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Characterization, mechanistic analysis and improving the properties of denture adhesives

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ABSTRACT

Objective. Denture adhesives are widely used to avoid the detachment and sliding of dentures. However, the adhesion properties can be affected by variation in mouth conditions such as the level of salivation. The objective of this study was to understand the effect of environmental conditions on the adhesion properties of a commercially available denture adhesive named as Poligrip® Free manufactured by GlaxoSmithKline Ltd., UK and to identify the reasons for the observed variation in its adhesion strength.

Methods. The failure mechanisms of denture adhesive have been assessed through using different physical, mechanical and thermal characterization experiments. All methods were used in different pH, temperatures, and salivation conditions and at the end, a strategy was proposed to overcome the failure of the paste in hyposalivation as well.

Results. *In vitro* models mimicking the denture gingival interface were designed to evaluate the adhesion properties of the investigated adhesive. Changes in the adhesion strength in response to three major factors related to the oral conditions including level of salivation, pH, and temperature were measured. The results of lap shear, tensile test, and internal interactions suggested a cohesion failure, where the lowest adhesion strength was due to hyposalivation. Fourier transform infrared spectroscopy (FTIR) and rheological analysis confirmed the importance of hydrogen bonds and hydration in the adhesion strength of the paste.

Significance. The investigated scenarios are widely observed in patient using denture adhesives and the clinical reports have indicated the inconsistency in adhesion strength of

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the commercial products. After identifying the potential reasons for such behavior, methods such as the addition of tripropylene glycol methyl ether (TPME) to enhance internal hydrogen bonds between the polymers are proposed to improve adhesion in the hyposalivation scenario.

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1. Introduction

Dentures are commonly used especially by elderly population. Approximately, 600 million people are 60 years or older all around the world. This number is projected to be about two billion by 2050. Almost 80% of this population are living in developing countries [1,2]. Through the next decades, dental specialists should solve the challenge of preparing dental support for a rising number of elderly who fail to keep their own natural teeth. To avoid the unwanted movement and slide of dentures in the mouth, adhesives which are shear thinning pastes are widely employed. Proper adhesion of dentures to gum (or gingival tissue) can improve patients' comfort. In addition, the use of denture adhesives can result in a reduction of denture mediolateral movement and dislodgment as well as a greater bite force [3,4].

A denture adhesive should be ideally biocompatible non-irritating, and could adhere properly to the oral mucosa. They should be easy-to-apply and easy-to-remove, and maintain adhesion strength for 12–16 h. A denture adhesive interacts with the denture surface from one side and the underlying oral mucosa from the other side over a certain period of time. To apply the adhesive, a thin layer of the material is applied to the interior surface of denture, which is then placed on top of gum (Fig. 1a). The adhesion strength of denture adhesives is maximized shortly after their application [5]. Immediately, after adhesive application and exposure to saliva, paste's water content increases which results in the enhancement of paste viscosity and adhesion. Thus, it is expected that the level of saliva affects the adhesion properties of the paste. This is in line with clinical observation showing the significant impact of saliva level on the performance of denture adhesives in different patients [6–8]. The adhesive, however, should maintain its properties in various conditions such as variation in the level of pH, temperature induced by different foods, and level of salivation [9,10].

In this study, the adhesion strength of Poligrip[®] Free manufactured by GlaxoSmithKline Ltd. (GSK, UK) was characterized. The adhesive is in the form of a shear thinning paste (Fig. 1b). The tested adhesive is comprised of carboxymethyl cellulose (CMC) and poly(methyl vinyl ether/maleic acid) (PMVEMA) as hydrophilic components and mineral oil and petrolatum as hydrophobic compounds. The hydrophilic compounds absorb and maintain water to enhance the adhesion strength and the hydrophobic compounds prevent excessive swelling and dissolution of the paste [11–13].

To measure the adhesion properties, *in vitro* models mimicking the denture oral mucosa interface were developed and used for measuring lap shear and tensile adhesion strength of the paste in various conditions including different pH values, levels of salivation, and temperature. Also, Fourier transform infrared spectroscopy (FTIR), modulated temperature differential scanning calorimetry (MTDSC), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), denture surface morphology, and viscosity measurement were performed to identify the mechanisms resulting in the observed properties.

2. Materials and methods

2.1. Materials

All materials and chemicals were purchased from Sigma–Aldrich Co. (St. Louis, USA) and were used as received without further purification unless mentioned otherwise. The artificial saliva used in the experiments was an aqueous solution containing 0.4 g/L KCl, 0.4 g/L NaCl, 0.906 g/L CaCl₂·2H₂O, 0.690 g/L NaH₂PO₄·2H₂O, 0.005 g/L Na₂S·9H₂O and 1 g/L Urea based on Fusayama Meyer Formula (Table 1) [14]. The pH of the saliva was adjusted by using the hydrochloric acid and sodium hydroxide 1 M solution. The Super Poligrip[®] Free denture adhesive was used throughout the experiments. The denture adhesive contained PMVEMA, CMC, petrolatum, cellulose gum, and mineral oil. The commercial denture resin made of heated poly methyl methacrylate and monomer ethylene dimethacrylate (Dentorium convertible acrylic-heat cure, Dentorium[®]) was purchased from Dentorium Products Co., Inc. (Farmingdale, NY) and used according to manufacture recommendation [15]. CMC (Fig. 1c) and PMVEMA (Fig. 1d) were obtained from Ashland Inc. Company (Covington, USA) and were prepared with concentrations of 24% (w/v) and 30% (w/v), respectively.

Table 1 – Artificial saliva composition.

Saliva composition	g/L
KCl	0.4
NaCl	0.4
CaCl ₂ ·2H ₂ O	0.906
NaH ₂ PO ₄ ·2H ₂ O	0.690
Na ₂ S·9H ₂ O	0.005
Urea	1

¹ These authors contributed equally to this work.

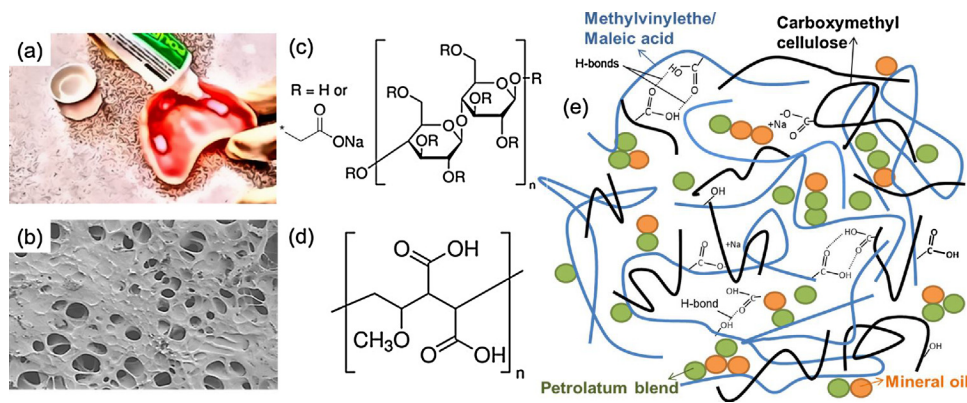


Fig. 1 – Poligrip[®] Free denture adhesive, its application and components. (a) Thin layer of the shear-thinning adhesive is applied on the denture and then placed on the gum; (b) SEM image of the freeze-dried paste showing the presence of pores within the material (scale bar = 100 μ m); (c) chemical structure of CMC; (d) chemical structure of PMVEMA; (e) schematic showing various components of the paste and the interactions between these components ranging from the entanglement of polymeric chains to weak hydrogen and hydrophobic interactions.

2.2. Methods

2.2.1. In vitro model development for adhesion measurement

Flat sheets of polyacrylate denture resin (Dentorium[®]) was used to mimic the denture surface, while a porcine skin was used to mimic surface properties of the oral tissue [16]. Two different set of molds were designed for characterization of the adhesion strength of the denture adhesive against tensile and lap shear loading. Based on ISO 10873: 2010 (testing of denture adhesives) protocol, a circular mold with the diameter of 24 mm was used, where a porcine skin was attached to the surface [17]. A similar circular mold was fabricated from PMMA and coated with denture resin to mimic the denture surface. Following the American Standard Test Method (ASTM) F2255-5 for lap shear experiments [18], rectangular PMMA sheets (40 mm \times 22 mm \times 2 mm) were cut and covered by porcine skin (Fig. 2b). A notch of 0.7 mm size was formed on the sample holders to facilitate the alignment of the two sides. A similar PMMA sheet was coated with denture resin to mimic the denture surface. 200 mg of paste was applied on the surface of denture side [13]. After that, the samples were placed in an incubator with 100% humidity and 37 $^{\circ}$ C for 30 min. After this period, the sample holder with denture adhesive was submerged in 200 mL of artificial saliva with different pH values, temperature and duration based on the test conditions. The study parameters are listed in Table 2. Also, all different formulations (F1–F7) are thoroughly explained in Table 3. To mimic hyposalivation [19–22], the samples were kept in incubator for 15 min and submerged into saliva for 5 min. On the other hand,

the hypersalivation was achieved by incubating the samples for 45 min follow by submerging them into saliva for 15 min. Subsequently, the adhesive was pressed gently (2N initial force by placing a known weight on the samples) onto the skin side and was kept under pressure for 30 s before mechanical testing.

2.2.2. Tensile method for measuring adhesion strength

The adhesion strength was determined using an Instron Mechanical Testing Machine (Norwood, USA) by measuring the maximum load. The test condition was based on ISO 10873. The test was performed first on bare PMMA surface and then was repeated with the PMMA mold covered with porcine skin as described above.

In the tensile test, 200 mg Poligrip[®] Free was applied over sample holder. The samples were prepared as described before. The sample holder with adhesive and cylinder were attached to the mechanical tester's grips. Tensile load was applied at the rate of 5 mm/min. The adhesive strength was measured based on maximum force per unit area. The test was repeated 10 times per condition and mean and standard deviation (SD) were calculated and reported. The number of samples per test group sufficient for drawing conclusion is suggested to be 5 in the ISO 10873 standard. However, we used 10 replicates for each experiment and performed statistical analysis on the collected data.

2.2.3. Lap shear method for measuring adhesion strength

The lap shear was conducted to evaluate the adhesion strength in shear movement. Lap shear tests were performed initially with bare PMMA molds and then with molds covered with denture resin and porcine skin. The sample preparation was the same as the tensile test and similarly, the stretching rate was set at 5 mm/min. The minimum load before sample detachment was measured as the adhesion strength. The maximum shear bond stress (Pa) was also calculated as the maximum force (N) divided by the area covered with adhesive (mm²) [23]. The tests were repeated 10 times per condition and the means and SDs were reported. The covered areas were visually inspected through comparison with a standard

Table 2 – Study parameters in three low, medium and high levels of moisture, pH and temperature.

Factors	Low level	Normal level	High level
Oral moisture degree	<0.1 mL/min	0.2 mL/min	>0.35 mL/min
pH	2	7	10
Temperature	0 $^{\circ}$ C	37 $^{\circ}$ C	60 $^{\circ}$ C

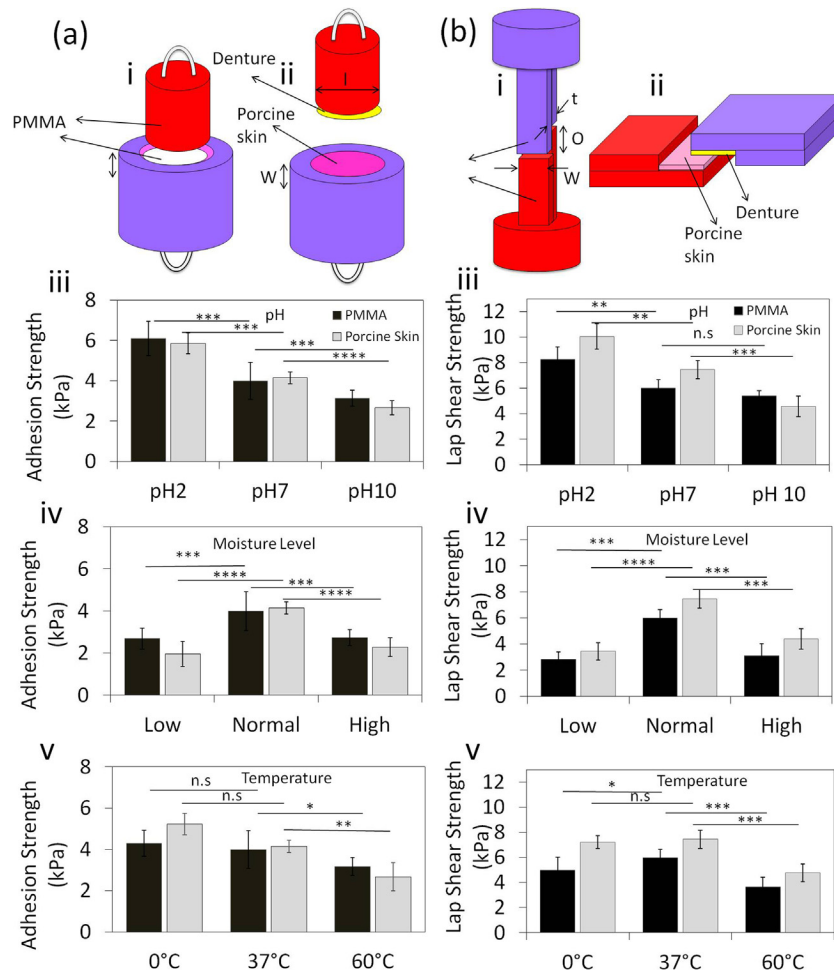


Fig. 2 – Adhesion properties of the paste in different working scenarios. (a) Adhesion strength at maximum load in two different set-ups: “w” represents the width and “l” is the length, (i) schematic of the standard PMMA-PMMA setup and (ii) schematic of the modified setup with porcine skin-denture covered grips (iii) different pHs, (iv) different moisture levels, (v) different temperatures; (b) lap shear test in two different set-ups: “w” represents the width and “t” the thickness of PMMA piece and “o” is the overlap length, (i) schematic of the standard PMMA-PMMA setup and (ii) schematic of the modified setup with porcine skin-denture covered grips (iii) different pHs, (iv) different moisture levels, (v) different temperatures.

marked area and the uncertainty for the covered area was less than 10% of the area.

2.2.4. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were acquired using a Bruker Hyperion 3000 FTIR

Microscope (Bruker, Ettlingen, Germany) equipped with ATR accessory (64 scans, wavenumber range 400–4000 cm^{-1}). The samples for each group were prepared the same as mechanical tests. Milli-Q water with different pH values was used as the

Table 3 – A full factorial design table showing 7 runs for tensile bond strength and lap shear tests (formulation codes describe different environmental conditions as: hyposalivation (low salivation mode: <0.1 mL/min), normal salivation mode (0.2 mL/min), hypersalivation (high salivation mode: >0.35 mL/min), acidic (pH 2), basic (pH 10), low temperature (0 °C) and high temperature (100 °C)).

Formulations in different environmental conditions	Salivation	pH	Temperature	Incubation time (min)	Submerging time in saliva (min)
Hyposalivation	Low	7	37 °C	15	5
Normal	Normal	7	37 °C	30	10
Hypersalivation	High	7	37 °C	45	15
Acidic (pH 2)	Normal	2	37 °C	30	10
Basic (pH 10)	Normal	10	37 °C	30	10
Low temperature (0 °C)	Normal	7	0 °C	30	10
High temperature (60 °C)	Normal	7	60 °C	30	10

background. The resolution was 1 cm^{-1} and 100 scans were performed and averaged for each sample.

2.2.5. Scanning electron microscopy (SEM)

Morphological characteristics of freeze-dried samples prepared with different amount of plasticizers were obtained by Field Emission Scanning Electron Microscope (FESEM, Zeiss Ultra 55, Germany). Samples were sputter coated with a 5 nm layer of Pt/Pd using the EMS 300 T Dual Head Sputter Coater.

2.2.6. Thermal characterizations

2.2.6.1. Modulated temperature differential scanning calorimetry (MTDSC). MTDSC studies were performed using a TA Q1000 modulated machine (TA Instruments®, Delaware, USA) over the temperature range from 0°C to 150°C . Lyophilized samples were typically between approximately 2.4–3.6 mg. The samples were heated from room temperature up to 100°C at a heating rate of $5^\circ\text{C}/\text{min}$. The nitrogen flow rate was $20\text{ mL}/\text{min}$.

2.2.6.2. Thermogravimetric analysis (TGA). TGA was performed using a thermogravimetric analyzer (TA Q500 TGA, TA instruments®, Delaware, USA) under nitrogen atmosphere at a heating rate of $5^\circ\text{C}/\text{min}$ and temperature range from 25°C to 300°C . The nitrogen flow rate was kept at $20\text{ mL}/\text{min}$.

2.2.7. Rheological analysis

Rheological measurements were carried out with AR-G2 rheometer (TA Instruments®). Samples were contained between two horizontal parallel stainless steel plates of 20 mm diameter. Shear rate and frequency sweep tests were performed at 0, 37 and 60°C , sweeping frequencies in the range of 0.001–100 Hz at 1% strain and shear rates from 0.001 to 100 s^{-1} with 10 points/decade. The frequency sweep tests were performed using a cone-plate rheometer (25 mm diameter, 1° angle). Samples were analyzed at different pHs as well as different temperatures based on sample preparation method for each condition.

2.2.8. Swelling and degradation assessment

The Poligrip® Free paste was weighed (300 mg each) in the beginning of the experiment. The samples were added into $70\text{ }\mu\text{m}$ cell stariners (5 samples per condition) which were placed into 6-wellplates containing with 4 mL saliva with 3 different pH values of 2, 7, and 10. The samples were kept in incubator for the duration of experiment. Measurements were obtained in certain time points of 2, 5, 10, 30 min for 4 h. The swelling ratio percentage were calculated and reported for each group [24]. The swelling ratio was calculated based on the following equation (Eq. (1)) whereas, W_d is the initial weight and W_s is the final weight in each time point.

$$\text{SwellingRatio}\% = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

2.2.9. Statistical analysis

The statistical significance was determined by an independent Student t-test for two groups of data or analysis of variance (ANOVA). Data were calculated as mean \pm standard deviation (SD). T test was performed and differences were considered

statistically significant when p values resulted lower than 0.05. $P < 0.05$ (*), $P < 0.01$ (**), $P < 0.001$ (***), $P < 0.0001$ (****).

3. Results

3.1. Developing an *in vitro* model for denture adhesives

In this study, *in vitro* models are developed that extend existing standards to better mimic the interface of gingival tissue and dentures as illustrated in Fig. 2a (i), (ii) for tensile adhesion strength measurement and Fig. 2b (i), (ii) for lap shear tests. In our models, one surface is coated with denture resin, which was prepared as per manufacture's recommendation to mimic the service properties of dentures. The other side made from a PMMA sheet covered by a piece of porcine skin to mimic the gum tissue. Following ASTM F2255-5 and the International Organization for Standardization (ISO) 10873 for characterization of medical adhesives, two sets of experiments were designed to measure the adhesion strength against tensile and shear forces.

To shed light on the effect of all these condition, the developed *in vitro* models were used to measure the adhesion strength of the adhesive paste. In all experiments, the *in vitro* model was exposed to artificial saliva, prepared according to Fusayama Meyer formula [14], with different pH values and temperatures. To mimic different mouth conditions, the hydration time, level of pH and temperature of the saliva were changed as described in Section 2.2. Briefly, in the case of hyposalivation, the samples were kept in incubator for 15 min and submerged into saliva for 5 min. These values were 30 min and 10 min for normal conditions. The hypersalivation was mimicked by incubating the samples for 45 min followed by submerging them into saliva for 15 min. All tests were carried out at the pH of 7 and a temperature of 37°C . To investigate the effect of pH, artificial saliva with pH values of 2, 7, and 10 were used for hydration of the paste. In this case, the samples were submerged in artificial saliva for 10 min. The effect of temperature was investigated by submerging the samples in artificial saliva kept at 0, 37, and 60°C .

3.2. Adhesion strength in tensile and lap shear experiments

Fig. 2a (iii) shows the tensile adhesion strength of Poligrip® Free in response to variation in the saliva pH values, temperature, and its generation rate [25]. The adhesion strength at 37°C and 0°C were not significantly different. However, the tensile experiments showed that the temperature of 60°C significantly reduced the adhesion strength of the paste. Another interesting observation was that the adhesion strength measured using the *in vitro* models with and without the incorporation of the porcine tissue was not significantly different. This observation suggests an insignificant interaction between the paste and gingival tissue. A similar trend was observed for the lap shear tests and no significant difference was detected between the adhesion strength of the samples tested using the model covered with porcine tissue and the values obtained using the model with bare PMMA

surface (Fig. 2b (iii)). Another important observation was that the failure of the paste was mainly due to cohesion as layers of paste remained on both denture and tissue sides. The cohesion failure suggests that improving the internal interactions between paste components can potentially improve the detachment force [25].

Both tensile and lap shear experiments suggested a lower adhesion strength in alkaline environment with pH of 10, as shown in Fig. 2a (iv) and b (iv). The paste had the highest adhesion strength in acidic environment and the values at pH 2 were almost two times higher than those measured for the control group at pH 7. Fig. 2a (v) and b (v) shows the effect of hydration rate on the adhesion properties of the paste. The condition mimicking hyposalivation resulted in the lowest adhesion strength in both tensile and lap shear experiments. Similarly, hypersalivation resulted in lower adhesion strength in comparison to the control group. Similar to previous cases, the failure was due to cohesion insufficient stability of the paste. All the results are also listed in Table 4.

3.3. Paste characterization

Fig. 3 shows some physical characterizations of the paste and its ingredients. The swelling and the dissolution of the paste and CMC at different pH values are shown in Fig. 3a and b. Since PMVEMA has a low viscosity, it was not possible to characterize its swelling and degradation properties [26,27]. As illustrated in Fig. 3, the paste showed the lowest swelling rate in acidic environment in Fig. 3a [28]. Once the swelling ratio reached to 200% of the dry weight, the paste started to dissociate and to partially degrade, thus, a reduction in samples' mass was observed beyond that point. The swelling and the dissolution rates were faster in alkaline environment and the dissolution started after 40 min in comparison to 70 min at neutral pH. The same trend was seen for CMC, which is one of the hydrophilic components of the paste. However, CMC showed a higher swelling ratio (almost 400%) in comparison with the paste in the same environments (Fig. 3b).

TGA curves of the paste and its ingredients, which demonstrate the thermal stability and gradual decomposition of the paste, are presented in Fig. 3c [29–31]. The TGA results showed that the thermal stability of CMC was more than PMVEMA and the degradation of all materials was completed in almost two steps. Based on TGA data, all components were stable up to $\sim 100^\circ\text{C}$. Hydrated paste showed 40% weight loss around 100°C , which was due to rapid evaporation of water molecules as well as potential degradation of ingredients (shown as blue and green curves in Fig. 3c). The weight loss was increased to $\sim 60\%$ at the next step around 130°C since the degradation of ingredients started especially for CMC. DSC diagram of the paste up to $\sim 200^\circ\text{C}$ shown as an inset in Fig. 3c, displayed transition temperatures and melting points [32] of the paste at different pH values. The results suggested that at pH 10, the amorphous paste underwent a faster melting and degradation at lower temperatures. At pH 7, two main transitions were observed. However, at pH 2, the paste experienced a smoother transition that could be due to stronger internal interactions with water molecules and hydrogen bonds. Hence, bonded water molecules gradually evaporated at temperatures higher than normal 100°C . The proposed mechanism for different

Table 4 – Tensile and lap shear properties of the paste in different conditions.

	Normal			pH 2			pH 10			Hyposalivation			Hypersalivation			Temperature 0°C			Temperature 60°C		
	PMMA	Porcine skin		PMMA	Porcine skin		PMMA	Porcine skin		PMMA	Porcine skin		PMMA	Porcine skin		PMMA	Porcine skin		PMMA	Porcine skin	
	Ave	SD		Ave	SD		Ave	SD		Ave	SD		Ave	SD		Ave	SD		Ave	SD	
Tensile test	4.00	0.91		6.10	0.84		3.14	0.41		2.68	0.50		2.74	0.38		4.30	0.63		3.18	0.43	
Lap shear test	6.00	0.65		8.22	1.01		5.38	0.41		2.81	0.60		3.10	0.94		4.99	1.00		3.66	0.78	
				10.03	1.00		4.55	0.81		0.66	0.66		4.40	0.78		7.22	0.50		4.77	0.72	
				5.85	0.52		2.66	0.36		1.96	0.6		2.28	0.44		5.23	0.52		2.67	0.69	

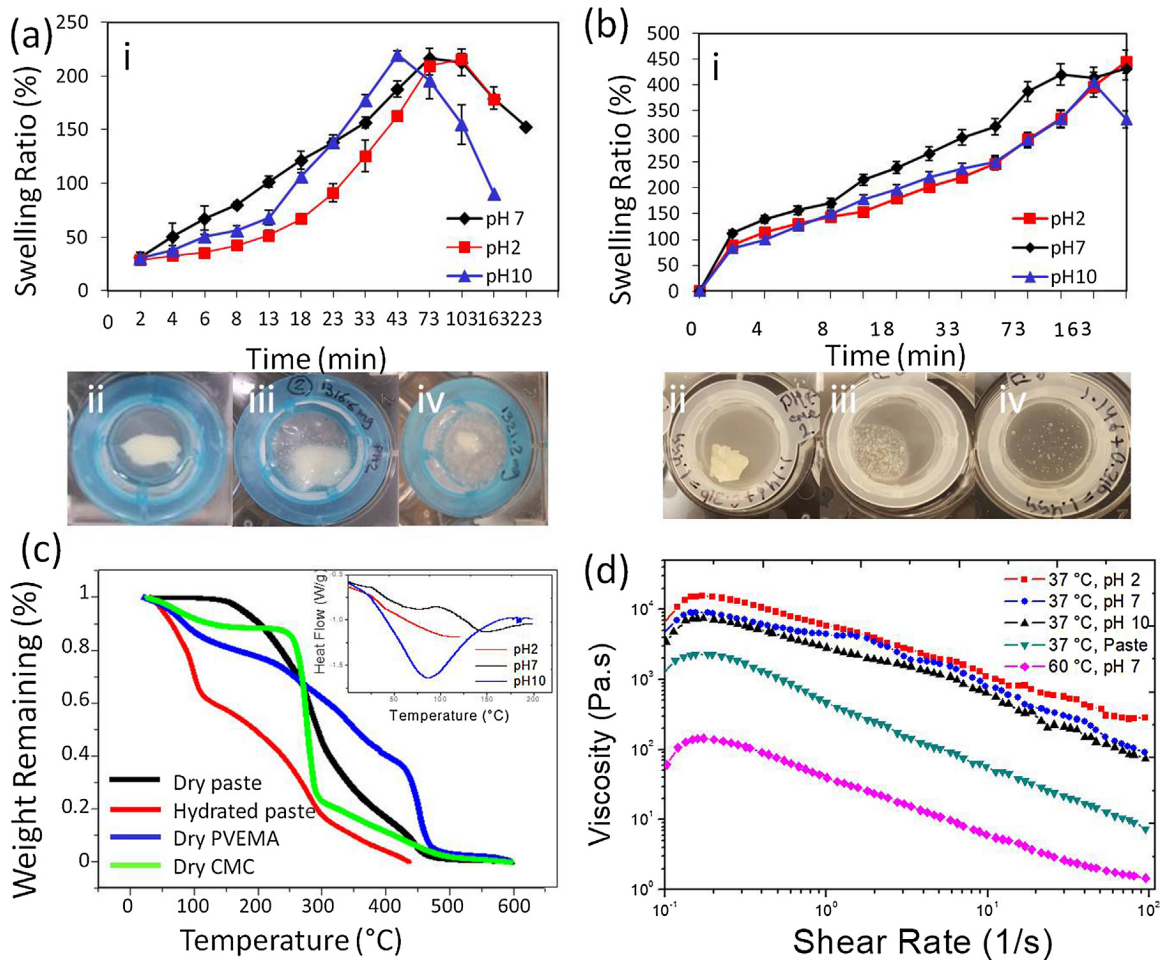


Fig. 3 – Physical characterization of the paste. (a) Swelling ratio of the Poligrip[®] Free paste in artificial saliva (i), and images showing the physical appearance of the paste at the beginning of the experiment (ii), after 30 min (iii), and after 60 min (iv); (b) (i) swelling ratio of CMC in artificial saliva (i), and images showing the physical appearance of CMC at the beginning of the experiment (ii), after 30 min (iii), and after 60 min (iv); (c) weight loss (TGA) diagram of paste, PMVEME and CMC; DSC diagrams (inside); (d) viscosity of the paste at different pHs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

observations will be discussed in detailed in the following section.

Rheological properties provide a measure of cohesion properties of soft materials. In the case of Poligrip[®] Free, our mechanical tests for measuring the adhesion strength of the paste, showed a cohesion failure. Thus, it was expected that the paste viscosity could provide an additional measure for verification of the failure mechanism of the paste. The viscosity of the paste was measured at different pH values and temperatures. As illustrated in this figure, hydration in saliva with pH 2 resulted in the highest viscosity. Increasing the pH resulted in a reduction in paste viscosity, which was consistent with the mechanical data. The lowest viscosity of the paste was observed for the tests performed at 60 °C.

3.4. Mechanistic analysis of the paste adhesion properties

The vibrational peaks for carbonyl groups of carboxylate and carboxylic acids appeared at different wavenumbers in

range of 1400–1750 cm^{-1} spectral window in Fig. 4. However, it is difficult to quantify the amount of each component using FTIR [33–35]. Saliva in different environmental conditions has a significant effect on the adhesion or cohesion properties by changing the strength of O–H and –COOH bonds or formation of an amorphous extended structure which cannot create strong hydrogen bonds (schematic of high temperatures or hypersalivation cases). Higher entropy of polymer chains at high temperatures reduces the formation of strong and long lasting bonds in comparison with physiologic or lower temperatures. It is speculated that at higher temperatures or high pH values, the non-bonding or free carboxylic group peaks of PMVEMA and CMC are more predominant around 1700 cm^{-1} , but they transform to bonding anhydride C–O types and lower wavelengths in acidic environments and lower temperatures. As shown in Fig. 4a, at different temperatures, a shift can be seen for C–H bends, alcoholic C=O and stretching C=O bonds from 1753 cm^{-1} at 60 °C to 1748 cm^{-1} at 37 °C and then to 1733 cm^{-1} at 0 °C. The intensity of this peak was reduced by decreasing the

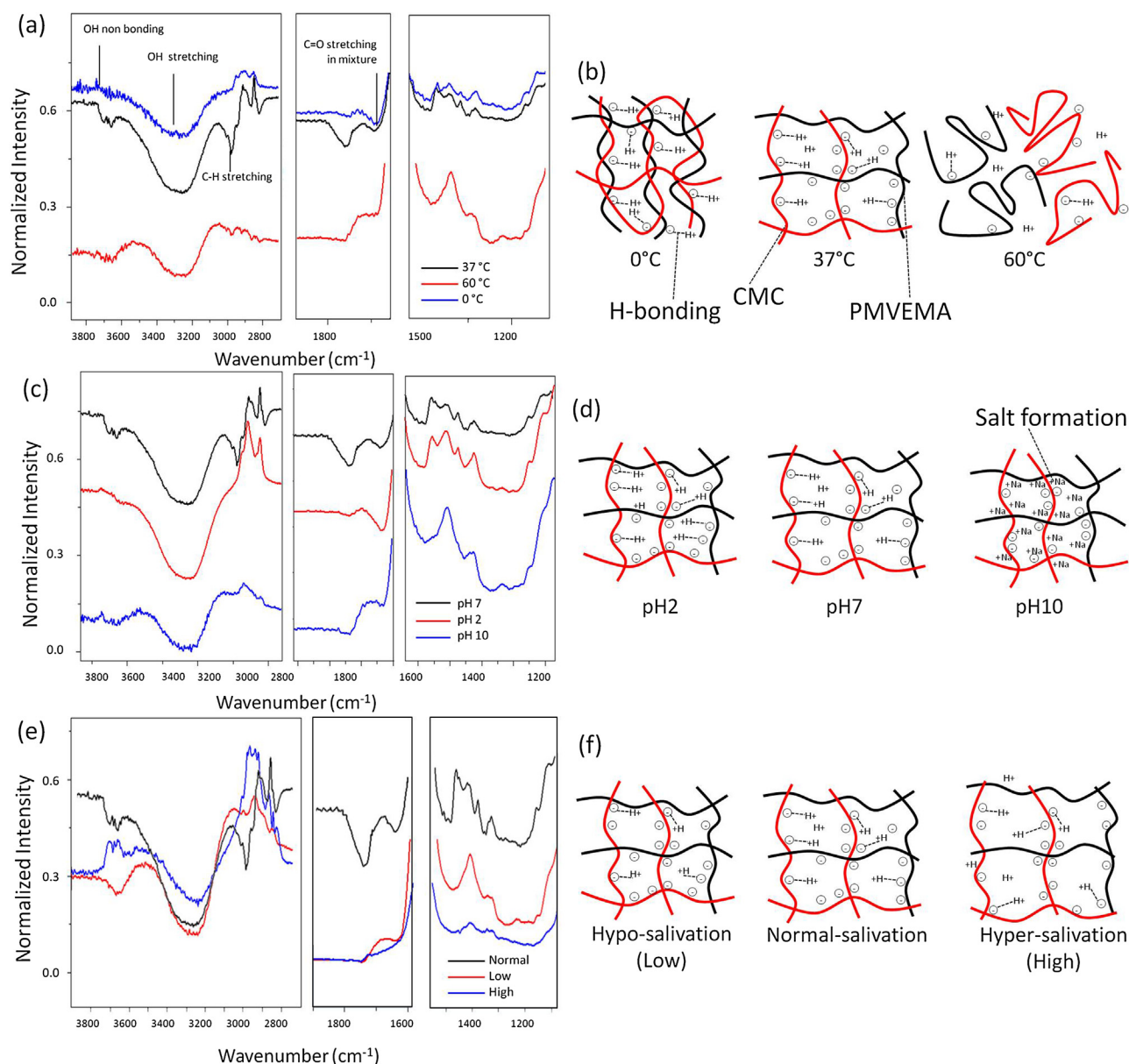


Fig. 4 – The interactions of various hydrophilic components of the adhesive paste. (a) Normalized FTIR spectra showing the interactions between two different hydrophilic components of the paste at various temperatures; (b) schematic showing polymeric network rearrangements in response to temperature variations. CMC is shown in red and PMVEMA is shown in black; (c) FTIR spectra showing the interactions between two different hydrophilic components at various pH values; (d) schematic showing polymeric network structure and internal interactions within two hydrophilic polymer parts; (e) FTIR spectra showing the interactions between two different hydrophilic components of the paste at various moisture contents; (f) schematic showing potential mechanism of inter- and intra-chain interactions and hydrogen bonds at different moisture contents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature. By decreasing the temperature from 60 °C to 37 °C, another growing peak appeared at 1640 cm^{-1} , which got shifted to 1636 cm^{-1} at 0 °C. Also, as the temperature decreased, the stretching O–H bonds showed a shift from 3277 at 60 °C to 3253 at 37 °C and then to 3248 cm^{-1} at 0 °C. The non-bonding O–H peak around 3700 cm^{-1} almost disappeared at 0 °C, which suggests better bonding formation between polymer chains at lower temperatures. For different pH values,

O–H stretching bond became sharper at pH 2 in comparison to pH 7 and pH 10; C=O stretching at pH 2 had more intensity with a little shift, and O–H and C=O stretching in the paste was noticeable around 1400–1700 cm^{-1} . C–O stretching and C–O–H stretching, bending and deformation peaks around 1100–1400 cm^{-1} were also more remarkable at pH 2. At pH 10, almost all peaks became shallow with some shifts indicating

more non-bonding C=O and O–H bonds compared to internal bonds at pH 7 and pH 2.

For hypersalivation condition, almost all peaks became broader with less intensity that might have been due to placement of samples inside the saliva for longer time and paste dissolution. These observations are in agreement with the mechanical and physical properties of the paste. Less strong internal interactions were observed in the paste at the hyposalivation condition in comparison to the paste receiving sufficient hydration as demonstrated in the FTIR data. In presence of insufficient amount of saliva, the –OH non bonding peak is noticeable around $3600\text{--}700\text{ cm}^{-1}$ and another peak existed around $1700\text{--}800\text{ cm}^{-1}$ which could be associated with the presence of –COOH non bonding groups that may formed as a result of oxidation of –OH groups.

3.5. Reinforcing internal interactions by addition of TPME

To investigate the benefit of enhancing hydrogen bonds in the paste on the adhesion strength, TPME was mixed with the paste, which is a hydrophilic macromolecule with ether and hydroxyl groups. TPME is also hygroscopic and could further improve the attraction of water molecules from the oral tissue. Fig. 5a shows the set-up used for measuring the tensile adhesion strength of the paste in normal condition and Fig. 5a (ii and iii) shows a typical image of the paste containing 2.5% (w/v) and 5% (w/v) TPME, respectively. The pristine paste failure was mainly a cohesion failure of the paste, while the addition of 2.5% (w/v) TPME improved the cohesive strength of the paste and after adding 5% (w/v) TPME the paste was detached from the surface showing an adhesion failure, confirming our hypothesis of the importance of hydrogen bonds and internal interaction for higher mechanical properties. In Fig. 5c, the adhesion strength of the paste after adding 2.5% (w/v) and 5% (w/v) TPME is demonstrated under all the scenarios discussed before. It was observed that the addition of TPME in general had a positive effect on the adhesion strength of the paste, especially at hyposalivation condition.

Fig. 5d shows SEM micrographs of casting films of (i) pristine paste, (ii) paste containing 2.5% (w/v) TPME, and (iii) paste containing 5% (w/v) TPME. SEM images suggested that the addition of TPME reduced the porosity of the paste, which could be another indication of increasing internal interactions between various compounds due to the increased number of hydrogen bonds between ether groups of TPME and the polymers within the paste. Fig. 5b shows FTIR spectra of pristine paste and paste containing two different concentrations of TPME. The adhesive paste was hydrated based on method representing hyposalivation. A red shift occurred for bonding C=O peaks and the intensity of peaks were also increased. Also another bonding peak appeared around 1400 cm^{-1} . For –OH bonds around 3300 cm^{-1} , after adding 2.5% (w/v) TPME polymeric bonding –OH peak intensity enhanced and non-bonding peaks around 3600 cm^{-1} were decreased or disappeared. The improved adhesion strength seen in Fig. 5d could be due to low melting point of TPME, which allowed it to act as a plasticizer to improve the interaction between the compounds. Due to excessive intra- and intermolecular hydrogen bonding of ether groups and more

water uptake after adding 5% (w/v) TPME, swelling and tensile adhesion strength was higher in the paste containing 2.5% (w/v) TPME.

4. Discussions

Denture adhesives are widely used by patients to facilitate the use of dentures and improve their quality of life. However, it has been reported that the performance of these adhesives can change based on patient diet and underlying conditions. This study was designed to shed light on the adhesive strength of the paste at various pH values, temperatures, and salivation levels.

Previous publications have suggested a series of *in vitro* testing methods to evaluate the performance of denture adhesives [13,36–38]. These models were designed to simulate the *in vivo* conditions by repeatedly measuring the tensile adhesion strength of the adhesive over time. However, the lack of a generally accepted *in vitro* testing model for denture adhesives complicates the comparison of their performance based on results reported in the literature. The model that we developed here was an extension of existing standards by using coating one side with denture material and covering the other side with skin tissue with similar texture as gum.

In real applications, once the adhesive is applied, saliva penetrates the material and according to manufacturer's guideline the material will reach its targeted strength within 30 min. Water content plays a key role on the function of denture adhesives [7,8,39]. Water comes from saliva and thus the rate of saliva production can affect the water content of the paste after its application [6,40,41]. In addition, mouth pH and temperature can also impact the adhesion strength of the paste. These values in the mouth are regulated by saliva and are temporarily affected by the consumption of foods and beverages [42,43]. For example, the pH of sparkling soft drinks is around 3. The consumption of ice-cold drinks and hot beverages can also affect the denture temperature and consequently the adhesion strength of the paste. It has been reported that a regular hot beverage can elevate the average of oral temperature to $\sim 54^\circ\text{C}$ and a regular cold beverage can drop this temperature to less than 4°C [43]. The rate of saliva generation varies between different patients. In normal patients, the unstimulated rate of saliva generation is between 0.1 to 0.2 mL/min. In patients suffering from dry-mouth the saliva generation rate is less than 0.1 mL/min, while in patients with ptyalism the saliva generation rate is more than 0.35 mL/min [44,45]. However, since there was no established protocol for simulating the hypo and hypersalivation, we changed the hydration time to capture these conditions during our experiments.

The mechanical data confirmed the previous reports and demonstrated that the paste adhesive properties were affected by the pH, temperature, and water content. After analyzing all these mechanical data, it was speculated that the environmental conditions affected the paste intrinsic properties and its adhesion strength. The paste was comprised of multiple components including CMC, PMVEMA, mineral oil, and petrolatum. Thus, to find potential solutions for improving the adhesion strength, the interactions between

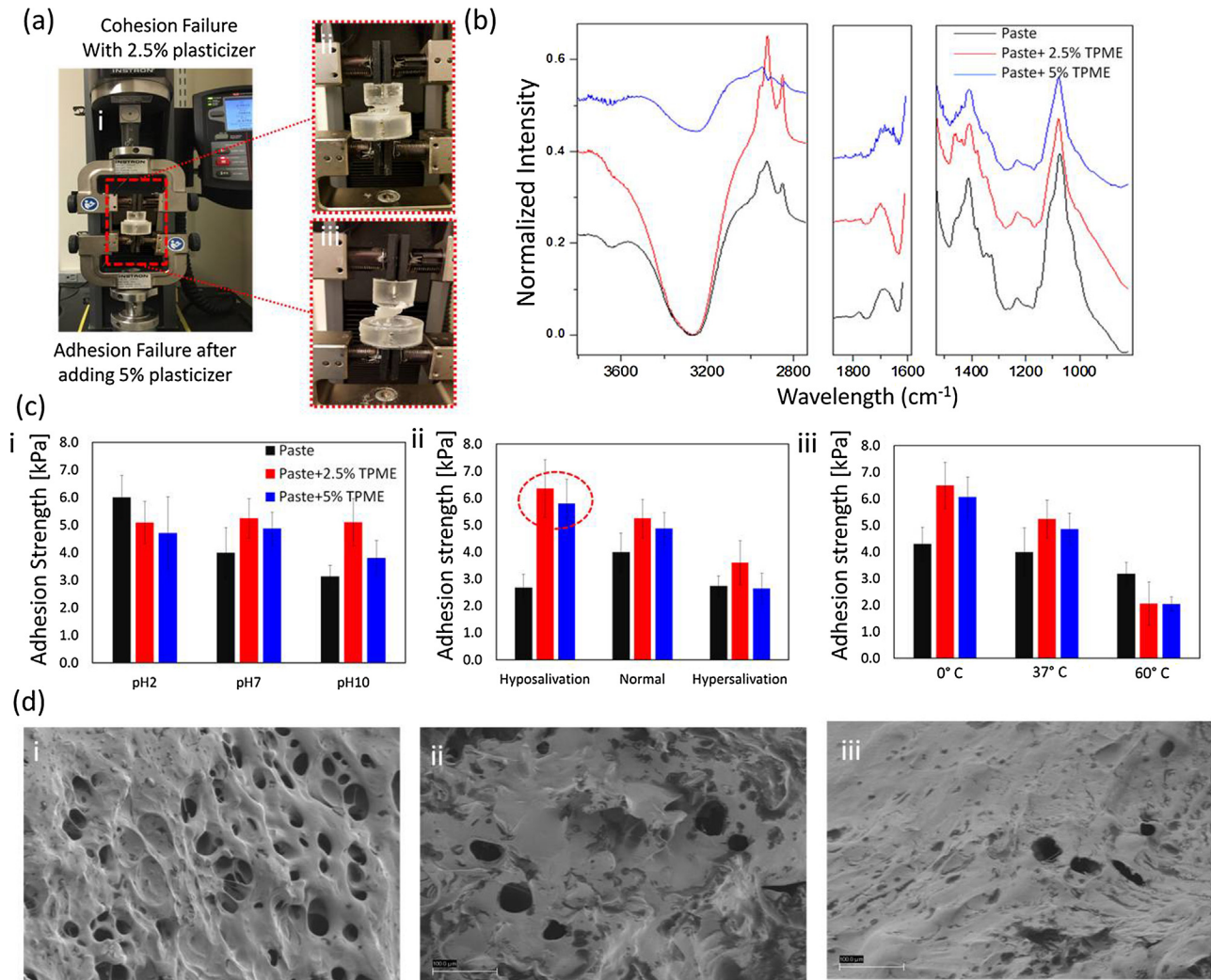


Fig. 5 – Adhesion properties of the paste after incorporation of TPME at two different concentrations in different working scenarios. (a) (i) Experimental set-up used for adhesion strength measurement, (ii) cohesion failure of the paste with applying 2.5% (w/v) TPME in the paste, (iii) adhesion failure of the paste after adding 5% (w/v) TPME; (b) FTIR of the paste before and after adding TPME in hyposalivation scenario; (c) mechanical properties of the paste (+2.5% (w/v), 5% (w/v) plasticizer) in different pHs, (ii) different hydration states, (iii) different temperatures; (d) SEM micrographs of casting films of (i) formulation A (paste + 0% (w/v) TPME) on which cracks can be observed, and (ii) formulation B (Paste + 2.5% (w/v) TPME) and (iii) (Paste + 5% (w/v) TPME) (scale bar = 100 μm).

various components and the saliva were studied over the wide spectrum of scenarios discussed above. Initially, the swelling and degradation rate of the paste and its ingredients were investigated and the rheological properties of the paste were measured in different conditions.

The different water uptake behavior of the paste and CMC in basic conditions compared with acidic and neutral conditions revealed that H-bonding appeared important in this study. Electrostatically charged carboxylic acid groups has key effect on the water uptake and swelling, dissociation and degradation rate of the paste. At low pH values, the hydrophilic parts of the paste can form hydrogen bonding in protonated $-\text{COOH}$ forms, repel entering water molecule inside the structure and slower water uptake. On the contrary at higher pH values, more ionized COO^- attracts more water molecules inside the network. It will show faster water uptake as well

as more rapid network dissociation. Comparing the amount of water uptake in the paste and CMC shows that larger mesh size and porosity of the CMC are also responsible for increased water uptake inside CMC network.

Based on the rheological analysis showing a reduction in paste viscosity by temperature increase, it was postulated that long chains were more cross-linked with stronger internal interactions at 0 °C. The chains however might have been reshaped into a relatively aligned network at 37 °C, but eventually it should have been deformed into a dynamic amorphous scaffold at 60 °C. It was observed that in acidic conditions, there was more hydrogen bonding between the polymer chains. However, alkaline saliva potentially led to ionic bondings and neutralization of all internal bonds and reducing adhesion. At low pHs, the hydrophilic parts of the paste can form hydrogen bonding in protonated $-\text{COOH}$ forms, repel

entering water molecule inside the structure and reduce the water uptake and degradation rate as confirmed by the FTIR data.

At basic pH values, the carboxylic groups were completely dissociated and made the network negatively charged based on COO⁻ and OH⁻ groups inside the structure. Because of the presence of high negative electrostatic repulsion charges and neutralization with Na⁺ ions, the network became more accessible for water molecules and consequently the materials dissociated faster [46,47].

The Poligrip[®] Free paste mainly consisted of CMC and PMVEMA as hydrophilic ingredients and mineral oil and petrolatum to prevent excessive swelling of the active compounds. The hydrophilic components of adhesive paste uptook saliva, swell, and became sticky [12]. The increased volume of the swollen hydrophilic ingredients also allows filling of the cavities and spaces between the denture material and the oral gingiva. CMC is highly hydrophilic and rapidly uptakes saliva to generate hydrogen bonds to provide an initial adhesion. However, CMC has high water uptake capacity and dissolves in saliva if not combined with less hydrophilic compounds. PMVEMA is less hydrophilic than CMC and is more stable, it can help with the long-term preservation of the saliva content within the paste essential for formation of hydrogen bonds within the paste [48]. Our study on pristine CMC samples showed an initial high adhesion strength, which was significantly reduced after 10 min immersion in water. The initial adhesion strength of the PMVEMA was lower, but augmented progressively over time. These results are in agreement with the data reported by Han et al. [12] and Kulak et al. [49]. The mixture of CMC and PMVEMA offered both high initial adhesive strength and longer effectiveness.

Our tensile and lap shear experiments suggested the necessity of sufficient hydration for proper adhesion of the paste and showed low adhesion strength in sample prepared under hyposalivation condition. Since the hyposalivation is frequently observed in elderly population, which are the main age group using dentures, finding solutions for improving the adhesion strength of the paste under hyposalivation condition was one of the major points of current study as well. It is speculated that the low adhesion strength under hyposalivation condition was due to the low hydrogen bonds due to lack of sufficient water or moist in the paste [48]. Thus, adding a compound that could form hydrogen bonds with the components of the paste could potentially improve the adhesion strength in the absence of sufficient water content. The addition of a compound that forms hydrogen bonds with the paste components may reduce the hydrogen bond formation between the polymer and the substrate, resulting in an adhesion failure, but at a higher value [50]. A similar trend was observed in samples after incorporation of 2.5% (w/v) TPME as illustrated in Fig. 5a (ii). The results reported here can shed light on the mechanisms resulting in inconsistent performance of denture adhesives and can be used to develop solutions to prevent that.

5. Conclusion

In this study, the adhesion and cohesion properties of Poligrip[®] Free manufactured by GSK were investigated with different

characterization methods. Evaluating the adhesion properties of the paste, using tensile and lap shear tests in various conditions including different pH values, levels of salivation, and various temperatures revealed that paste had the highest adhesion strength at pH 2, normal salivation condition, and at 0 °C. Different FTIR, DSC, TGA and SEM analysis were performed to identify the mechanisms arising observed properties. It was speculated that the mechanism leading to variation in the adhesion strength is based on internal interactions of hydrophilic ingredients of the paste namely CMC and PMVEMA, amount and strength of polymers' inter and intra-chain entanglements and hydrogen bonds. It was also observed that acidic conditions resulted in more effective hydrogen bonds between the polymer chains. However, alkaline saliva potentially led to ionic bondings and neutralization of all internal bonds and reduced the adhesion. Saliva content had a significant effect on the adhesion through affecting internal O–H and –COOH bonds or formation of an amorphous extended structure which cannot create strong hydrogen bonds (hypersalivation case). Also, at higher temperatures, based on higher entropy of the chains, no strong and long-lasting internal interactions were formed compared with normal or low temperatures. Incorporation of 2.5% (w/v) TPME enhanced the formation of hydrogen bonds and can potentially overcome the low adhesion strength of the paste in patients suffering from hyposalivation.

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