Photoswitchable Wetting Properties in Bifunctional Metavanadate-Promoted Chitosan/Cassava Biopolymer Films: A Mechanistic Study

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Smart materials that adapt to external stimuli hold great potential for applications in biomedical coatings, responsive packaging, and optical sensors. This study presents a novel photo-responsive biopolymer film derived from starch and chitosan, infused with vanadium salts to create a metallopolymer system. Upon exposure to visible light, these films exhibit a noticeable color shift from yellow to green, signaling changes in vanadium's oxidation state. Structural analysis reveals significant morphological alterations following vanadium incorporation, which further evolve under visible light illumination. A key functional property observed is enhanced hydrophobicity, with water contact angles reaching up to 103° after irradiation. X-ray photoelectron spectroscopy (XPS) confirms that photoreduction renders vanadium from V5+ (VO_3^-) to lower oxidation states. Initially, V5+ ions form electrostatic interactions with chitosan's $-NH_3^+$ groups, but upon photoreduction to V4+ (VO^{2+}), these forces weaken, allowing greater polymer chain interactions due to increased degrees of freedom of the freed polymer chains leading to subsequent surface restructuring. Atomic force microscopy (AFM) shows reduced root mean square (RMS) roughness upon vanadium incorporation due to constrained polymer configurations, with a slight roughness increase post-irradiation as the constraints are lifted, consistent with our proposed physical model. The surface properties of these films demonstrate reversible behavior through alternating irradiation and oxidation treatments, with water contact angles cycling between >100° and ˜60°. These findings open new possibilities for the design of biodegradable, photo-switchable, smart soft materials.

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