

Enhancing the Properties of Smart Sustainable Materials Through Atmospheric Plasma Deposition of Bio-Based Coatings

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Abstract. Presently, the emphasis on environmental sustainability is directed towards minimizing the ecological impact of human activities and advocating for the efficient utilization of natural resources. In the pursuit of enhancing sustainability in industrial coatings, our investigation utilized ultrasonic nebulization, liquid-assisted and vapor deposition in conjunction with atmospheric plasma polymerization. Bio-based coating formulations as monomer precursors were applied to natural fiber reinforcement and paper substrates to augment properties, such as improving interfacial adhesion, hydrophobicity for the release function, barrier properties against oxygen and water vapor transmission and antimicrobial activity. Characterization techniques, including FTIR, HR-MS, profilometry, were employed to assess chemical composition and thicknesses of the deposited coatings, SEM studies were conducted to observe morphological features. Contact angle measurements were carried out for the investigation of hydrophilic / hydrophobic behavior, and bending tests were scrutinized for mechanical properties of reinforced composites. For barrier papers and release liners, oxygen and water vapor transmission rates and release functions were tested. The feasibility study aimed to comprehend how the deposition of nanosized particles on porous or renewable substrates could enhance the macroscopic behavior of the substrate. The applications primarily target the composite and paper industries, aiming to replace conventional thick coatings with relatively thin coatings. While the results indicated an improvement in the properties of the modified substrate, optimization is required before considering complete substitution for conventional pretreatment or wet coating techniques. Additionally, the developed coatings show potential for sensor applications, where their tailored surface properties could enhance sensitivity and functionality in various sensing technologies.

Key words: Sustainable materials, Plasma deposition, Bio-based coatings, Functionalization

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1 INTRODUCTION

Research on reducing the ecological impact of industrial processes and maximizing the use of renewable resources has been prompted by the growing emphasis on environmental sustainability on a global scale. The traditional petroleum-based formulations used in the coatings industry, in particular, have given way to bio-based substitutes that are more environmentally friendly and consistent with the circular economy [1], [2]. The use of solvent-based formulations or thick polymer layers in traditional coating techniques presents problems with waste production, emissions of volatile organic compounds (VOCs), and processing that requires a lot of energy [3]. As a result, there has been a lot of interest in creating effective and sustainable deposition techniques for bio-based coatings.

In this work, we investigated the use of atmospheric plasma polymerization in conjunction with advanced coating techniques such as liquid-assisted, vapor deposition, and ultrasonic nebulization. These techniques lower waste and material consumption while enabling the creation of uniform, ultra-thin coatings with customized functions. Bio-based monomer precursors were applied to natural fiber reinforcements and paper substrates to enhance interfacial adhesion, hydrophobicity, barrier properties, and antimicrobial activity that are key attributes for applications in composite materials and the paper industry.

To evaluate the coatings' chemical makeup and thickness, characterization methods including Fourier-transform infrared spectroscopy (FTIR), high-resolution mass spectrometry (HR-MS), and profilometry were used. While bending tests and contact angle measurements assessed mechanical and hydrophobic qualities, respectively, scanning electron microscopy (SEM) provided information on morphological features. The functional enhancements made possible by the deposition techniques were further confirmed by an analysis of the oxygen and water vapor transmission rates for barrier papers. Determining how nanoscale coatings can improve the macroscopic behavior of porous or renewable substrates in order to substitute high-performance layers for traditional thick coatings with relatively thin coating, was a key goal of this study. The results indicate that although notable enhancements in substrate characteristics were attained, additional refinement is necessary to fully replace traditional wet coating methods. Moreover, the developed coatings show promise for sensor applications, where their engineered surface properties may enhance functionality and sensitivity in a range of sensing technologies [4]. By leveraging innovative deposition methods and bio-based precursors, this study contributes to the ongoing transition toward sustainable coatings, offering solutions that balance performance with environmental responsibility.

2 MATERIALS AND METHODS

The renewable precursor vanillyl alcohol methacrylate (VAM) was synthesized from vanillyl alcohol following the procedure outlined below. 30 g of vanillyl alcohol (VA), 60 g of methacrylic anhydride, and 0.2 g of DMAP (dimethyl aminopyridine) were added to a round-bottom flask equipped with a thermometer and a magnetic stirrer set at 200 rpm. The reaction mixture was purged with nitrogen for 20 minutes and then allowed to react at 45°C for four

days. Following the reaction, the mixture was diluted with a blend of ethyl acetate and dichloromethane, then purified using a 3% sodium bicarbonate solution and water. Finally, the solvents were removed by distillation.

The reinforcement nanocrystalline cellulose (NCC) were modified according to the adopted procedure from the reference [5]. NCC were dried in an oven at 90 °C for 1 hour and then functionalized with (3-chloropropyl) trimethoxy silane (CPTMS). Subsequently a mixture of ethanol and water (75:25, 300 ml Et:100 ml H₂O) was prepared and mixed with a magnetic stirrer (300 rpm) for 5 minutes. 2g of CNC particles was first added to the solution and after their dispersion 2g of CPTMS was added afterwards. The mixture was left to mix for two hours (300 rpm). After two hours, the solution was poured in a dish and left over the night in an oven at 70°C to evaporate the solvent.

The plasma-polymer coatings were grown using an atmospheric pressure dielectric barrier discharge plasma set-up described in previous works [6], [7]. The plasma was generated by a 10 kHz, 8 kV sinusoidal generator (SOFTAL 7010R) using Argon (Ar) as plasma gas with a flow of 20 l min⁻¹ and a power ranging from 50 to 200 W. Silicon or paper substrates (Barrier paper 60g) were coated with the monomers (VAM) or a suspension of VAM containing 1 w. % of reinforced NCC using a 120 kHz ultrasonic atomizing nozzle (Sono-Tek), fed by a syringe pump (10 µl min⁻¹) and shaped into a 10 cm wide fan spray using an impact spray shaper supplied with 20 l min⁻¹ of N₂. Substrates were mounted on a variable-speed moving stage. The spray-curing cycle was repeated 100 times at a stage speed of 50 mm s⁻¹ to reach coating thicknesses in the range of several micrometers.

FTIR spectra were acquired using a Bruker Vertex 70 spectrometer with a DTGS detector. Transmission mode was used for coatings on silicon wafers, otherwise ATR mode was used. All spectra were recorded from 4000 to 400 cm⁻¹ at 4 cm⁻¹ resolution under nitrogen purge. To evaluate the effect of plasma on the polymerization, the degree of double bond conversion was determined by means of FTIR using Equation (1) by calculating the ratios between the vinyl $A_{C=C}$ band intensity against the carbonyl $A_{C=O}$ bands for the monomer and polymer layers. These ratios are then compared to obtain the degree of conversion (DC).

$$DC (\%) = \left(1 - \frac{(A_{C=C}/A_{C=O})_t}{(A_{C=C}/A_{C=O})_0} \right) \times 100 \quad (1)$$

Matrix-assisted laser desorption/ionization high-resolution mass spectra (MALDI-HRMS) measurements were performed on an AP-MALDI PDF+ ion source from MassTech, Inc. coupled to an LTQ/Orbitrap Elite from Thermo Scientific. α -Cyano-4-hydroxycinnamic acid diluted in THF (10 mg l⁻¹) was used as the matrix. A total of 0.1 µl of the matrix was then spotted on the thin films to form a co-crystal with the soluble part of the film when the THF evaporated. Due to the numerous side peaks resulting from the plasma side-mechanisms, the relevant peaks corresponding to oligomeric repetitions were isolated for better depiction.

Scanning electron microscopy (SEM) images were obtained using a Hitachi SU-70 FE-SEM.

To prevent distortions caused by charge effects, the samples were coated with a 5 nm thick platinum film under vacuum conditions prior to SEM observations.

3 RESULTS AND DISCUSSIONS

The synthesized vanillyl alcohol methacrylate (VAM) monomer was initially characterized using Fourier-transform infrared spectroscopy (FTIR), which confirmed the successful incorporation of the methacrylate group. To further analyze the surface modification of nanocrystalline cellulose (NCC), X-ray photoelectron spectroscopy (XPS) was employed (Figure 1). The XPS survey spectrum revealed characteristic peaks of oxygen (26.4% at 533.0 eV) and carbon (48.3% at 286.0 eV), which are consistent with the chemical structure of cellulose and the modifying agent CPTMS.

Importantly, successful surface functionalization was evidenced by the appearance of chlorine (14.2% at 201.0 eV) and silicon (11.0% at 103.0 eV) signals, indicating effective grafting of CPTMS onto NCC. For comparison, [8] reported only 4.06% silicon content when modifying cellulose nanocrystals with 3-aminopropyltriethoxysilane. This comparison highlights the efficiency of the applied silanization process, which yielded a substantial proportion of modified hydroxyl groups available for further reaction.

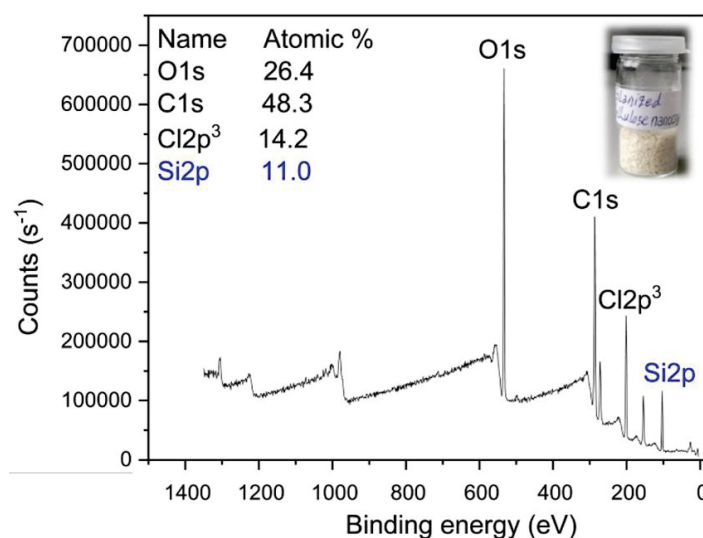


Figure 1: XPS spectrum of CPTMS-modified nanocrystalline cellulose

3.1 Plasma Polymerization and Characterization of VAM

To evaluate the conversion of VAM into a polymer layer, FTIR analysis was carried out following plasma polymerization at different power levels (Figure 2). Key functional group transitions were monitored in the 1600–1800 cm⁻¹ region. The carbonyl (C=O) stretching band was observed at 1714 cm⁻¹, and the vinyl (C=C) stretching band at 1633 cm⁻¹. Residual peaks from the monomer synthesis (MAA and MA) appeared at 1782 cm⁻¹ and 1693 cm⁻¹, respectively.

In plasma-treated samples, the vinyl band at 1633 cm^{-1} showed a significant reduction, indicating effective polymerization. Additionally, the carbonyl band shifted to a higher wavenumber (1724 cm^{-1}), suggesting free-radical-induced crosslinking of the methacrylate groups. The near disappearance of the MAA and MA peaks suggests their decomposition or evaporation during plasma exposure.

The degree of conversion (DC) of double bonds was calculated from FTIR spectra as the ratio of the C=C and C=O bands. Plasma powers of 50, 100, and 200 W resulted in DC values of 76%, 77%, and 79%, respectively, indicating that even at lower plasma powers, high polymerization efficiency was achieved. The slight increase in DC at higher power reflects improved fragmentation and radical formation, which enhances crosslinking.

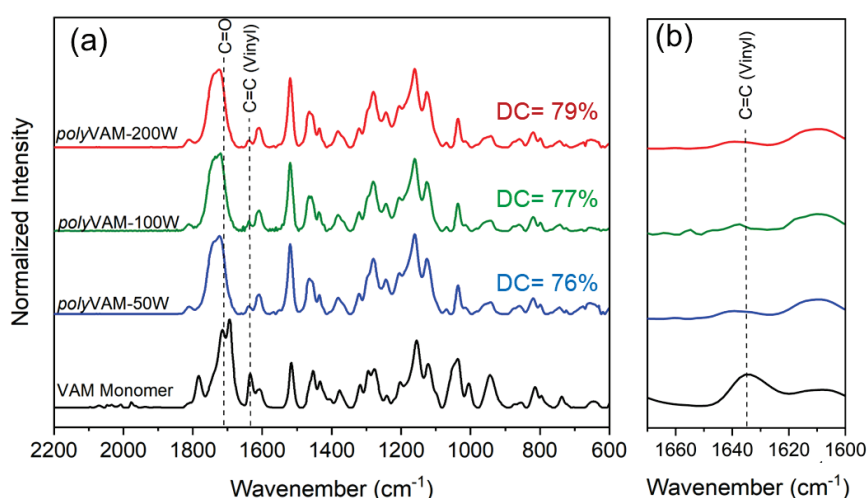


Figure 2: FTIR spectra comparing VAM monomer and plasma-polymerized films at different powers

3.2 Molecular Characterization via MALDI-HRMS

Matrix-assisted laser desorption/ionization high-resolution mass spectrometry (MALDI-HRMS) was used to identify the molecular structure of the resulting polymers (Figure 3). The spectra revealed oligomers composed of mono- and di-methacrylated vanillyl alcohol (mono-VAM and di-VAM) repeating units. At 50 W plasma power, the oligomers consisted of up to three mono-VAM and four di-VAM units. At 100 W, longer chains were formed (up to six mono-VAM and seven di-VAM), while at 200 W, a higher incorporation of di-VAM (eight units) and fewer mono-VAM (four units) was observed. These findings suggest that plasma power influences not only polymer chain length but also the balance between mono- and di-functional incorporation, with 100 W offering a well-balanced structure.

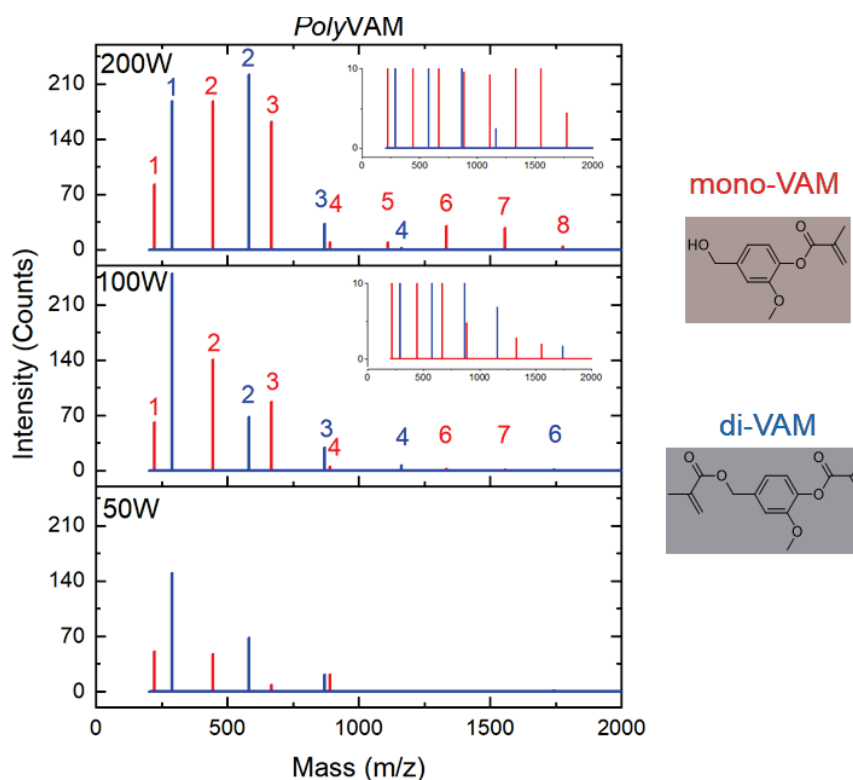


Figure 3: MALDI-HRMS spectra showing mono- and di-VAM oligomer distributions under varying plasma conditions

3.3 Coating Performance and Barrier Properties

Based on polymerization and structural analysis, a plasma power of 100 W was selected as the optimal condition for coating VAM and NCC formulations onto paper substrates. A film thickness of approximately 3 μm was achieved after 100 deposition cycles.

Water vapor transmission rate (WVTR) testing revealed that uncoated paper had a high WVTR of $\sim 350 \text{ g m}^{-2} \text{ day}^{-1}$ (Figure 4). Coating with plasma-polymerized VAM significantly reduced the WVTR to $\sim 70 \text{ g m}^{-2} \text{ day}^{-1}$, demonstrating the formation of an effective barrier layer. Surprisingly, the incorporation of NCC into the VAM matrix resulted in a slightly increased WVTR ($\sim 90 \text{ g m}^{-2} \text{ day}^{-1}$). This may be attributed to poor dispersion or incompatibility between NCC and the polymer matrix, possibly leading to microstructural defects and compromised barrier performance.

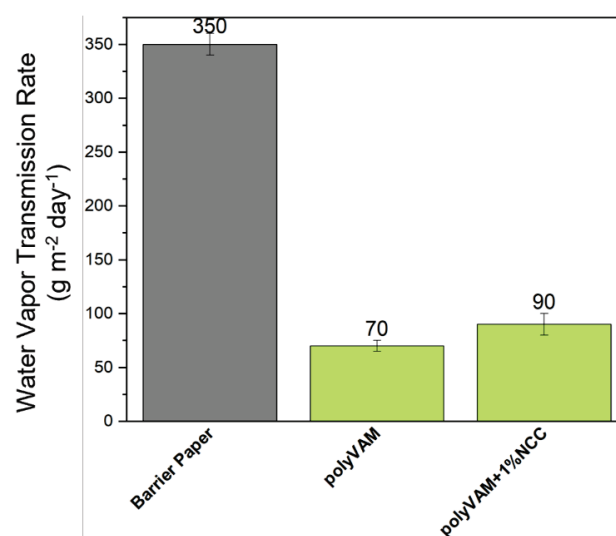


Figure 4: Water Vapor Transmission Rate (WVTR) values of paper samples: uncoated, VAM-coated, and VAM/NCC-coated

4 CONCLUSIONS

The synthesized VAM monomer was successfully polymerized using plasma polymerization, with FTIR and MALDI-HRMS confirming efficient conversion and oligomer formation. An optimal plasma power of 100 W provided balanced incorporation of mono- and di-functional units, ensuring effective crosslinking. Coating the VAM polymer onto paper significantly improved its barrier properties, although the addition of NCC did not enhance performance as expected, likely due to dispersion or compatibility issues. These findings demonstrate the potential of plasma-polymerized VAM as a bio-based coating material for moisture-sensitive applications, with further optimization needed for composite formulations involving nanocellulose.

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