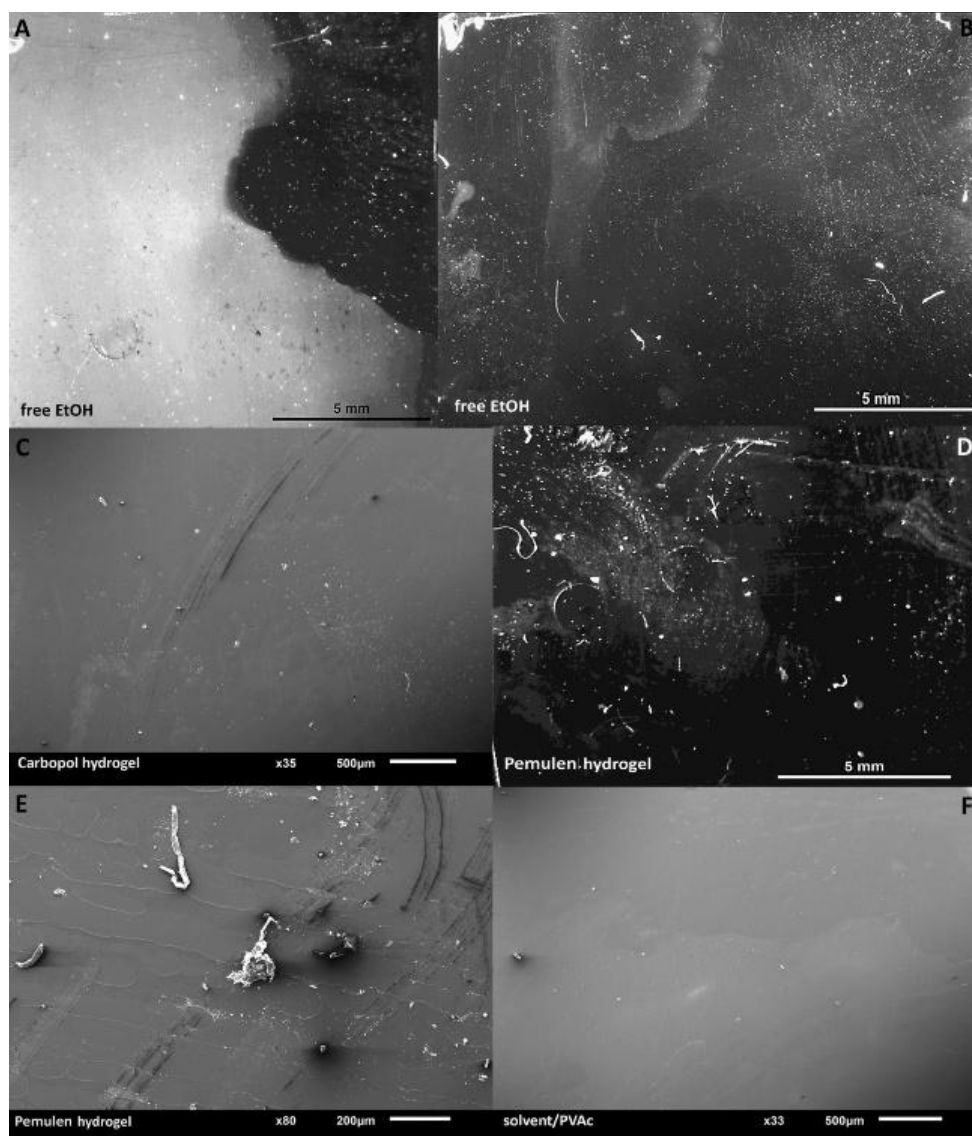


FIG. 1 (A) Raking light image showing clear and dull surfaces upon EtOH. (B) Raking light image showing dull areas upon ethanol (EtOH). (C) SEM image reveals scratching after Carbopol/Ethomeen hydrogels. (D) Raking light image showing greasy surfaces after Pemulen hydrogels and solvent/Pemulen; (E) SEM image reveals Pemulen residues; (F) SEM image reveals discoloration after solvent/PVAc (images: Stefani Kavda).

(accuracy 0.01 mg). Gloss measurements were performed with a Konica Minolta Multi Gloss 268 Plus, and Fourier transform infrared (FTIR) spectroscopy with a diamond Universal Sampling Accessory for attenuated total reflectance (ATR) on a Perkin Elmer Frontier spectrometer from 4000 to 400 cm^{-1} , processed with Perkin Elmer Spectrum software.

Results

Visual and microscopical observation

Free DI water and PET induced negligible blemishes. Application of free EtOH resulted in two distinct behaviours: clear/transparent surfaces after 5 minutes and non-uniform opaque areas and blemishes after 60 minutes (Fig. 1 A and B). Samples cleaned with IPA performed similarly to EtOH

cleaned samples. Agar hydrogels caused limited scratching only visible with high magnification under the SEM. Opacity caused by free EtOH and IPA was significantly reduced when the solvents were introduced in agar gels. Agar left negligible residues visible under the SEM. Sample behaviour after PET gel cleaning resembled that of samples after free solvent application. Carbopol/Ethomeen hydrogels caused intense scratching visible under the SEM, and left considerable amounts of residues (Fig. 1C). Samples treated with Carbopol/EtOH exhibited non-uniform opaque areas characteristic of the action of the free solvent. All solvent/Carbopol gels left residues rendering surface appearance dull. All Pemulen gels left surfaces scratched and greasy (Fig. 1D), with residues which rendered surfaces stained (Fig. 1E). The samples were visually inferior to those treated with other solvent gels. Surfaces treated with water-based PVAc-borax were minimally blemished. This condition was aggravated upon addition of solvents, along

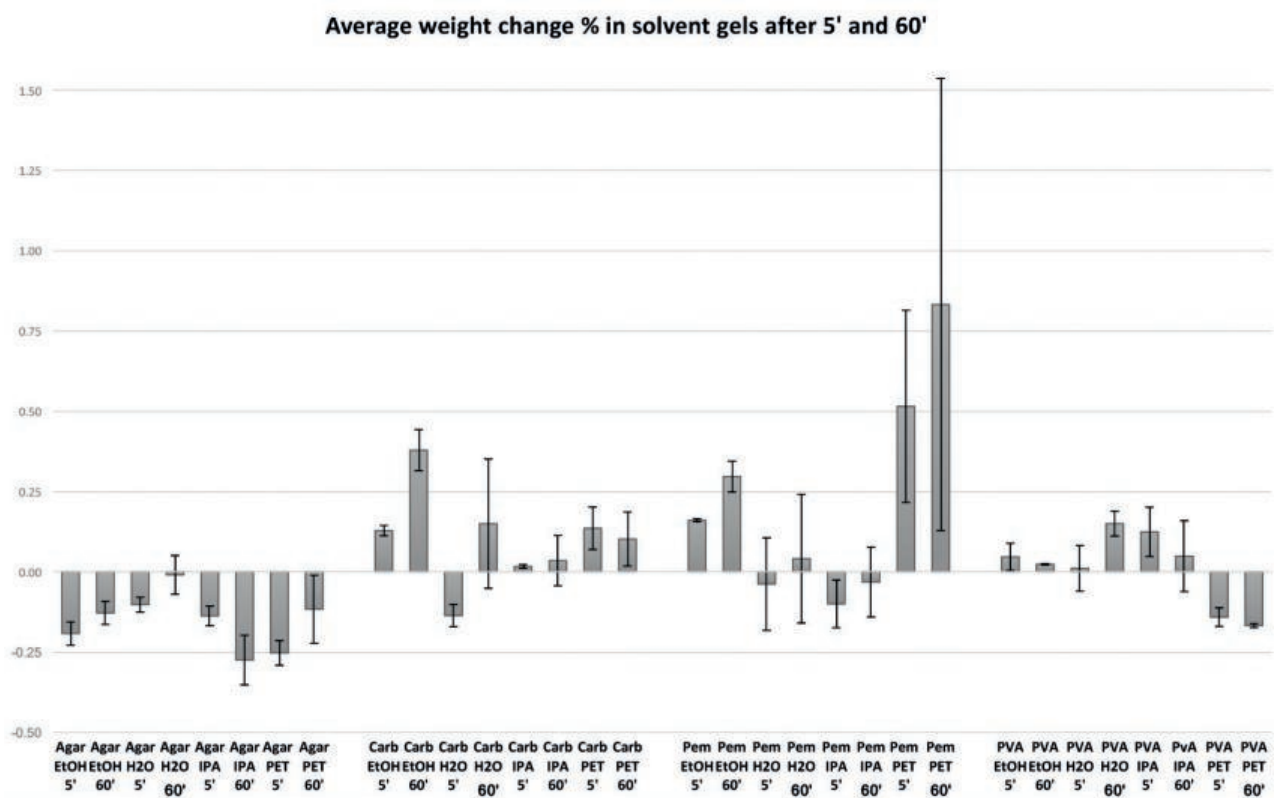


FIG. 2 Average weight change % of samples after solvent gels for 5 and 60 minutes.

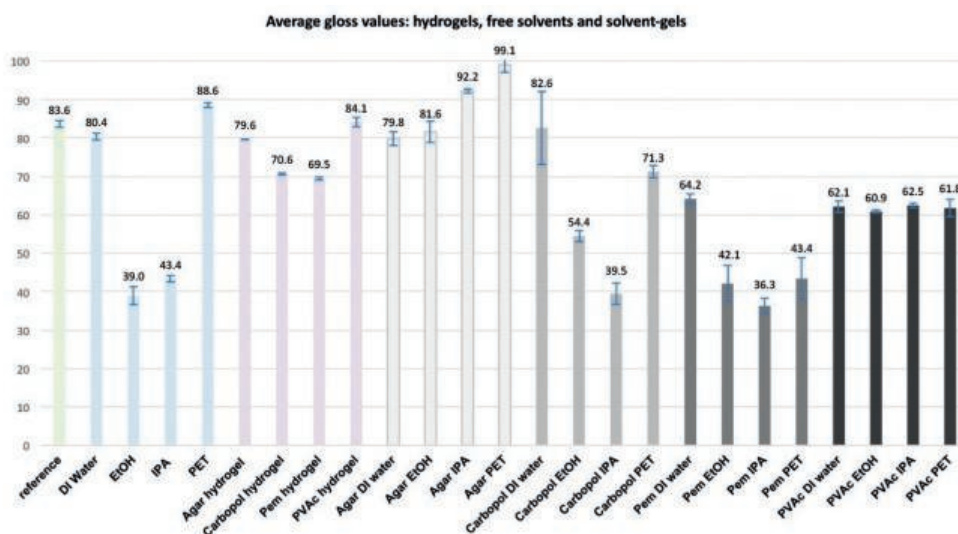


FIG. 3 Average gloss values of reference PMMA and treated samples, averaged from five measurements at five different surface spots at an incident angle at 20°, against a black matte background.

with scratching. Occasionally, solvent/PVAc gels caused areas of discoloration on PMMA (Fig. 1F). Minimal gel residues were observed after solvent-PVAc gel treatment. No swelling of samples was visually detected on any of the treated samples.

Weight change

There was no clear pattern of weight change with free DI water and PET. Application of PET for 5 minutes resulted in

the smallest weight fluctuations (Fig. 2). Samples showed an overall trend of weight loss after hydro- and solvent/agar gel treatments, which was more pronounced than with free solvents. Carbopol/Ethomeen and Pemulen hydrogels appeared more consistent upon addition of solvents. PVAc-borax hydrogels induced mostly weight gain while solvent/PVAc exhibited the least alterations. EtOH was identified as the solvent having the greatest effect on the treatments; gel type was shown to be the most significant factor in the solvent-gel systems while application time did not impact the outcome (Kavda *et al.* 2017).

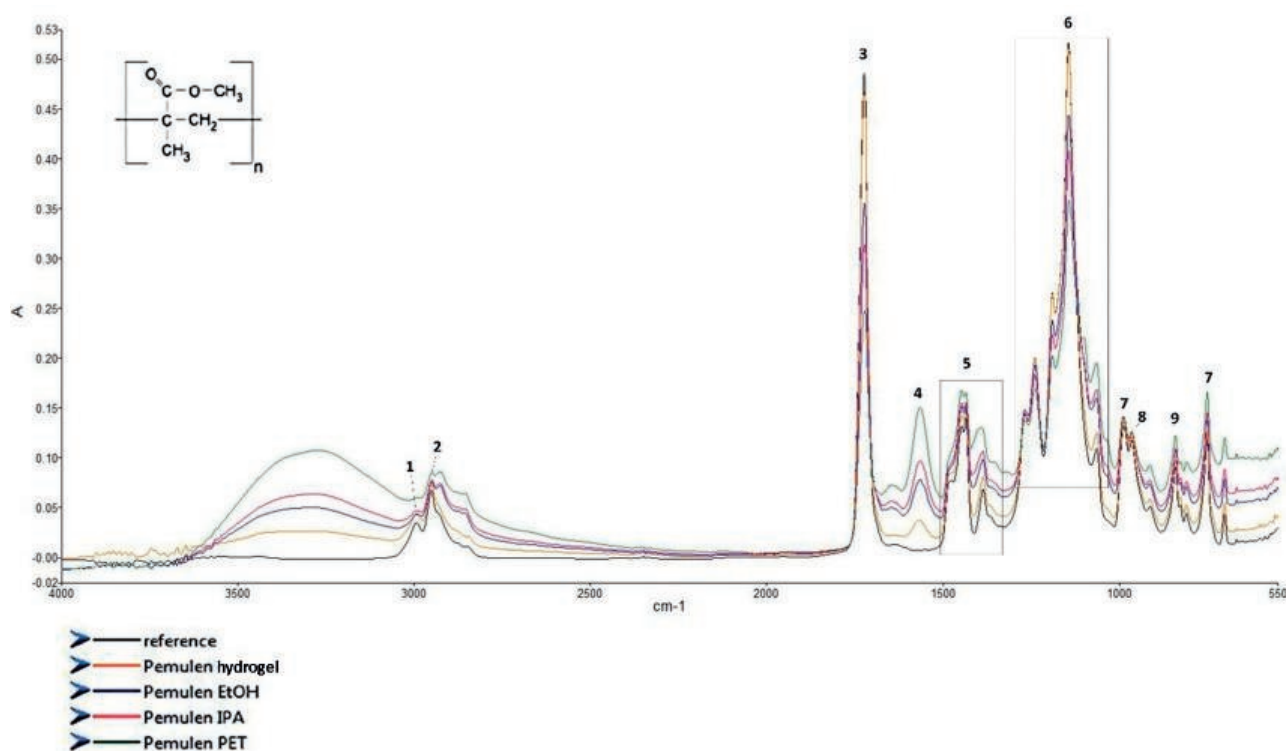


FIG. 4 Spectra of reference PMMA and samples after solvent/Pemulen with 32 scans at ambient temperature and pressure, with a resolution of 4 cm^{-1} equating to a penetration depth of $1.66\ \mu\text{m}$. Labelled primary absorption bands correspond to assignments in Table 1. The methyl methacrylate (MMA) monomer unit is inset.

TABLE 1 Assignments of diagnostic IR absorptions of reference PMMA (Haris *et al.* 2010).

Labels	Wavenumber (cm ⁻¹)	Assignment	Functional group
1	2993	C–H symmetric and asymmetric stretch	CH ₃
2	2951	C–H symmetric and asymmetric stretch	CH ₂
3	1723	C=O stretch	COOCH ₃
4	1556	C–O asymmetric stretch	COO ⁻
5	1500–1300	C–H deformation	CH ₃ and CH ₂
6	1400–1100	C–O stretch	COOCH ₃
7	987/750	C–H out of plane bend	CH ₃
8	965	C–C	CH ₃
9	840	C–H rock	CH ₂

Gloss measurements

The use of free DI water did not significantly alter the PMMA surface gloss. The visibly dulled surfaces after treatment with free EtOH showed the greatest variation in specular reflectance. Free IPA cleaning increased opacity while treatment with free PET showed a marginal increase in surface gloss (Fig. 3). DI water/agar and EtOH/agar offered the closest gloss values to the reference PMMA, while IPA/agar and PET/agar increased the gloss. In Carbopol hydrogel treated samples the large deviations of the measurements indicated that replicates were significantly affected. With the addition of solvents, Carbopol exhibited a fluctuation in gloss. Even though Pemulen hydrogels caused small losses, with the presence of solvents, samples behaved poorly with the lowest gloss values

among solvent gels tested. PVAc-borax hydrogels resulted in insignificant changes, but once solvents were added, a consistent drop in gloss occurred.

FTIR-ATR

Fig. 4 shows the FTIR spectra acquired from the PMMA control sample and 72 hours after the samples were treated with solvent-Pemulen mixtures. The structure of the MMA monomer is also illustrated in Fig. 4 and the peak assignments are described in Table 1. Agar and Carbopol with EtOH, IPA and PET, as well as Pemulen and PVAc with all four solvents, caused alterations to the PMMA surfaces, demonstrated by changes to the IR absorptions of treated samples. The principal

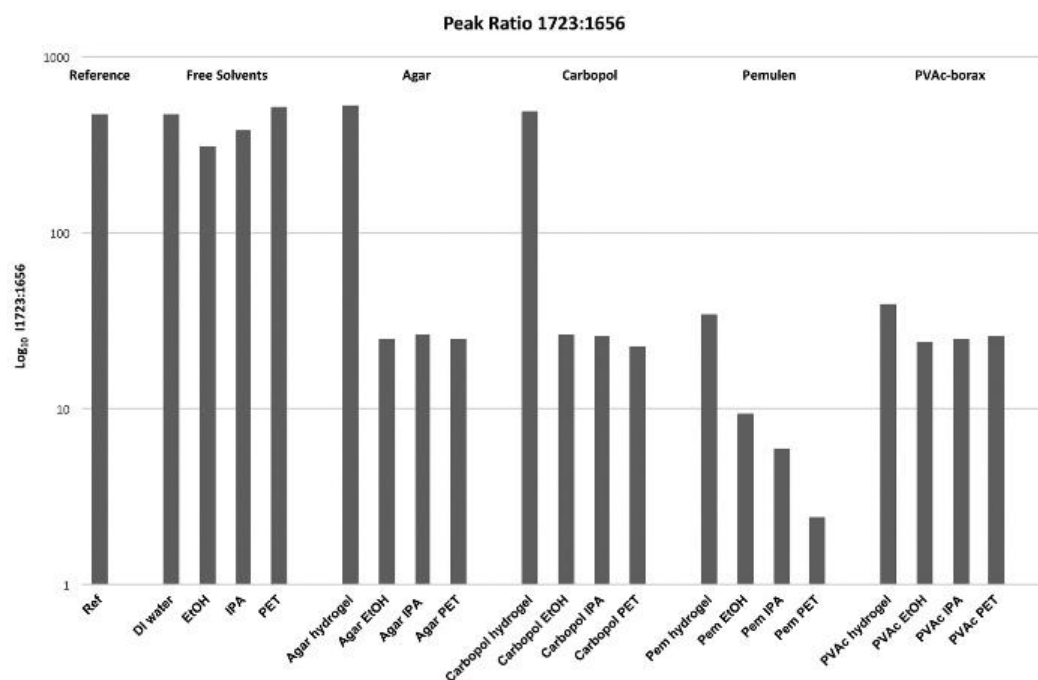


FIG. 5 Ratio between the peak heights at 1723 cm^{-1} and 1656 cm^{-1} of reference PMMA and treated samples.

changes were the formation of absorption bands at 3335 cm^{-1} and 1565 cm^{-1} , also seen after treatment with Pemulen and PVAc-borax hydrogels. The broad bands centred around 3400 cm^{-1} indicate the presence of oxidized structures, in particular hydroxyl groups ($-\text{OH}$) (Kaczmarek *et al.* 2010: 1600), and the absorption at 1560 cm^{-1} is assigned to the presence of a carboxylate ion (Grassie and Fortune 1973: 15). It is apparent from the spectra that an increase in the 1560 cm^{-1} band is accompanied by a decrease in the principal carbonyl band at 1723 cm^{-1} (peak 3), suggesting ester side-group elimination (Kaczmarek and Chaberska 2006: 8189). Decay of absorption at 1239 cm^{-1} and 1144 cm^{-1} (peak 5) is also associated with the cleavage of ester groups. Their decomposition has been shown by Chiantore *et al.* (2000: 1660) to relate to loss of polymer, especially to volatile compounds. They demonstrated that most of the changes in carbonyl band intensity relate to the production of methyl formate, while other gaseous products are methane, hydrogen and carbon oxides (Çaykara and Güven 1999: 226). In addition, an increase in the intensity of the shoulder at 2920 cm^{-1} and 1645 cm^{-1} , indicates the formation of $\text{C}=\text{C}$ bonds associated with main chain scission reactions (Ayre *et al.* 2014: 83).

The ratio between the peak height at 1723 cm^{-1} and 1656 cm^{-1} (Fig. 5) is used as a measure of change in the samples, showing the progression between the relative decrease of carbonyl groups and increase in carboxylate ion. However, it needs to be borne in mind that the vibrational band at 1656 cm^{-1} also corresponds to functional moieties present in all of the synthetic gel formulations and resulting from solvent cleavage of the glycosidic link in agarose, the gelling fraction in agar. Therefore, the increase in carboxylate ion may be in part due to surface residues. The free solvents of EtOH and IPA were seen to cause a slight decrease in the peak ratio, suggesting ester decomposition, exacerbated by the reduced

evaporation rate in the presence of the gels. Further work is under way to establish the depth of the residue layers and the relationship between solvent type and gel deposition.

Discussion

Elastic PVAc gels, together with rigid agar gels, proved the easiest to prepare. PVAc was harder to apply, but easy to remove, and agar gels were the easiest to place and remove due to their rigidity. Agar was not particularly compatible with PET, as exhibited by the gel dissociation, however its introduction did not prevent gellation. In the preparation of Carbopol/Ethomeen gels, difficulties were encountered due to dissociation of the system. Carbopol and Pemulen gels are in paste form that was easy to apply, but prone to leaving residues.

The poor appearance of samples after Carbopol and Pemulen gel cleaning appears comparable. Gloss measurements of the samples after application of the hydrogels presented similar values. Samples after the solvent-gel treatments followed the same pattern of hydrogels having the highest gloss, followed by PET, IPA and lastly EtOH. All gloss values were slightly lower in the Pemulen-based gels. Samples treated with solvent-based Carbopol and Pemulen gels showed a similar pattern of weight fluctuation. The results of poor surface appearance of Pemulen-based gels are in agreement with the gloss and weight measurements, which presented the most deviating values. Samples treated with PVAc gels offered similar visual observations throughout the use of the different solvents, which were comparable to other solvent gels. Interestingly, solvent-PVAc rendered PMMA surfaces equally glossy in a consistent manner. This might

suggest that treatment with PVAc gels offers more consistency, and that their action might be quite controlled.

IPA/Carbopol and EtOH/PVAc gels showed the least weight change. In theory, this appears to be a positive result, as it indicates that the solvent-gel action has no net effect on the treated material. Further investigations will determine whether more than one process might be occurring concurrently, as gravimetric analysis is completely insensitive to simultaneous extraction and deposition of material, if this occurs.

Weight changes in samples induced by free solvents were occasionally intensified or moderated by gellation. This suggests that gels influenced the performance of the solvents possibly by slowing their evaporation, while increasing control over their action. This, however, is not always a desirable characteristic: in the case of EtOH, which appears to be aggressive on these PMMA samples, this mechanism would increase solvent diffusion and contact time, aggravating the condition of the sample. Based on the FTIR results, this solvent interaction with PMMA can lead to extraction and/or dissolution of volatile components.

EtOH, followed by IPA, caused the highest visual and physical alterations, supported by gloss and weight measurements. Nonetheless, FTIR showed a similar degradation between PMMA treated with most solvent gels. When coupled with Pemulen, PET instigated the greatest change, followed by IPA and then EtOH (Fig. 5). This might indicate that when added in Pemulen, PET's action is intensified, an assumption also supported by gravimetric data (Fig. 2).

Conclusion

Visual observations, gravimetric and gloss measurements, and chemical analysis showed that hydrogels did not cause significant damage to PMMA surfaces. EtOH influenced the surfaces to the largest degree, appearing unsafe for use on PMMA. The application time did not affect the result of treatments at this stage of the study. FTIR-ATR showed that gels with EtOH, IPA and PET mainly caused cleavage of ester groups in PMMA, increasing its degradation. Overall, solvent-agar gels appeared to be the most effective and safe for use on PMMA, while solvent-based Carbopol and Pemulen performed poorly. Samples after treatment with solvent/PVAc-borax gels generally displayed more consistent behaviours with the least variations.

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