Biopolymer Gelation Mechanisms in Alginate-Pectin Systems: Role of Polyvalent Ions Revealed by ssNMR and FTIR

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Introduction

Alginate and pectin represent the most widely used polyuronates due to their flexibility, biodegradability, biocompatibility, and non-toxic nature. Their crosslinked forms are of particular interest for biomedical and pharmaceutical applications, especially in drug delivery systems, tissue engineering scaffolds, and encapsulation technologies. Gelation of alginate has long been described by the egg-box model, but recent findings reveal notable differences in the gelation pathways of alginate and pectin. In particular, Ca^{2+} ions interact preferentially with guluronic G-blocks via electrostatic interactions, while Zn^{2+} ions can coordinate with both mannuronic and guluronic blocks, forming mixed covalent-coordination bonds. These ion-specific interactions critically affect the structure of hybrid alginate - pectin networks. This study focuses on unraveling the structural motifs governing the gelation process of alginate - pectin systems crosslinked by polyvalent ions.

Experimental

Alginate–pectin hybrid beads with varying ALG/PEC ratios were prepared through a multistep process involving mixing, filtration, hardening, and drying. Crosslinking was performed with $Ca^{2+}$and Zn^{2+} ions. The samples were denoted as ALG/PEC/x/y_X^{2+}, where x and y represent the fraction of alginate and pectin, respectively, and X^{2+} the crosslinking ion.

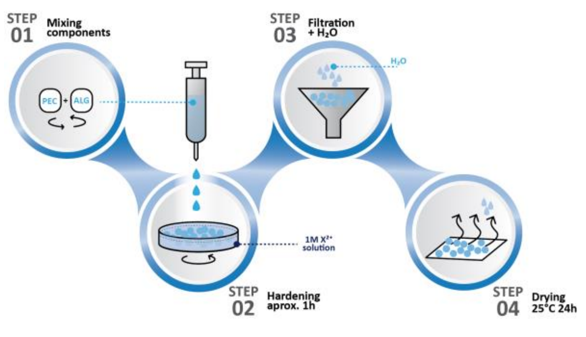
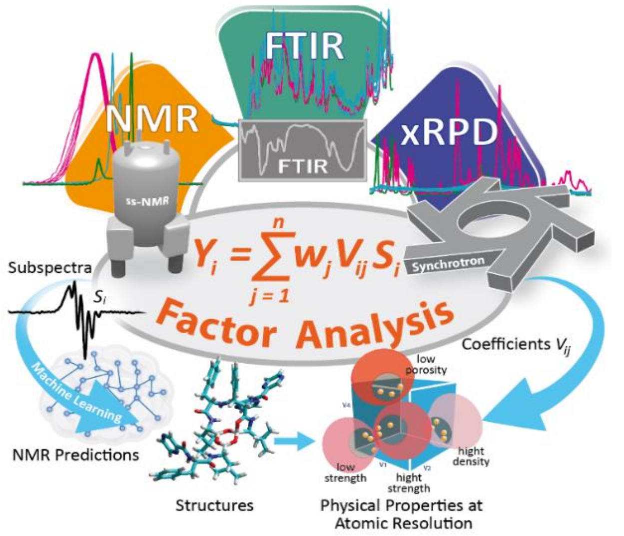


Figure 1. Scheme of preparation alginate-pectin systems

Structural characterization was carried out using: i) Solid-state NMR spectroscopy: ^1H, ^{13}C CP/MAS, ^{23}Na MAS, and ^{13}C MAS experiments and FTIR spectroscopy: vibrational analysis to detect functional group modifications.

Multivariate analysis: Principal Component Analysis (PCA) - Factor Analysis were applied to reveal hidden spectral features in overlapping resonances of polysaccharides.



$$Y_i = \sum_{j=1}^{n} w_j V_{ij} S_j$$

Y_i - residual errors
w_j - singular value
S_j – subspectra
V_{ij} – coefficients

Figure 2. Equation of Principal component analysis/Factor analysis

Results and Discussion

Direct visual interpretation of ^{13}C CP/MAS and FTIR spectra was hindered by overlapping signals and the amorphous nature of alginate and pectin. PCA allowed deconvolution into subspectra S1–S5 with corresponding coefficients V_{i1}–V_{i5}.

Ion-specific effects: Ca^{2+} crosslinked systems displayed characteristic changes in guluronic-block resonances, confirming electrostatic interactions consistent with the egg-box model. Zn^{2+} ions induced broader structural changes, affecting both mannuronic and guluronic units, reflecting coordination-covalent contributions.

Correlation analysis: Plots of V_{ij} coefficients from ^{13}C CP/MAS, ^{23}Na MAS, and FTIR revealed strong correlations, suggesting that similar structural motifs are detectable across different spectroscopic techniques. The high-amplitude signals in subspectra S2–S5 identified the most prominent changes in network formation.

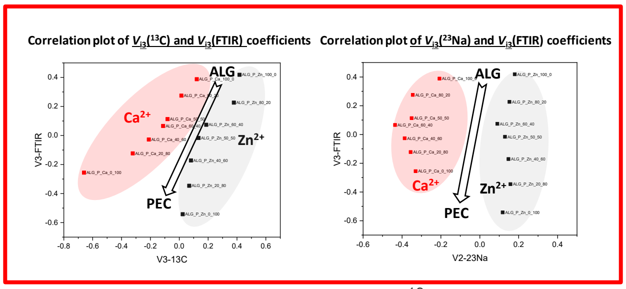


Figure 3. Correlation plot of V_{i3}(^{13}C) and V_{i3}(FTIR) coefficients and correlation plot of V_{i3}(^{23}Na) and V_{i3}(FTIR) coefficients

These results demonstrate that combining ssNMR, FTIR, and factor analysis provides a powerful approach to distinguish subtle ion-specific crosslinking mechanisms in hybrid polysaccharide gels.

Conclusion

This study provides a detailed structural characterization of alginate–pectin networks crosslinked by polyvalent ions. The findings highlight that while Ca^{2+} induces classical egg-box structures, Zn^{2+} promotes more complex hybrid interactions. Understanding these mechanisms is crucial for tailoring the mechanical and functional properties of biopolymer gels for pharmaceutical and biomedical applications.

Acknowledgments

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