



# Quantitative analysis of molecular interactions in $\kappa$ -carrageenan-Isovanillin biocomposite for biodegradable packaging and pharmaceutical applications using NMR, TOF-SIMS, and XPS approach

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## ABSTRACT

This study explores the molecular interactions and structural changes in  $\kappa$ -carrageenan crosslinked with isovanillin to create a biocomposite material suitable for hard capsule and bio-degradable packaging applications. Proton Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) spectroscopy revealed chemical changes in the conjugate molecule, indicating improved electronegativity due to intermolecular hydrogen bonding between  $\kappa$ -carrageenan and isovanillin. Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis revealed enhanced ion intensity due to intermolecular interactions, particularly between sulphate and hydrogen ions. X-ray Photoelectron Spectroscopy (XPS) study demonstrated that  $\kappa$ -carrageenan and isovanillin form stronger hydrogen bonds, with a shift in binding energy indicating higher electronegativity. These findings shed light on the molecular mechanisms that underpin the formation of the biocomposite material, as well as its potential for use in hard capsule and biodegradable packaging materials, addressing the need for sustainable alternatives in the pharmaceutical and packaging industries while also contributing to environmental conservation.

## 1. Introduction

There are two types of crosslinking in carrageenan namely physical and chemical crosslinking. Physical crosslinking is commonly established through the development of weak bond such as hydrogen bond molecular interaction, while chemical crosslinking is established through covalent bond (Kontou, Spathis, Niaounakis, & Kefalas, 1990; Krumova, Lopez, Benavente, Mijangos, & Perena, 2000). In physical crosslinking, “bridges” form between polymer chains; however, these connections are not rigid and can be disrupted by environmental factors like rising temperatures or shifts in ionic strength (Krumova et al., 2000). Besides, swelling of physical crosslinking is lower than chemical crosslinking which resulting in poor water retention capabilities (Yegappan, Selvaprithiviraj, Amirthalingam, & Jayakumar, 2018).

Intermolecular crosslinking can occur in two mechanisms- (1) both ends of crosslinker and (2) one end of crosslinker react with polymer chain (Sonker et al., 2018). In a study conducted by Sonker et al. (2018), the first mechanism is suggested to crosslink between agar and

diisocyanates through formation of carbamate crosslinks. The result showed that the crosslinking introduced carbamate crosslink bond (amide (II) band) by reducing the number of hydroxyl groups of agar chains (Krumova et al., 2000; Sonker et al., 2018). Carbamate crosslink forms when hydroxyl group (-OH) of agar crosslinked with isocyanate group (-N=C=O) of crosslinker, thus decrease the number of -OH groups. The mechanism of crosslinker is in R-N=C=O sequence. The nitrogen (N) from crosslinker is negatively charged and carbon (C) from agar is positively charged. If R, an alkyl substituent attached to isocyanate group is aromatic, then the negative charge gets delocalized into R (Sonker et al., 2018). A rigid aromatic crosslinker will impart restriction to the mobility of polymer chain, thus increase the film tensile strength and reduce elongation at break (Sonker et al., 2018). The result is vice versa for linear structure of crosslinker.

Crosslinking can also increase the junction zones at shorter average length in the crosslinked matrix. In carrageenan, crosslinked with sugar sol-gel, the carrageenan was stabilized by formation of intermolecular hydrogen bonding between OH-groups of both materials and cause the

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