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Introduction

PVM/MA is a copolymer of methyl vinyl ether and maleic acid known to improve the delivery of hydrophobic active ingredients. It is known as a mucosal adhesive, and interactions with the enamel surface may occur, as well. The objective of this work was to identify interactions of PVM/MA with buccal mucosa (BM) and enamel surfaces.

Methods

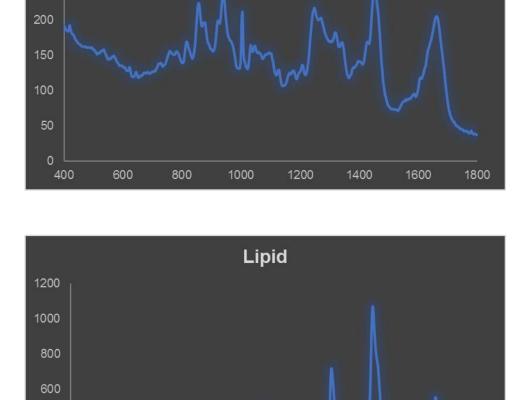
Data Collection

Confocal Raman spectroscopy (CRS) was used to probe the surface of substrates after treatment with artificial saliva followed by PVM/MA solution. CRS was selected for its functional group specificity, spectral resolution, and sensitivity of individual bands to interactions such as hydrogen bonding. Spectra in the region from 400cm⁻¹ to 1800cm⁻¹ were acquired using a RiverD Gen2-SCA confocal Raman spectrometer. The spectral resolution was 4.5 cm⁻¹. The z-axis resolution (perpendicular to the surface) was 5µm. All spectra were recorded in triplicate. Difference spectra were acquired by subtracting substrate spectra treated with artificial saliva only from those subsequently treated with polymer solution. Enamel samples were dried prior to data collection.

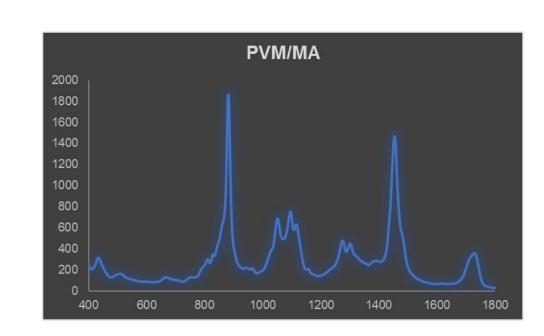
Data Analysis

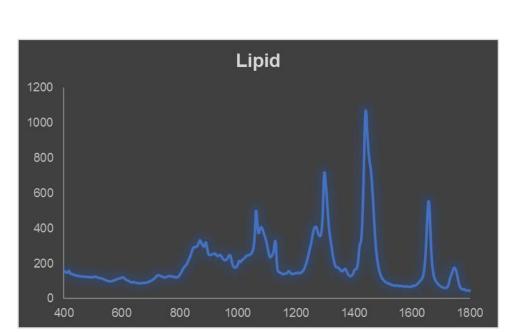
Multivariate Curve Resolution (MCR) was used to isolate spectra of PVM/MA in BM samples due the complexity of BM spectra. Experimental spectra were modelled using component spectra from BM protein, PVM/MA, water, and lipids. Relative concentration is expressed as fit coefficients of component spectra. Spectral bands arising from polymer on enamel surfaces were visible upon subtraction, as were band shifts indicative of interaction.

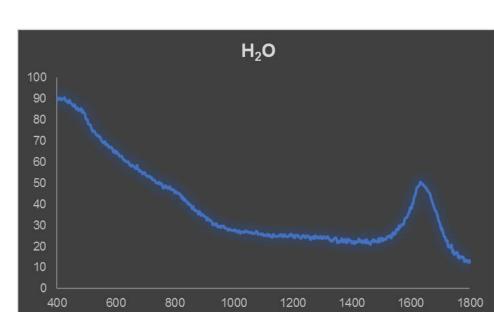
Figure 1. Component spectra used in MCR of BM spectra. The fit coefficients of the spectra are proportional to relative concentrations.



Buccal Mucosa







Sample Preparation

Figure 2. Schematic representation of preparation of bovine enamel samples

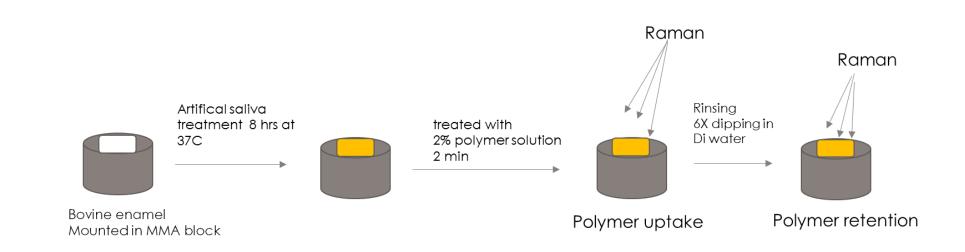
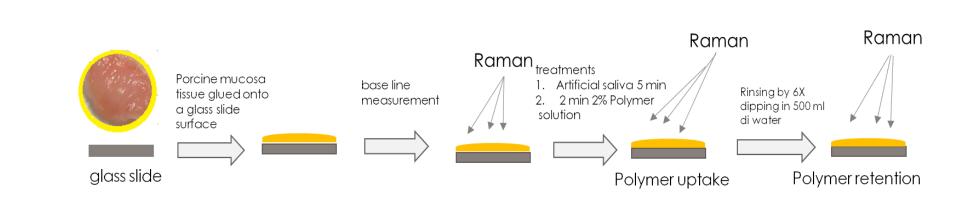


FIGURE 3. Schematic representation of preparation of porcine buccal mucosa samples

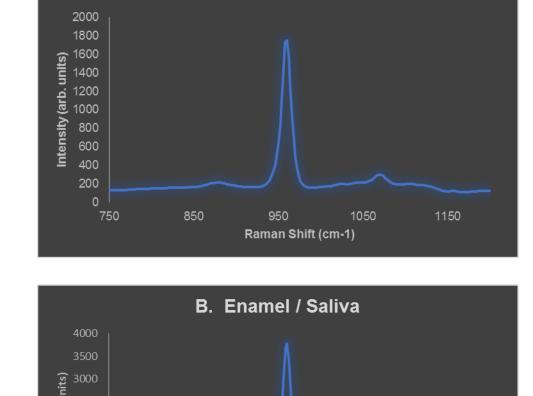


Results

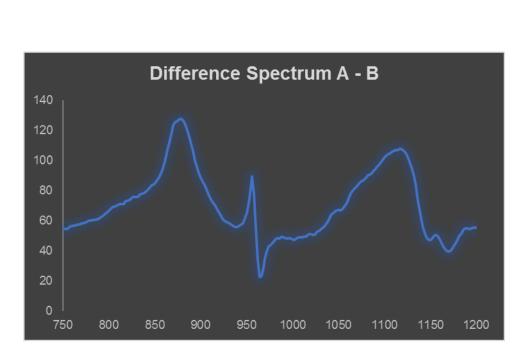
Surface interactions between PVM/MA and enamel or BM were observed with CRS and were manifested by shifts of the PO_4^{3-} mode to lower frequency or changes of spectral line shape, respectively. Raman spectroscopy was particularly useful in detecting interactions between enamel and PVM/MA due to the sharp, prominent PO_{4}^{3-} band, for which a shift in band position is more readily observed. The spectra of BM treated with saliva and the lipid were subtracted from the spectrum of BM treated with PVM/MA and saliva. The second derivative shape indicates broadening due to more protein conformational possibilities in the presence of PVM/MA.

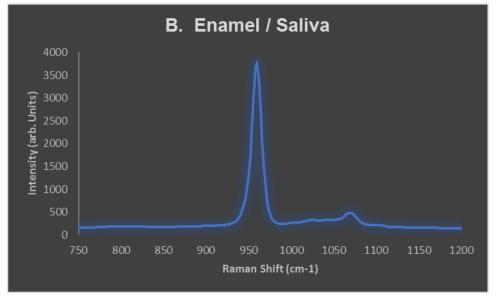
Enamel

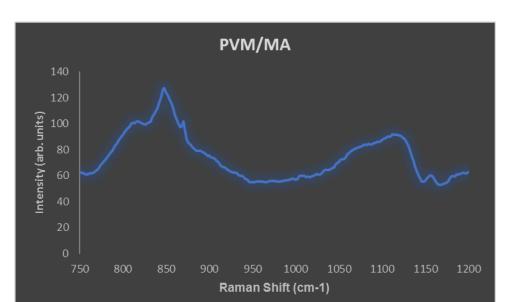
Figure 3. A prominent first derivative-shaped feature centered at the position of the 960 cm⁻¹ PO $_{4}$ ³- mode of hydroxyapatite resulted from subtraction. This is due to a shift of the PO_{4}^{3-} mode to 956 cm⁻¹, indicative of non-covalent interaction (H-bonding).



A. Enamel / PVM/MA / Saliva







Buccal Mucosa

Figure 4. PVM/MA is present on BM after six washes.

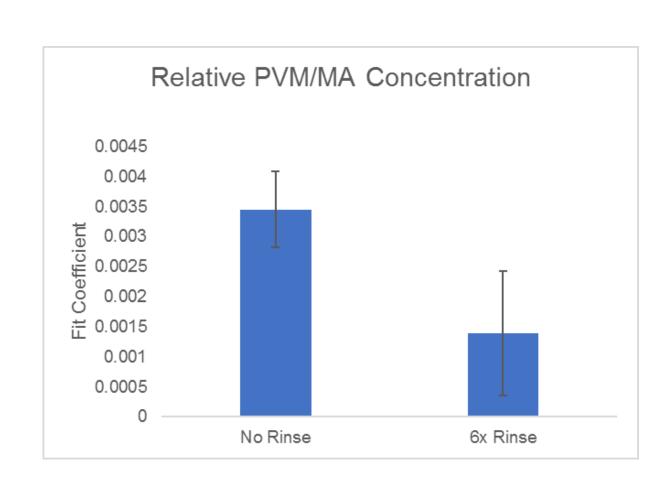
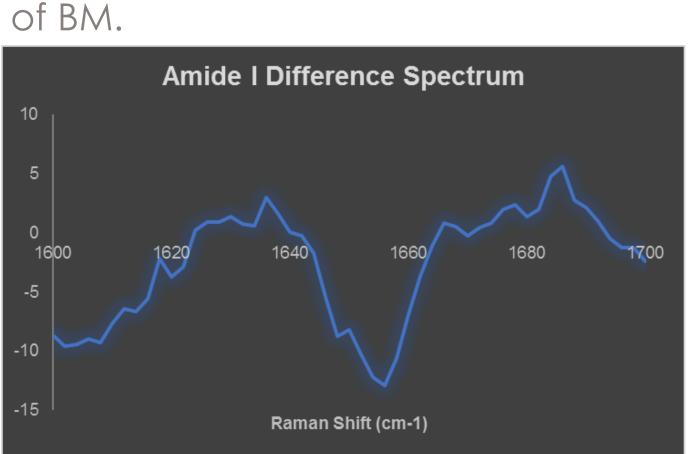


Figure 5. Broadening of the protein Amide I band (1650 cm⁻¹)



Conclusions

The interactions of PVM/MA with enamel or buccal mucosa have been observed using confocal Raman spectroscopy. They are indicated by a shift of the phosphate PO_4^{3-} by 4 cm⁻¹ from 960 cm⁻¹ to 956 cm⁻¹ and is attributed to H-bonding. In the case of buccal mucosa, interaction is observed by a broadening of the protein Amide I band attributed to increased conformational freedom in the presence of PVM/MA.

Mark A. Davies, Surya Kamin, Petros Gebreselassie, and Hani A. Fares are employed by Ashland Specialty Ingredients G.P. Ashland Specialty Ingredients G.P. is the manufacturer of PVM/MA tested herein.



