The effects of cross-linking agent and surfactant on the tear strength of novel vinyl polysiloxane impression materials

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1. Introduction

Tear strength (TS) is an important property of dental impression materials, which indicates their ability to withstand rupture while the impression is removed from mouth [1-3]. Impression materials are subject to both compressive and tensile forces while being removed from the mouth [4]. The removal forces for an impression of dentate arches are higher compared to edentulous arches and these become more complex with individuals who have angulated teeth, anterior protrusions and severe undercuts [5]. Impressions are more vulnerable to tearing in thin sections, such as the interproximal areas and subgingival regions [3, 5]. One of the common reasons for rejecting an impression is due to tearing while removing from the mouth [3, 6]. Tearing causes defects in the impression leading to the construction of a faulty final restoration [7]. Furthermore, a broken piece of impression material left embedded within the gingival sulcus can cause periodontal problems [8, 9]. Fragments of impression materials left in the mouth are difficult to detect in radiographs because most are not radiopaque, with the exception of polysulphide, which contain lead dioxide [9, 10].

There are a variety of impression materials currently on the market with varying properties. An ideal impression material should have excellent physical, mechanical and clinical properties. However, no single impression material on the market possesses all the desired properties for all applications [11-14], and therefore it is crucial to select one which satisfies several properties, taking in to consideration the patient's needs. Hydrocolloid (Agar and Alginate) impression materials are dimensionally unstable due to syneresis and imbibition, and their TS is also poor.

Elastomeric impression materials have improved physico-mechanical properties compared to hydrocolloids and non-elastic impression materials. These include polysulphides, condensation silicones, polyethers and vinyl polysiloxane (VPS) [15].

Among all the elastomeric impression materials, VPS impression materials are widely used because of their superior elastic recovery [14], excellent dimensional stability and greater accuracy [16, 17]. However, they do have some limitations such as their TS, although higher than hydrocolloids, it is lower than polysulphide impression materials [18]. Their % elongation-at-break is also lower than polysulphide impression materials [19, 20].

The VPS impression materials contain a conventional cross-linking agent [poly(methylhydrosilane)] which polymerises with the pre-polymer [vinyl-terminated poly(dimethylsiloxane)] in the presence of platinum catalyst. Little work has been carried out to improve the TS of VPS impression materials as demonstrated by the lack of literature available. However, Esteves *et al* [21] prepared formulations of vinyl-terminated poly(dimethylsiloxane) (pre-polymer) with a novel cross-linking agent [tetrakis(dimethylsiloxane)]. Tetrakis(dimethylsiloxane) is a four-functional silane-terminated cross-linking agent which can bond with four different molecules of vinyl-terminated poly(dimethylsiloxane). They prepared cross-linked formulations (not impression materials) through a hydrosilylation reaction between vinyl-terminated poly(dimethylsiloxane) and tetrakis(dimethylsiloxane) in the presence of a platinum catalyst. They used Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy to study the cross-linking of formulations containing different

concentrations of tetrakis(dimethylsiloxane) (1.0, 1.7 and 2.7) with vinyl-terminated poly(dimethylsiloxane), by measuring the consumption of the Si–H and C=C bond. It was observed that the Si–H concentrations used were directly proportional to the total integrated area of the band being used to follow the changes in the Si–H concentration, confirming that tetrakis(dimethylsiloxane) contributed to the cross-linking reaction.

Patents on Aquasil, by Dentsply Research and Development Corporation, [22] claimed the incorporation of a quadri-functional (multi-functional) vinyl-terminated poly(dimethylsiloxane) (pre-polymer) in their VPS impression materials to increase TS. Quadri-functional polysiloxane contains tetra-functional vinyl groups and one molecule of this pre-polymer can engage with four molecules of the cross-linking agent, providing vertical, as well as horizontal, cross-linking in the resulting cured VPS impression material. After polymerisation, this composition showed improved TS compared to the materials which contained only conventional vinyl-terminated poly(dimethylsiloxane).

Ud Din *et al,* [23] also formulated their own novel experimental VPS impression materials to investigate the effect of incorporating a tetra-functional di(methylsilyl) orthosilicate (TFDMSOS) cross-linking agent, on the materials % elongation-at-break. They found that % elongation-at-break of the formulations containing TFDMSOS, was significantly higher compared to the control [containing a conventional crosslinking agent-poly(methylhydrosiloxane)]. Furthermore, on incorporating a novel surfactant (Rhodasurf CET-2) in the formulations resulted in a further significant increase in % elongation-at-break and this was also concentration dependent.

VPS impression materials are inherently hydrophobic due to their chemical structure [24]. To overcome their hydrophobicity, manufacturers have incorporated surfactants within these materials and have classed them as hydrophilic VPS impression materials. These materials have better wetting properties compared to conventional VPS impression materials [for example 25-27].

Researchers have studied the effects of surfactants on the wetting of elastomeric impression materials and found that non-ionic surfactants improved the hydrophilicity of these materials. As an example, Norling and Reisbick [28], incorporated nonylphenoxypoly(ethyleneoxy) ethanol (non-ionic surfactant) into the base paste of silicone and polysulphide impression materials to improve the wettability of these materials. They found that the addition of the surfactant increased the wettability by gypsum products and consequently resulted in less bubble entrapment in poured casts. However, they did not measure the effects of the surfactant on the TS of their materials.

Nonylphenoxypoly(ethyleneoxy) ethanol is a commonly used surfactant for impression materials. Oh *et al.* [29] developed their own compositions of VPS impression materials, in order to investigate the effect of nonylphenoxy poly(ethyleneoxy) surfactant, on the surface hydrophilicity of their materials. They found that the materials containing the surfactant had better wettability compared to the control. Lee *et al.* [30] also developed their own VPS compositions with different concentrations of nonylphenoxy poly(ethyleneoxy) surfactant. They

found that in addition to improvement in hydrophilicity, there was a strong negative correlation between the surfactant's concentration and contact angle; the higher amount of surfactant resulted in lowering of the contact angles. However, none of the above researchers studied the effects of the surfactant on the TS of their materials, nor did they evaluate the hydrophilicity of their materials after disinfection. Testing only some of the properties does not provide enough information on all the other relevant properties of VPS impression materials.

In an earlier article, the authors, Ud Din *et al,* [31] evaluated the effect of a non-ionic surfactant, Rhodasurf CET-2, (ethoxylatedcetyl-oleyl alcohol), and novel cross-linking agent, TFDMSOS, on the contact angles of experimental VPS impression materials. The surfactant did not leach readily in to the disinfecting solution and the experimental formulations retained low contact angles after disinfection, compared to commercial materials. The possible interaction of surfactant and cross-linking agent, on the TS of novel experimental VPS impression materials, was not reported.

So, the purpose of the current study is to evaluate the effect of the novel cross-linking agent, a tetra-functional (dimethylsilyl) orthosilicate (TFDMSOS) on the TS of experimental VPS impression materials, and also to investigate if the surfactant (ethoxylatedcetyl-oleyl alcohol) is helpful in further improving TS.

Hence, the aim and objectives of this study can be summarised as follows:

- To develop novel VPS impression materials incorporating a novel cross-linking agent, TFDMSOS, and a non-ionic surfactant, ethoxylatedcetyl-oleyl alcohol (Rhodasurf CET-2) to improve their TS.

- To study the effect of incorporating TFDMSOS crosslinking agent and ethoxylatedcetyl-oleyl alcohol surfactant on the TS of experimental VPS impression materials, and comparing them with commercial materials.

Therefore, the null hypotheses can be summarised as the mean TS for all novel experimental VPS impression materials was not improved following incorporation of a novel cross-linking agent, TFDMSOS, and there was no further improvement in the TS after addition of the non-ionic surfactant, Rhodasurf CET-2, (ethoxylatedcetyl-oleyl alcohol).

2.   Materials and Methods

The commercial VPS impression materials used in this study were:

(i) Aquasil Ultra Monophase (Medium-Bodied), (Aq M), from Dentsply, USA

(ii) Elite HD Monophase (Medium-Bodied), (Elt M), from Zhermack, Italy

(iii) Extrude (Medium-Bodied), (Extr M), from Kerr, USA.

The ingredients used for the preparation of two hydrophobic (Exp-I, II) and three hydrophilic VPS experimental materials (Exp-III, IV and V) were:

Vinyl-terminated poly(dimethylsiloxane) (pre-polymer; molecular weight-Mw 62700; (Fluorochem, UK), Aerosil R812S (filler - from Lawrence Industries, UK), Rhodasurf CET-2 (ethoxylatedcetyl-oleyl alcohol; non-ionic surfactant, from Rhodia, UK). The following were purchased from Sigma Aldrich, UK, poly(methylhydrosiloxane) (Mw 2270; conventional cross-linking agent), tetra-functional (dimethylsilylorthosilicate -TFDMSOS; Mw 328.73; novel cross-linking agent), platinum catalyst (0.05 M), palladium (<1 μm; scavenger).

2.1 Preparation of experimental (Exp) VPS impression materials

The Exp formulations were prepared following published methods [29, 30], where the researchers developed their own VPS impression materials. Consistency of pastes was regulated by adjusting the amount of filler (Aerosil R812S) and molecular weight (Mw) of the pre-polymer, vinyl (polydimethylsiloxane) (Exp-I). Palladium (hydrogen absorber) was included in the formulations to prevent the secondary reaction of Si-H groups with moisture, or with each other, which would result in porous surfaces. After this, different concentrations of a novel cross-linking agent, TFDMSOS, together with the conventional one, were incorporated to improve mechanical properties (e.g. TS; Exp-II,I II, IV and V). Incorporation of TFDMSOS appeared to have no adverse effects on the formulations.

Furthermore, a non-ionic surfactant, Rhodasurf CET-2, (ethoxylatedcetyl-oleyl alcohol) was also added to separate formulations (Exp-III, IV and V) to improve the wettability and potentially the TS of these materials. To match the delivery of commercial VPS impression materials, both experimental pastes (base and catalyst) were dispensed separately in a double barrel cartridge.

The detailed compositions of these formulations are given in Table1 (for Exp-I-V). All components were weighed on a four-figure balance (Mettler, Toledo Ltd, Model AG204, UK). The main differences between these five formulations included the incorporation of a novel cross-linking agent, TFDMSOS, to improve the TS, and a novel non-ionic surfactant (Rhodasurf CET-2; Ethoxylatedcetyl-oleyl alcohol) to also improve the wetting properties and possibly to further improve the TS of these materials. Exp-I (no TFDMSOS) was used as a control for Exp-II (TFDMSOS). The same catalyst paste was used for both formulations (Exp-I and II; Table1). Exp-II was used as a control for Exp-III, IV and V. The same catalyst paste was used for Exp formulations III, IV and V (Table1).

2.2   Sample preparation for testing tear strength

Samples were prepared in rectangular stainless steel metal moulds measuring 40 x 10 x 1 mm^3. An acetate sheet was placed on top of a metal plate, on to which the stainless-steel mould was positioned. The base and catalyst pastes (pre-packed in a double barrel cartridge) were mixed using an auto-mixing syringe, and extruded directly into the mould cavity. Another acetate sheet was placed on top followed by another metal plate. Then the whole assembly was placed under a hand-operated hydraulic press (MESTRA MOD-030350, Talleres Mestraitua, S.L) and the pressure was slowly increased to 100 bars in order to distribute the material evenly in the mould cavity, flush out excess material and expel air bubbles [32]. The materials were allowed to set (i) for the time specified by manufactures for commercial materials (these times were 5 minutes for Aq M and Elt M, and 5-6 minutes for Extr M), and (ii) for 4 to 11 minutes depending on the overall composition of the Exp materials. The samples were removed from the mould and stored in plastic bags at 23 ºC ± 1 ºC until further use. An incision measuring 30 mm, was made down

the middle of each sample to prepare "trouser test" specimens (American Society for Testing and Materials [ASTM] D 624) and TS was measured as described below.

2.3   Tear strength

The tear test for Exp and commercial VPS was performed on a calibrated mechanical testing machine (Tinius Olsen Ltd, Model H5KS, England, load cell 5kN). Trouser test specimens (n=12 per material, according to ASTM D624-00(2001) [33] number of specimens should be greater than 5) measuring 40 x 10 x 1 mm^3 were used.

The specimen was secured in position by placing the legs in opposite directions using the self-tightening grips to prevent slippage, and then extended at a constant test speed of 500 mm min^{-1}[4]. The force (N) required to tear the specimen was recorded. The tear test was carried out at four different time points as given below:

   (i)   Immediately after setting to mimic the removal of impression from mouth [4]

   (ii)   24 hours after setting to mimic the removal of the impression from the cast [4, 34]

   (iii)   72 hours after setting

   (iv)   168 hours (1 week) after setting

The latter two time points were introduced to investigate the effects of extended storage times on TS prior to pouring of the impression.

TS was calculated according to ASTM D624 (Standard Test Method for TS of Conventional Vulcanized Rubber and Thermoplastic Elastomers) using Equation 1.

$$TS = \frac{F}{t} \qquad\qquad Equation\ 1$$

Where

TS = tear strength (N mm^{-1}), F = force to tear specimen (N), and t = thickness of specimen (mm)

2.4 Formulations to study functional bonds (cross-linking) in VPS by FTIR:

A further set of Exp Formulations (1, 2 and 3) were prepared in order to identify the chemical functional bonds and cross-linking using FTIR spectroscopy. In this part of the study only the very basic constituents were used, which take part in the cross-linking polymerisation reaction (i.e. pre-polymer, conventional cross-linking agents and novel cross-linking agents, platinum catalyst and surfactant), according to Esteves *et al.* [21].

Formulation 1:

Three ratios (1, 2 and 3 g) of vinyl-terminated poly(dimethylsiloxane, Mw 62700) with 0.04 g of conventional cross-linking agent, poly(methylhydrosiloxane), and 0.0021 g of platinum catalyst.

Formulation 2:

Similar to Formulation 1 above but with 0.04 g of novel cross-linking agent (TFDMSOS) replacing the conventional cross-linking agent.

Formulation 3:

Three ratios (1, 2 and 3 g) of Rhodasurf CET-2 with 0.04 g of novel cross-linking agent (TFDMSOS), and 0.0041 g of platinum catalyst.

2.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy (Perkin Elmer Spectrometer Accessories Horizontal Attenuated Total Reflectance; HATR) was performed on Exp Formulations 1, 2 and 3 and commercial VPS. The wavelength range was set between 600 cm^{-1} to 2400 cm^{-1}. To minimise error, four scan cycles were used for each specimen. Before running each sample, a background spectrum was obtained. After mixing, each sample was placed on the HATR window and spectra were generated for the following components/materials:

1. Individual liquid components used to prepare Formulations 1, 2 and 3 such as vinyl-terminated poly(dimethylsiloxane), poly(metylhydrosiloxane), TFDMSOS and ethoxylatedcetyl-oleyl alcohol (non-ionic surfactant; Rhodasurf CET-2).

2. Formulations 1, 2 and 3, and commercial VPS immediately after setting

Each spectrum was superimposed on to the previous one to identify peak changes between Exp and commercial VPS impression materials.

2.5   Statistical analysis

Two-way analysis of variance (ANOVA, P < 0.05) was performed where the factors were different materials at 8 levels (Aq M, Elt M, Extr M, Exp I, II, III, IV and V), and time of the test at 4 levels (at immediately after setting, 24, 72 and 168 hours after setting). This was used to identify statistically significant differences in the mean TS values of commercial and Exp materials at different time points, and to further explore if there was an interaction between these two variables (material*time). Subsequently, one-way ANOVA followed by post-hoc Tukey test were employed to identify any significant differences in mean TS values between all materials

(Exp and commercial) at every time point (at immediately after setting, 24, 72 and 168 hours after setting; p < 0.05). They were also used to evaluate TS values of individual VPS (Exp and commercial) at different time points (at immediately after setting, 24, 72 and 168 hours after setting; p < 0.05). Statistical tests were performed under the assumptions of normally distributed measurements using Shapiro–Wilk test (p > 0.05) and equal variances between groups using Levene's test (p > 0.05).

3. Results

3.1   Tear strength (TS)

3.1.1   TS of Exp and commercial VPS at each time point

Two-way ANOVA analysis demonstrated that TS was significantly influenced by material type (p<0.001, ie P < 0.05) and a significant interaction was observed between material type and time (p<0.001; ie P < 0.05). Fig 1 and Table 2 show the TS of Exp and commercial VPS impression materials at different time points. One-way ANOVA followed by post hoc analyses demonstrated that Extr M had a significantly lower TS compared to all other Exp and commercial materials at all time points, with the exception of Elt M, in which case the difference was not significant. Elt M had the second lowest TS and it was significantly different to all Exp VPS.

Exp-II, which contained the conventional cross-linking agent, poly(methylhydrosiloxane), as well as the novel cross-linking agent, TFDMSOS, showed significantly higher (p<0.05) TS values (almost double) at all-time points (immediately after setting, 24, 72 and 1 week after setting), compared to Exp-I (control), which only contained the conventional cross-linking agent

(Table 2). On incorporating the surfactant (Rhodasurf CET-2) in the novel Exp hydrophilic VPS (Exp-III, IV and V), the TS further increased significantly at all-time points compared to Exp-II (control). With an increase in the amount of surfactant (2%, 2.5% and 3%) in the formulations, there was a significant increase in TS for Exp-III, IV and V respectively, at all-time points. Among all Exp and commercial materials tested, Exp-V showed significantly higher TS at all-time points (Fig 1).

The TS of Exp and commercial VPS after 24 hours of setting showed a similar pattern to those obtained immediately after setting (Fig 1), and there was a significant difference among the groups of the materials tested. The TS of Exp-II, III, IV and V after 72 hours of setting was significantly higher than all commercial products and Exp-I (Fig 1). After 168 hours (one week) of setting, the mean TS of all the materials were significantly different ($p<0.05$). On further analysis of the data (post-hoc Tukey) it was seen that Aq M, Elt M and Extr M had significantly lower TS than all Exp materials, with the exception of Exp-I (Fig 1), which contained a similar conventional cross-linking agent to commercial materials.

3.1.2 TS of individual VPS at different time points

A comparison of TS of individual VPS (Exp and commercial) at different time points (immediately after setting, 24, 72, 168 hours after setting) was performed to observe if there were statistically significant differences between these, and to see what happens when a material is stored for longer times after setting (Fig 1 and Table 2). Generally, Aq M and Elt M showed a different trend in TS at the four different time points compared to Ext M and Exp VPS. The two commercial brands showed higher TS values with longer setting times, but they were not

statistically different compared to immediately after setting. The increase in TS was only significant at one week after setting for Aq M (Fig 1). In the case of the Exp materials the TS decreased with extended storage times, but it was only significant for Exp III and Exp-V after one week of setting compared to immediately after setting ($p < 0.001$; Fig 1).

Fig 2 shows FTIR spectra for Formulation 1 which contained three ratios (1, 2 and 3 g) of vinyl-terminated poly(dimethylsiloxane, Mw 62700), 0.04 g of conventional cross-linking agent [poly(methylhydrosiloxane)] and 0.0021 g of platinum catalyst. Fig 3 shows FTIR spectra for Formulation 2, which was similar to Formulation 1 but with 0.04 g of novel cross-linking agent (TFDMSOS) replacing the conventional cross-linking agent.

Both cross-linking agents showed a band at 2135 cm^{-1} (Si–H bond) (Figs 2 and 3). However, TFDMSOS also showed another band at 890 cm^{-1} for the Si–H group, as shown in Figs 3 and 4 (the latter compares Formulation 2 and liquid TFDMSOS alone). With an increasing amount of vinyl-terminated poly(dimethylsiloxane), the peak at 2135 cm^{-1} decreased, indicating the consumption of Si–H as polymerisation progressed (Figs 3 and 4). However, on comparing the spectrum for the vinyl-terminated poly(dimethylsiloxane) (Fig 2) with TFDMSOS (Fig 4), in addition to a decrease in the band at 2135 cm^{-1}, there was also a decrease in the band at 890 cm^{-1}, signifying the consumption of Si–H following the cross-linking polymerisation reaction [21]. This indicates that with the addition of TFDMSOS a reaction (cross-linking) had taking place at two different points, presumably leading to an increase in the TS (Fig 3 and 4).

Fig 5 shows FTIR spectra for Formulation 3, which contained three ratios (1, 2 and 3 g) of ethoxylatedcetyl-oleyl alcohol (Rhodasurf CET-2; non-ionic surfactant) with 0.04 g TFDMSOS and 0.0041 g of platinum catalyst. Bands at 2135 cm^{-1} (Si–H bond), 1253 cm^{-1} (Si-CH_3) and 890 cm^{-1} (Si-H) are observed. With an increasing amount of Rhodasurf CET-2, all the three peaks decreased, signifying the consumption of Si–H at 2135 cm^{-1}, 890 cm^{-1} (Si–H) and 1253 cm^{-1}(Si-CH_3), signifying cross-linking, which contributed to an increase in TS for Exp VPS impression materials (Exp-III, IV and V; Fig 1).

On comparing the spectra of Formulations 1, 2 and 3 with commercial materials, it was observed that overall all spectra were similar (Fig 6). However, there were some minor differences seen at 900 cm^{-1}, 1090 cm^{-1} and 1220 cm^{-1}, presumably due to the different types of surfactants, fillers and other ingredients incorporated in the commercial VPS impression materials (Fig 6).

Therefore, both null hypotheses were rejected since the mean TS for all novel Exp VPS was improved following incorporation of TFDMSOS and ethoxylatedcetyl-oleyl alcohol (Rhodasurf CET-2; non-ionic surfactant).

4.   Discussion

VPS impression materials have superior elastic recovery [7, 35], excellent dimensional stability [17, 36, 37] and greater accuracy [17, 38]. However, they do have some limitations such as their tear strength (TS), and due to their hydrophobicity, they are not compatible with the oral moist environment and gypsum slurries. In order to address the former issue, experimental impression materials were developed, with known compositions, and incorporating novel cross-linking agent

and surfactant, so that the results could be argued with reference to the ingredients and compared with commercial VPS impression materials.

Impression materials with sufficient TS are required for impressions of dental arches containing large undercuts, or where thin sections of materials are present (tight interproximal areas and sub-gingival regions), otherwise tearing will result. In these situations, materials with sufficient TS are required to avoid defects in the impressions. Hence literature, (for example [19], and common clinical practise, suggest that impressions should be removed from the mouth rapidly and with a 'snap action' to minimise tearing. Previous studies have measured the TS of commercial impression materials by loading the specimens in tension, at a crosshead speed of 20 mm min^{-1}[1, 18] and 50 mm min^{-1} until failure [3]. These studies however, do not correlate with the clinical situation (ie 'snap action' removal mentioned). In the current study, all materials were subjected to tear testing using a crosshead speed of 500 mm min^{-1} until failure, also reported by Lawson *et al.* [4], in order to produce clinically relevant results.

It was assumed that commercial materials contained the conventional cross-linking agent, poly(methylhydrosiloxane). The results showed that Exp-I, containing the same cross-linking agent had comparable (to Aq M) or higher TS than the commercial materials (Elt M and Extr M). On introducing a novel cross-linking agent, TFDMSOS, together with the conventional one in Exp-II, the TS, measured at all-time points (immediately after setting, 24, 72 and 168 hours after setting), increased significantly compared to Exp-I and all commercial VPS impression materials. The improved TS resulting from the incorporation of TFDMSOS could be explained by its structure (Fig 7) and function.

TFDMSOS is a tetra-functional silane-terminated cross-linker, and one molecule of TFDMSOS can bond (cross-link) with four functional groups (C=C) of vinyl-terminated poly(dimethylsiloxane) pre-polymer, as shown in Fig 7. It can be seen that on setting the material results in chain extension as well as cross-linking, forming a well organised network of the polymerised/cross-linked material, while in the case of the conventional cross-linking agent, less cross-linking takes place. Similarly, Dentsply's (22) VPS impression materials also contain a quadri-functional (multi-functional) vinyl-terminated poly(dimethylsiloxane) (pre-polymer), which has improved their TS, compared to materials containing only conventional vinyl-terminated poly(dimethylsiloxane). They also report that this cross-linking agent provides vertical and horizontal, cross-linking in the set VPS impression material. Ud Din *et al,* [23] formulated their own novel experimental VPS impression materials to investigate the effect of TFDMSOS on the materials % elongation-at-break. They found that % elongation-at-break of these formulations was significantly higher compared to the control, which only contained the conventional cross-linking agent [poly(methylhydrosiloxane)]. An increase in the % elongation at break is also being attributed to an increase in cross-linking within the set materials.

On incorporating non-ionic surfactant, Rhodasurf CET-2, (ethoxylatedcetyl-oleylalcohol) in the experimental formulations resulted in a further significant increase in the materials TS and this was also concentration dependent. Ud Din *et al,* [31], used this surfactant in their VPS experimental formulations and reported that the ethoxylated-oleyl alcohol contains a double bond in its chemical structure, which presumably activates during the setting reaction. Thus this component contributed to a further increase in cross-linking and some of the materials physico-

mechanical properties, including TS and % elongation at break.

Hatzi *et al* [39] used FTIR for quantifying Si-H consumption, by studying the reduction in the peak heights of Si-H ($\sim$2158cm^{-1}) and Si-CH$_3$ (1256cm^{-1}) groups in VPS materials. Nyczyka *et al* [40] also used FTIR to study the crosslinking of vinylpolysiloxanes with tetrakis(dimethylsiloxane), by concentrating on peaks for the Si-H group (eg at $\sim$2132cm^{-1}). Esteves *et al.* [21], who first introduced the use of TFDMSOS, also reported an increase in cross-linking within their experimental silicone materials, by using ATR-FTIR spectroscopy. In the current study, their method was followed; ATR-FTIR spectroscopy was used to monitor cross-linking/chain extension of TFDMSOS, focussing on peak heights of the silane group (Si-H) at 2135 cm^{-1} and at 890 cm^{-1}. Both peaks decreased in the set material and these were concentration dependent. The additional peak at 890 cm^{-1} was only seen in formulations containing TFDMSOS (Figs 3 and 4), and not in those containing only the conventional crosslinking agent (Fig 2). The results of the current study agree with Esteves *et al.* [21] findings. Therefore, the increased cross-linking and chain extension attained with TFDMSOS contributed to the higher TS of the experimental materials.

FTIR spectra for Formulation 3, which contained three ratios (1, 2 and 3 g) of ethoxylatedcetyl-oleyl alcohol (Rhodasurf CET-2; non-ionic surfactant), also showed the consumption of Si–H at 2135 cm^{-1} and 890 cm^{-1}, and 1253 cm^{-1}(Si-CH$_3$; Fig 5). This indicates that there was a reaction between the double bond within the surfactant's structure and TFDMSOS, since only these two components, along with the platinum salt catalyst, were present within the formulation. It is therefore assumed that cross-linking took place and hence contributed to a further increase in TS

of experimental VPS impression materials. The current study is also supported by Ud Din *et al,* [31], who investigated contact angles of experimental VPS impression materials incorporating (Rhodasurf CET-2). Their results confirmed that Rhodasurf CET-2 was an effective surfactant since the impression materials retained low contact angles after immersion disinfection for 30 minutes and 24 hours, compared with commercial materials, in which case they increased. The authors attributed this to some partial polymerisation of the surfactant with the ExpVPS, preventing the former from leaching.

The results of this study have shown that TFDMSOS cross-linking agent and Rhodasurf CET-2 improved the TS of experimental impression materials compared to the experimental control and commercial materials. It could be assumed that both of these components are more suitable for use in dental VPS impression materials based on the promising findings of this work. There is no literature available on the use of Rhodasurf CET-2 surfactant in impression materials, and clearly this area merits further research.

5.   Conclusions

- The novel cross-linking agent, TFDMSOS, increased the tear strength (TS) of Exp-II VPS impression material significantly at all-time points compared to Exp-I (control).

- On incorporating the surfactant (Rhodasurf CET-2) into the novel Exp hydrophilic VPS (Exp-III, IV and V), the TS was further increased significantly at all-time points compared to Exp-II (control); the increase in TS was dependent on the amount of surfactant introduced.

- Among all the materials (Exp and commercial) tested, Exp-V showed significantly higher TS at all-time points.

- TFDMSOS and Rhodasurf CET-2 show promise and open pathways to further research on improving physico-mechanical properties of VPS impression materials and related elastomers.

Acknowledgements

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