Abstract:

Bioactive compounds from plants have been extracted and utilized by humans for many centuries. Polyphenols represent one of the most widely applied groups of such compounds in industry. They are responsible for defense mechanisms in response to biological factors such as phytophagous insects and phytopathogens, as well as abiotic stressors, including excessive UV radiation in plants. This group of chemical compounds encompasses both structurally simple phenolic acids and more complex flavonoids, including anthocyanins. Polyphenols primarily exhibit antioxidant properties, which depend on their chemical form (glycosidic/aglycone), as well as antibacterial and antifungal activities. They act as the signaling molecules for symbiosis with soil bacteria and serve as pigments responsible for flower coloration, acting as attractants for pollinators. However, outside plant cells, these compounds are highly susceptible to oxidation and degradation induced by light, temperature, and exposure to oxygen. Consequently, these substances frequently require a carrier matrix to stabilize them in the extracellular environment and fully exploit their biological potential.

Cellulose is the most abundant and widely extracted biopolymer from plants, possessing unique properties including low density, high mechanical strength, biocompatibility, and biodegradability. Cellulose-based materials have well-developed fabrication and modification methodologies. Cellulose modifications aim to improve unfavorable properties for food packaging applications, such as hydrophilicity, lipid absorption capacity, and lower elasticity than synthetic plastics. Such changes include the substitution of hydroxyl groups with carboxymethyl groups (to produce carboxymethyl cellulose) or with ethyl groups (for ethyl cellulose). Nevertheless, these modifications may negatively impact the biodegradability of such materials.

A literature review led to the conclusion that combining cellulose films with various polyphenol types would enable the investigation of molecular interactions between these components without compromising the bioactive properties of polyphenols and determining their effects on film properties. For this purpose, two types of cellulose were selected: micro- and nanofibrillated cellulose. Three polyphenol categories were deposited via adsorption: phenolic acids (chlorogenic, caffeic, and gallic acids), flavonoids (quercetin, rutin, naringenin,

and naringin), and anthocyanins derived from fruit pomace extracts (blackcurrant, black grape, and chokeberry).

This study demonstrated that enriching micro- and nanofibrillated cellulose films derived from apple pomace with phenolic acids and flavonoids altered their functional properties for food packaging applications. FT-IR and FT-Raman spectroscopy revealed characteristic bands for various flavonoid groups, facilitating the identification of individual bonds and providing insight into cellulose-polyphenol interactions.

Investigation of micro- and nanofibrillated cellulose films with selected phenolic acids (gallic, caffeic, chlorogenic) at two concentrations (450/900 ppm) demonstrated that caffeic acid addition improved barrier and mechanical properties while contact-inhibiting the growth of E. coli, S. capitis, and Botrytis cinerea. Higher acid concentrations led to increased intensity at 1410 cm^{-1} in FT-Raman spectra, corroborating the presence of intermolecular interactions.

Composites based on micro- and nanofibrillated cellulose with lecithin and liposomal formulations of two flavonoid pairs (glucoside/aglycone) adsorbed on film surface from distinct flavonoid classes - quercetin/rutin and naringin/naringenin - were synthesized and compared. Surface wettability properties, intermolecular interaction mechanisms via spectroscopy, water vapor barrier properties, light transmittance, antioxidant stability, and pathogen inhibition were evaluated. Quercetin-containing composites proved to be the most promising, nearly completely blocking UV light transmission, demonstrating high antioxidant capacity, and being the only compounds tested that exhibited distinct molecular bonding with cellulose. Despite increased surface hydrophilicity, water vapor permeability showed no significant deterioration. Microbiological analysis revealed inhibitory activity against S. aureus.

Supplementary studies employing nanofibrillated cellulose and extracts from three selected fruit pomaces - chokeberry, blackcurrant, and grape - demonstrated pronounced pH sensitivity in films, both upon exposure to pH-buffered solutions and in response to nitrogen-containing compounds released into the atmosphere (as food spoilage test). Films exhibited considerable hydrophobicity, with blackcurrant pomace extracts demonstrating optimal properties in both color intensity and water vapor permeability.

This work represents a comprehensive investigation that elucidates the molecular interactions and comparative functional properties of cellulose films enriched with various bioactive polyphenolic compounds for intelligent food packaging applications. The findings

provide insights into the development of advanced packaging materials that combine cellulose's structural advantages with the multifunctional bioactivity of polyphenols.

Keywords: Plant waste, apple pomace, polysaccharide-based composites, flavonoids, phenolic acids, microfibrillar cellulose, nanofibrillar cellulose, antioxidant properties, barrier properties, molecular structure, surface properties