Progress in Organic Coatings 208 (2025) 109511

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis, formulation, and characterization of a bio-based paint derived from TOCN and polypyrrole

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ARTICLE INFO

Keywords:
Biobased paint
TEMPO-oxidized cellulose nanofibers (TOCN)
Polypyrrole
Polyvinyl alcohol
Glycerol
Circular bioeconomy

ABSTRACT

This study presents the development of a biobased paint by integrating TEMPO-oxidized cellulose nanofibers (TOCN) with polypyrrole (PPy) and incorporating polyvinyl alcohol (PVA) as a binder and glycerol as a plasticizer. The TOCN-PPy composite was synthesized via in-situ polymerization, followed by a washing process to ensure compositional purity. High-shear mixing and controlled thermal treatment produced homogeneous and stable formulations. Scanning Electron Microscopy (SEM) revealed a well-dispersed nanofiber network, with increased glycerol content contributing to smoother surface morphology. This may correlate with improved flexibility observed during handling. Raman analysis further confirmed the presence of polypyrrole and revealed spectral shifts associated with enhanced polymer dispersion and hydrogen bonding influenced by PVA and glycerol. Contact angle measurements showed that higher glycerol content increased wettability, reducing hydrophobicity and enhancing adaptability for coating applications. Thermogravimetric Analysis (TGA) revealed multi-stage degradation, with polypyrrole improving thermal stability. The enhanced flexibility observed in glycerol-containing samples is attributed to its plasticizing effect, as evidenced by morphological and handling observations. DSC was also employed for glass transition, melting and thermal decomposition behavior, and thermal stability trends. These findings emphasize the tunability of TOCN-PPy coatings, balancing structural integrity, thermal performance, and wettability for various industrial applications. The results also highlight the potential of TOCN-PPy composites as high-performance, eco-friendly coatings, supporting innovations in green chemistry and the circular bioeconomy.

1. Introduction

The growing emphasis on bio-based coatings stems from the depletion of fossil resources and the environmental concerns associated with conventional petrochemical-based coatings. This shift is reflected in the increasing research on innovative binders derived from renewable sources such as plant oils, fatty acids, cellulose, and cardanol. As sustainability becomes a key driver of material innovation, the demand for eco-friendly alternatives to traditional coatings continues to rise [1]. The widespread use of conventional plastics has led to significant environmental concerns, as their persistence contributes to pollution and greenhouse gas emissions from incineration. This has driven the search for biodegradable alternatives in many applications [2]. Cellulose nanofibrils (CNFs) have emerged as promising bio-based nanomaterials for advanced composites due to their high aspect ratio, specific surface area, and mechanical properties. They also offer improved sustainability over synthetic reinforcements. However, their hydrophilicity complicates integration with hydrophobic polymers, often leading to agglomeration, void formation, and poor interfacial adhesion, which reduce composite performance. As a result, considerable research is focused on CNF surface functionalization to improve dispersion, minimize interfacial energy differences, and enhance fiber–matrix interactions for better mechanical integrity [3]. TEMPO-mediated oxidation functionalizes cellulose nanofibers (TOCNFs) with carboxyl groups and requires less energy than producing microfibrillated cellulose (MFC) or cellulose nanocrystals (CNCs). The

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https://doi.org/10.1016/j.porgcoat.2025.109511
Received 19 April 2025; Received in revised form 16 June 2025; Accepted 4 July 2025
Available online 11 July 2025

carboxyl groups enhance the physicochemical properties of TOCNFs, making them well-suited for applications in biomedicine, wastewater treatment, and bioelectronics [4].While CNFs themselves lack inherent conductivity, they are often used as sustainable substrates in combination with conductive additives for flexible and wearable electronics. Conductive polymers such as polypyrrole (PPy) and polyaniline (PANI) are commonly employed to impart conductivity to insulating matrices. Literature [5] indicates that PPy-coated fabrics exhibit lower cytotoxicity than PANI-based ones, making PPy more favorable for biocompatible applications. Consequently, PPy is widely used for its electrical conductivity, biocompatibility, and environmental stability. Recent advances in electrospun cellulose followed by in-situ PPy polymerization have enabled the development of cellulose/PPy composites for flexible strain sensors and other advanced electronics [5–7].

Polyvinyl alcohol (PVA) is a distinctive water-soluble polymer extensively utilized in papermaking, textiles, and various coatings. Known for its biocompatibility, it serves as a scaffold for cell cultures, embolic materials, contact lenses, and wound dressings. Additionally, PVA is increasingly being applied in environmental engineering and electrical materials [8–10]. Glycerol has been demonstrated to be an effective plasticizer for polyvinyl alcohol (PVA), significantly enhancing its processability and ductility. Among various polyol plasticizers, glycerol-plasticized PVA exhibits the greatest reduction in Young's modulus, improved toughness, and the lowest melting temperature (195 °C). In Xie et al. [11], structural analysis reveals that glycerol reduces crystallinity to 29 % and increases the amorphous layer thickness to 7.76 nm, indicating a significant impact on PVA's structural transformation. Additionally, molecular dynamics studies show that glycerol-plasticized PVA has a two-dimensional structure and the most heterogeneous chain dynamics, with the lowest rigid amorphous fraction (RAF) of 0.507 in the interphase. These findings highlight glycerol's crucial role in modifying PVA's physical and mechanical properties [11].

Paints generally consist of a pigment for color, a binding medium, and various additives that influence optical properties and workability. Over time, the characteristics of paint change, beginning as a liquid-like film and gradually transforming into a solid-like paint film. This transition occurs through two primary mechanisms: drying, where solvents evaporate from the paint film, or curing, which involves crosslinking and other chemical reactions that enhance stiffness. The duration of these processes varies significantly, ranging from a few hours (as seen in acrylics) to months (alkyds) or even decades (oil-based paints). During this transformation, the stiffness of the paint film can increase by several orders of magnitude [12]. Based on previous work for various application of TOCN-PPy films [13,14], we now explore the formulation of a biobased paint designed to unify conductivity, antibacterial activity, and moisture barrier properties in a single, surface-applicable system. This multifunctional paint is particularly suited for applications such as in smart wooden surfaces, antimicrobial indoor coatings, low-power conductive layers in sensors, and sustainable packaging solutions. Its film-forming capability, ease of application, and bio-based composition make it a promising candidate for eco-friendly coatings across electronics, furniture, and health-sensitive environments. Therefore, this study will aim to integrate TOCN with polypyrrole as a base additive and optimizing the composition using PVA (as binder), glycerol (as plasticizer) and water (as solvent). This work will focus on understanding the structural, thermal, and surface properties of the resulting composite coatings and access their potential for antibacterial and conductive applications. Through a combination of viscosity, scanning electron microscopy (SEM), Raman spectroscopy, contact angle measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and qualitative electrical conductivity testing, we have evaluated the material's performance and potential. While previous studies have focused on the development of TOCN-PPy composites as conductive films or coatings, these typically lacked optimization for real-world application as a paint-like formulation. In contrast, our work integrates TOCN and PPy within a fully water-based system, incorporating polyvinyl alcohol (PVA) as a binder and glycerol as a plasticizer. This formulation approach enables direct application to substrates, offering tunable viscosity, improved flexibility, and enhanced adhesion. By systematically varying glycerol content, we demonstrate how to balance network cohesion and plasticity to achieve a versatile, eco-friendly coating. This novel bio-based paint formulation not only preserves the key functional properties of TOCN-PPy but also extends its practical applicability—representing a significant step forward in green coatings for smart surfaces and sustainable packaging.

2. Materials and methodology

2.1. Materials

Pyrrole (C_4H_5N), iron (III) chloride ($FeCl_3$), poly(vinyl alcohol) and glycerol were procured from Sigma Aldrich and Fisher Scientific, and used without further purification. TOCN were prepared from a commercially available never-dried bleached Kraft wood pulp from a methodology developed by our research group [15,16]. From previous work, these treatments resulted in a typical carboxyl content of 1600 mmol/kg, facilitating nanofibers extraction from the oxidized cellulose matrix, and exhibited an estimated width of 3.5 ± 1.0 nm and a length of 306 ± 112 nm with a minor fraction of MFC remaining in the final material [17].

2.2. Synthesis of TOCN-Polypyrrole (TOCN-PPy)

To enhance the functional properties of the composite material, polypyrrole (PPy) was incorporated into the TOCN matrix through an in-situ oxidative polymerization process. The polymerization reaction commenced with the dispersion of 5 ml of pyrrole (4.835 g) in 100 ml of a 0.45 wt% TOCN suspension, followed by stirring for 10 min to mitigate premature polymerization, resulting in an approximate PPy:TOCN mass ratio of 10.7:1. Subsequently, 25 ml of a 0.3 M $FeCl_3$ solution was gradually introduced under continuous stirring, initiating the polymerization process over a period of 30 min. Following polymerization, the TOCN-PPy composite underwent an extensive purification protocol to eliminate residual $FeCl_3$. During each washing cycle, the pH of the water was monitored, and washing was continued until the pH stabilized near the level of distilled water, indicating effective removal of $FeCl_3$. This involved four times sequential washing cycles with 1000 ml of deionized water over a filtration apparatus (Whatman filter paper, Grade 202)) to ensure compositional purity, with pH stabilization being monitored as an indicator of $FeCl_3$ removal.

2.3. Preparation of paint formulations incorporating TOCN-PPy, PVA, and glycerol

The development of paint formulations utilized TOCN-PPy as a functional additive, polyvinyl alcohol (PVA) as a binder, glycerol as a plasticizer, and water as a solvent. The formulation process involved several key steps.

2.3.1. Preparation of the PVA base formulation

A homogeneous solution was prepared by dissolving 5 g of PVA in 100 ml of water, followed by the incorporation of the washed TOCN-PPy composite. High-shear mixing (Silverson L4RT-A, USA) was employed a period of 3 min at room temperature to ensure uniform dispersion of the composite within the PVA matrix.

2.3.2. Incorporation of glycerol

To modify the mechanical and rheological properties of the paint, glycerol was introduced in varying concentrations: 1 ml (Gly1), 2 ml (Gly2) and 5 ml (Gly5). Each formulation was subjected again to high-shear mixing (Silverson L4RT-A, USA) for a period of 3 min at room temperature to achieve thorough integration of TOCN-PPy, PVA, water, and glycerol.

2.3.3. Thermal processing

To facilitate complete dissolution of PVA and promote homogeneous blending of all components, the formulations were heated at 75 °C for a duration of 50 min to 1 h under continuous stirring. This thermal treatment ensured uniform dispersion of TOCN-PPy within the polymer matrix, yielding a stable and homogeneous paint formulation suitable for further applications.

2.3.4. Experimental design for paints development

This structured approach, illustrated in Fig. 1, has enabled composite synthesis and formulation development of TOCN-PPy into a paint system. In the developed paint formulations, each component plays a distinct functional role in achieving the desired material properties. The TOCN-polypyrrole serves as a functional additive, contributing to the active properties. Polyvinyl alcohol (PVA) functions as the binder, ensuring strong adhesion and film-forming capabilities essential for coating applications. Glycerol acts as a plasticizer, improving the flexibility and workability of the paint, thereby preventing brittleness and enhancing durability. Water serves as the solvent, enabling uniform dispersion of all components and facilitating efficient mixing and processing throughout the formulation. Together, these components create a stable and homogeneously blended paint system.

2.4. Making of paint films

The paint formulations were used to prepare films by casting 20–25 ml of the paint solutions into Fisherbrand disposable aluminum weighing pans (10 cm diameter). The samples were then left to dry at room temperature (23 ± 2 °C) for a period of two days, allowing complete solvent evaporation and film formation without thermal acceleration. Once fully dried, the films were carefully peeled from the pans and stored under ambient conditions prior to characterization. This method yielded self-standing films suitable for structural, surface, thermal, and conductivity analyses.

2.5. Substrate coating

In this study, we evaluated the coating performance of various formulations, including TOCN-PPy, TOCN-PPy-PVA, TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2, and TOCN-PPy-PVA-Gly5, on wood substrates, the paints were applied via brush and let it dry over the period of 1 day at room temperature. While the TOCN-PPy formulation alone failed to adhere properly—forming a brittle film that detached from the wood surface upon drying—the inclusion of PVA and varying concentrations of glycerol significantly improved film formation and adhesion. The paint formulations containing PVA and glycerol remained well-adhered to the wood surface, demonstrating their potential for effective painting applications.

2.6. Characterisations

The following sections are describing the apparatus and specific methodology used to characterise the suspension and films.

2.6.1. Rheometer

The rheological properties of the paint formulations were assessed using a Rheologica Stresstech HR Rheometer (ATS RheoSystems) equipped with a C40 cone–plate geometry. Measurements were conducted at a controlled temperature of 25 °C, with the shear rate ranging from 0.1 to 1000 s^{-1}. Apparent viscosity (η_{app}) was determined as the slope of the shear stress (τ) versus shear rate (γ) curve, calculated using the relationship $\eta_{app} = \tau / \gamma$. Each formulation underwent three measurements to ensure data reliability, with average viscosity values reported.

2.6.2. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was performed using a Hitachi SU1510 microscope. Non-conductive samples were sputter-coated with a thin layer of gold using an International Scientific Instruments PS-2 coating unit to prevent charging and enhance imaging quality. The SEM operated in secondary electron mode at an accelerating voltage of 15 kV and a beam current of 100 μA, providing detailed imaging of surface features.

2.6.3. Raman spectroscopy

Raman spectroscopy was conducted using a Thermo Fisher DXR3 Raman Microscope to analyze the molecular composition and chemical structure of the paint films. The instrument was equipped with a 785 nm excitation laser and a full-range grating covering approximately 300 to 3000 cm^{-1}. Optimal spectral data were obtained by setting the laser power to 30 mW, utilizing an exposure time of 30 s per scan, and performing three accumulations. A 50 μm slit aperture and a 10× objective were employed to focus the laser on the sample surface. Three replicate measurements were collected for each sample at various locations to ensure data reliability. The DXR3 Raman Microscope features automatic X-axis calibration, enhancing measurement reliability and stability. .

2.6.4. Contact angle

The wettability of the paint films applied to wood surfaces was evaluated through contact angle measurements using the sessile drop method. A Microdrop Contact Angle Analyzer FTA4000 (First Ten Angstroms, USA) was employed for this purpose. Deionized water droplets of 5 μl were carefully deposited onto the coated wood surfaces using the analyzer's precision dispensing system. The contact angles were measured at ambient temperature by capturing the droplet profiles

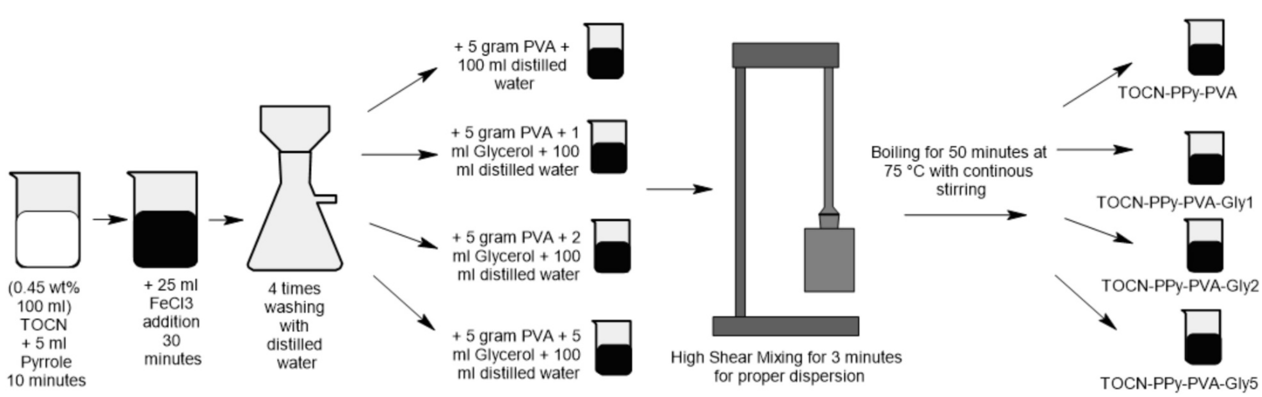

Fig. 1. Formation of TOCN-PPy-PVA-Glycerol based paints.

with the instrument's high-resolution camera. The instrument's software analyzed the droplet images to determine the contact angle at the liquid-solid-air interface. To ensure reliability and account for surface heterogeneity, measurements were performed at five different locations on each sample, and the average contact angle was reported.

2.6.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted using a Perkin Elmer TGA-8000 (USA) thermogravimetric analyzer to evaluate the thermal stability and composition of the paint films. Samples were placed in ceramic crucibles and subjected to a temperature program under a nitrogen atmosphere with a flow rate of 50 ml/min. The program included equilibration at 40 °C for 3 min, heating from 40 °C to 105 °C at 10 °C/min to remove adsorbed moisture, an isothermal hold at 105 °C for 20 min, followed by heating to 900 °C at 10 °C/min for polymer decomposition and carbonization, an isothermal hold at 900 °C for 20 min, and finally cooling back to 40 °C at 200 °C/min. Weight changes were continuously recorded to assess the thermal stability and compositional characteristics of the samples..

2.6.6. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was conducted using a TA Instruments DSC 2500 to analyze the thermal transitions of the paint films. Under a nitrogen atmosphere maintained at a flow rate of 50 ml/min to prevent oxidative degradation, the samples were heated from 40 °C to 200 °C at a rate of 10 °C/min.

2.6.7. Qualitative conductivity analysis

To qualitatively assess the electrical conductivity of the paint films, a simple circuit was constructed comprising a 9 V battery and a LED bulb as an indicator. Initially, the circuit was tested in an open configuration without any connecting material; as expected, the bulb remained unlit, confirming that a continuous conductive path is necessary for current flow. An aluminum disk was then introduced into the circuit, completing the electrical pathway and causing the bulb to illuminate, thereby validating the setup's functionality. Subsequently, paint film samples measuring 30 mm in length and 15 mm in width were placed into the circuit in place of the aluminum disk. This result reinforces the reliability of the experimental setup and ensures that the observed conductivity in the TOCN-PPy-PVA-based composites was due to intrinsic material properties rather than experimental artifacts.

3. Results and discussion

As the application of this study is develop a paint-like coating, measurements of the suspension properties and the resulting film was undergone.

3.1. Rheological measurements (Suspensions)

Viscosity measurements on a rheometer enable determination of the viscosity values at a given shear rate but also accurate characterization of shear-dependent flow behavior. Fig. 2 presents the flow behavior for all the TOCN-PPy-PVA-Glycerol formulations as described in the methodology; an apparent viscosity can be extracted from the data of the

Table 1
Viscosity of TOCN-PPy-PVA-Glycerol based paints.

Sample	Viscosity (Pa.s) Measure 1	Measure 2	Measure 3	Mean	Standard deviation
TOCN-PPy-PVA	0.73	0.59	0.59	0.64	0.08
TOCN-PPy-PVA-Gly1	5.93	10.20	12.60	9.58	3.40
TOCN-PPy-PVA-Gly2	2.77	4.76	3.35	3.63	1.00
TOCN-PPy-PVA-Gly5	0.87	0.95	0.86	0.90	0.05

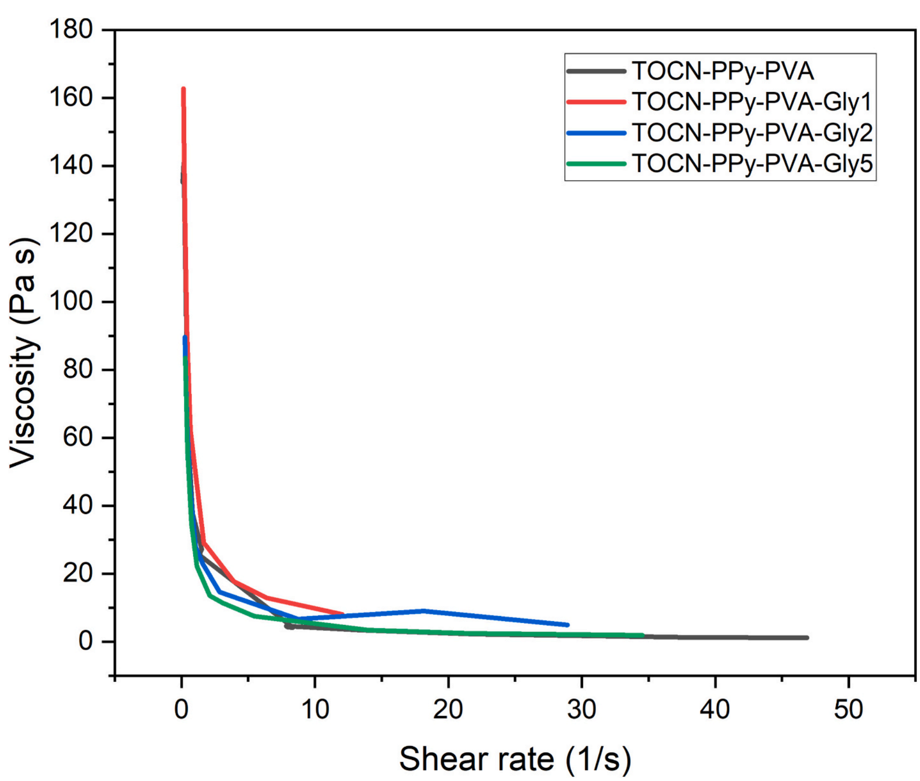

Fig. 2. Rheological behavior of TOCN-PPy-PVA-Glycerol based paints.

shear stress vs. shear rate curves (Table 1).

The variation in viscosity observed across the TOCN–PPy–PVA–glycerol system can be attributed to the complex interplay between hydrogen bonding, polymer chain mobility, and filler dispersion. In the base formulation containing TOCN, polypyrrole (PPy), and polyvinyl alcohol (PVA), the viscosity remains relatively low due to limited molecular entanglement and weak physical interactions. The incorporation of a small amount of glycerol (Gly1) results in a significant increase in viscosity, which is attributed to reduced polymer chain mobility by hydrogen bonding between PVA and TOCN nanofibers. This facilitates the formation of a more cohesive and entangled network, while also improving the dispersion of PPy within the matrix. The increase in viscosity observed with the addition of a small amount of glycerol (Gly1) is supported by the [18] findings that glycerol enhances hydrogen bonding and decreases crystallinity, which reduces chain mobility and promotes polymer network cohesion, especially between PVA and other matrix components. As the glycerol content increases further (Gly2 and Gly5), it now assumes a dominant plasticizing role, disrupting interpolymeric hydrogen bonds and reducing the effective network density. Consequently, the viscosity decreases, although it remains higher than the PVA-only formulation. This nonlinear rheological behavior highlights glycerol's dual functionality, acting as a network enhancer at low concentrations and as a plasticizer at higher concentrations, enabling tunable viscosity. This biphasic effect has been documented in a study [19] showed that adding 22 % *w*/w glycerol to PVA initially increased crystallinity due to hydrogen bonding, while higher concentrations (36–55 % *w*/w) disrupted the polymer network, reducing flow resistance. Similarly, another study [20] found that while polyvinylpyrrolidone increased viscosity in transdermal patch formulations, increasing glycerol concentrations led to decreased viscosity due to its plasticizing effects.

The rheological behavior of TOCN-PPy-PVA-Glycerol formulations exhibited typical shear-thinning characteristics observed from Fig. 2, where viscosity decreased with increasing shear rate, demonstrating suitability for paint applications due to ease of application under shear and film stability at rest. The incorporation of glycerol significantly influenced viscosity, with the Gly1 formulation showing the highest viscosity due to enhanced hydrogen bonding and polymer network formation between TOCN, PVA, and glycerol. However, further addition of glycerol in Gly2 and Gly5 reduced the viscosity, as excess glycerol acted as a plasticizer, disrupting the hydrogen bonding network and increasing polymer chain mobility. This biphasic behavior highlights glycerol's dual role—initially strengthening the matrix at low concentrations and later reducing structural cohesion at higher concentrations—allowing tunable rheological properties for tailored coating performance. Furthermore, The viscosity measurements for the TOCN-PPy-PVA-Gly1 formulation (5.93, 10.2, 12.6 Pa·s) exhibit variability due to the inherent complexity and heterogeneity of the paint system. This formulation contains multiple components (TOCN, PPy, PVA, and glycerol), which can lead to local differences in dispersion and microstructure in each replicate, impacting flow behavior. Additionally, as a non-Newtonian, shear-thinning fluid, slight variations in shear history and rest periods during rheological testing can cause differences in the reported viscosity values. Instrumental factors, such as torque resolution and sample loading, can also contribute to this normal experimental variability. Nevertheless, these differences do not affect the overall trends and conclusions from the rheological characterization.

The rheological profiles of the TOCN-PPy-PVA-Glycerol formulations (Fig. 2) clearly exhibit shear-thinning behavior, characterized by a decrease in apparent viscosity with increasing shear rate. This behavior is typical of pseudoplastic fluids and is crucial for paints, as it facilitates ease of application under mechanical shear while enhancing stability at rest. Shear thinning in these formulations can be attributed to the alignment and disentanglement of polymer chains (TOCN, PVA, and PPy) and the disruption of transient hydrogen-bonded networks under shear forces. During shear application (e.g., brushing, mixing), viscosity decreased, enabling smooth application, and upon resting, the viscosity of the system appeared to partially recover—indicating reversible structural rebuilding. This is consistent with typical behavior of waterborne polymeric and nanocellulose-based paints, which exhibit structural network rebuilding driven by hydrogen bonding, polymer chain entanglement, and van der Waals interactions (as described by [21,22]).

Since the structure of the suspension is proving to be of importance, we want to investigate the structure of the final's products. Therefore, films were made from the above solutions of TOCN-PPy-PVA, TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2 and TOCN-PPy-PVA-Gly5.

3.2. Scanning electron microscopy (Films)

The SEM micrographs reveal significant morphological variations across the TOCN-PPy-based composites, highlighting the structural influence of PVA and glycerol on the material. The Fig. 3 shows the SEM for the surface of TOCN-PPy, TOCN-PPy-PVA, and TOCN-PPy-PVA-Gly2. The TOCN-PPy (Fig. 3a) sample exhibits a highly rough, porous, and fibrous surface morphology, indicative of an interconnected polypyrrole (PPy) network embedded within the TOCN matrix. The presence of visible voids and irregularities suggests a high surface area, but could lead to increased mechanical fragility. Upon the incorporation of PVA (TOCN-PPy-PVA), Fig. 3b, show that microstructure appears significantly smoother and more compact, suggesting improved polymer matrix integration, thus potential enhanced mechanical stability. PVA likely acts as a binder, reducing phase separation and improving structural cohesion. However, minor surface irregularities may still imply localized polymer aggregation. In Fig. 3c, further modification with glycerol (TOCN-PPy-PVA-Gly2) show an even more cohesive microstructure, characterized by a smooth morphology with visible fibrillar structures. The plasticizing effect of glycerol appears to enhance polymer blending, reducing surface roughness while maintaining an interconnected network. The presence of elongated streaks or fibrils suggests polymer chain alignment, potentially improving mechanical flexibility while preserving electric conductive pathways.

3.3. Raman spectroscopy (Films)

The Raman spectra of TOCN-PPy, TOCN-PPy-PVA, and glycerol-modified composites (TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2, and TOCN-PPy-PVA-Gly5) were analyzed and compared with reported literature values to assess structural and electronic variations (Fig. 4).

The key Raman peaks of interest observed in this study were at 922, 1042, 1230, 1318, 1408, 1507, and 1597 cm^{-1}, corresponding to fundamental vibrational modes associated with polypyrrole (PPy) and its composites. The observed Raman bands were compared with previously reported assignments [23,24]. The comparison suggests that the molecular structure and oxidation state of PPy were influenced by the presence of TOCN, PVA, and glycerol modifications.

Raman spectroscopic analysis of the TOCN-PPy-PVA composites revealed spectral shifts and peak broadening, indicating complex molecular interactions between the polypyrrole (PPy) backbone, TOCN, polyvinyl alcohol (PVA), and glycerol. A notable shift is observed in the C—C ring deformation associated with bipolaron formation, where the peak appears at 922 cm^{-1}, slightly downshifted from the reported 933–939 cm^{-1} range [24]. This shift may be influenced by interactions between TOCN and PVA. Similarly, the C—H in-plane deformation associated with polaronic structures is observed at 1042 cm^{-1}, downshifted from the typical 1050–1056 cm^{-1} range [23]. The shift may be attributed to hydrogen bonding interactions between the polypyrrole chains and TOCN or PVA, which alter the local electronic environment and influence charge delocalization. Further modifications in conjugation are evident in the ring stretching and antisymmetric C—H bending modes, with a peak at 1230 cm^{-1}, compared to the literature-reported 1241–1253 cm^{-1} [24]. This shift suggests changes in electronic density along the PPy backbone, likely due to TOCN-PVA interactions.

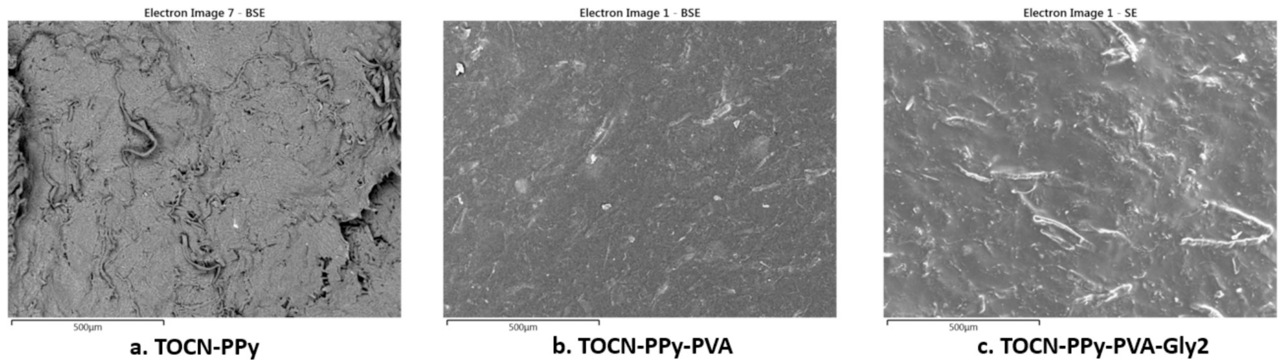

Fig. 3. Scanning electron microscopy for the TOCN-PPy, TOCN-PPy-PVA and TOCN-PPy-PVA-Gly2.

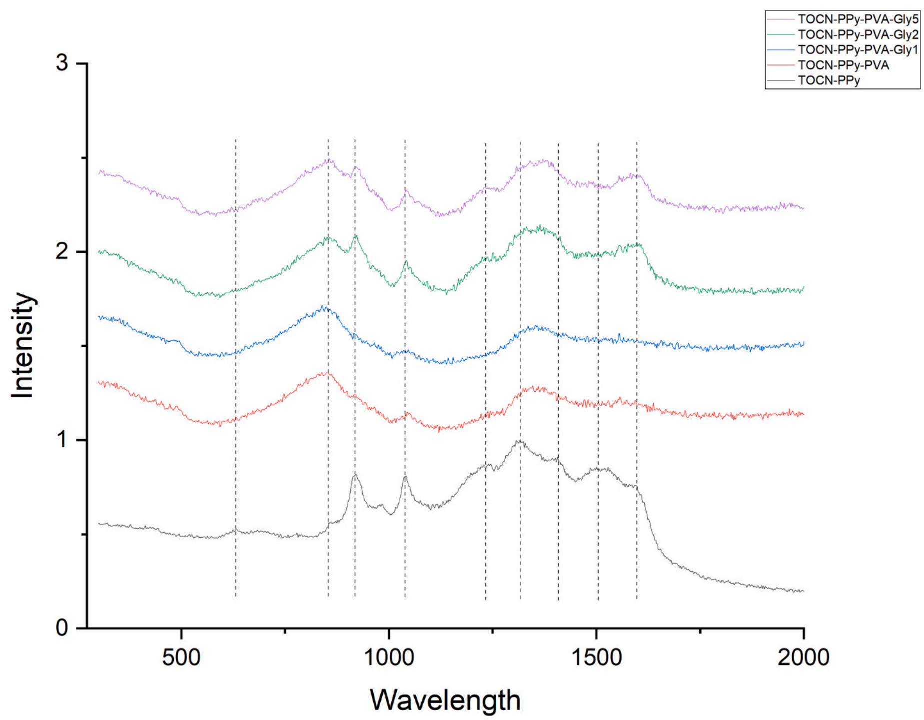

Fig. 4. Raman spectroscopy of TOCN-PPy-PVA-Glycerol based paints.

Similarly, the C—C in-ring and antisymmetric C—N stretching vibrations, detected at 1318 cm^{-1} (compared to 1330–1333 cm^{-1} in literature), indicate slight variations in conjugation length. These modifications may result from hydrogen bonding interactions or steric effects introduced by the polymeric matrix.

A more pronounced shift is observed in the C—C in-ring, C—N stretching, and N—H bending vibrations, where the 1408 cm^{-1} peak is significantly upshifted from the expected 1372–1389 cm^{-1} range [24]. This shift suggests possible changes in the oxidation state of PPy, with increased oxidation levels typically leading to higher peak intensities in this region [23]. The presence of PVA and glycerol appears to influence the electronic charge distribution within the polypyrrole framework, potentially modifying its conductivity and charge transport properties. The C—C and C═N stretching vibrations, appearing at 1507 cm^{-1}, align well with the literature values of 1492–1498 cm^{-1} [24], confirming the integrity of polypyrrole's characteristic vibrational modes within the composite structure. Similarly, the C═C in-ring and C—C inter-ring stretching mode, observed at 1597 cm^{-1}, remains consistent with reported values of 1583–1609 cm^{-1} [24]. While these observations indicate that the main polypyrrole backbone remains intact, the small spectral shifts observed could be associated with interactions between PVA, TOCN, and glycerol. However, minor shifts indicate that while PVA and glycerol modifications do not disrupt the primary PPy backbone, they do influence charge delocalization.

Finally, the Raman spectra show increased broadening in TOCN-PPy-PVA and TOCN-PPy-PVA-Gly1, particularly in the peaks around 1408 cm^{-1} and 1597 cm^{-1}. This broadening is indicative of enhanced molecular interactions, possibly due to increased hydrogen bonding or polymeric entanglement effects. The spectral broadening is more pronounced in Gly1, suggesting an initial increase in molecular disorder and charge delocalization due to glycerol incorporation. With Gly2 and Gly5, the peaks become more defined, indicating a stabilization effect as the glycerol content increases. This suggests that at higher glycerol concentrations, the molecular interactions become more structured, possibly leading to better charge transport properties.

3.4. Contact angle (Wood painted surfaces)

While not being a chemical analysis, the water droplet contact angle give relevant information about the surface hydrophobicity. The results from Table 2 show how glycerol content affects the surface properties of TOCN-PPy-PVA composites, with a clear trend toward increased

Table 2
Contact angle measurement of TOCN-PPy-PVA-Glycerol based paints.

Sample	Static contact angle (°)
TOCN-PPy-PVA	85.40 ± 4.22
TOCN-PPy-PVA-Gly1	93.09 ± 6.50
TOCN-PPy-PVA-Gly2	86.46 ± 5.23
TOCN-PPy-PVA-Gly5	79.89 ± 4.09

hydrophobicity and reduced wettability as glycerol concentration increase.

The control sample (TOCN-PPy-PVA) exhibits moderate hydrophobicity with a contact angle of 85.40° ± 4.22. With the addition of glycerol, the contact angle increases to 93.09° ± 6.50 for the Gly1 sample, indicating enhanced hydrophobicity, though variability is observed due to higher standard deviation. For the Gly2 sample, the contact angle decreases to 86.46° ± 5.23, suggesting a slight reduction in hydrophobicity and improved wettability. The highest glycerol content (Gly5) leads to the lowest contact angle (79.89° ± 4.09), reflecting a shift toward hydrophilicity and enhanced wettability. Overall, as glycerol content increases, there is a consistent reduction in hydrophobicity and an increase in wettability, with lower variability observed at higher glycerol concentrations.

3.5. Thermogravimetric analysis (Films)

Thermogravimetric analysis (TGA) was performed to investigate the thermal stability, decomposition behavior, and residual mass content of TOCN-based composites, including pure TOCN, TOCN-PPy, TOCN-PPy-PVA, and glycerol-modified composites (TOCN-PPy-PVA-Gly1, Gly2, Gly5). The thermogravimetric analysis (Fig. 5) of TOCN-based composites revealed distinct thermal degradation profiles reflecting the influence of added components.

Pure TOCN exhibited two main degradation stages: moisture loss below 105 °C and cellulose decomposition between 200 and 350 °C, leaving residue at 900 °C. TOCN-PPy exhibited the highest thermal stability, with a residual mass of approximately 44 % at 900 °C, indicating the formation of a stable carbonaceous structure due to polypyrrole's conjugated aromatic backbone. Pure TOCN retained about 22 %, reflecting typical cellulose char formation after thermal degradation. Incorporating PVA reduced the final residue to 11 %, indicating a more complete thermal decomposition of the polymeric matrix. The introduction of glycerol further reduced thermal stability, with residual masses decreasing progressively to 10.5 % (Gly1), 8 % (Gly2), and 6.5 % (Gly5). This trend is consistent with glycerol's known plasticizing effect, which lowers the thermal decomposition onset and enhances volatility, leading to lower char formation. These results underscore the trade-off between flexibility and thermal resistance, as the addition of glycerol improves processability but diminishes structural integrity under thermal stress. The enhanced char yield in PPy-containing samples confirms its role in improving high-temperature performance, crucial for applications requiring both conductivity and thermal durability. Glycerol lower decomposition temperature (∼150–250 °C) and high volatility result in significant mass loss at earlier stages and reduced carbonaceous residue. Incorporating polypyrrole (PPy) improved thermal stability, with a delayed onset of degradation and increased residue due to stable carbonaceous content. The addition of polyvinyl alcohol (PVA) and glycerol introduced overlapping degradation steps and increased moisture loss at 105 °C, highlighting their hydrophilic nature. In the end, glycerol reduced overall thermal stability due to its lower decomposition temperature, while PPy enhanced stability by delaying decomposition.

These results underscore the trade-off between flexibility, hydrophilicity, and thermal performance, critical for tailoring composites for applications in biobased coatings and packaging. The lower residual mass observed in the glycerol-modified composites (TOCN-PPy-PVA-Gly1, Gly2, and Gly5) indicates a greater degree of thermal degradation and reduced char yield compared to TOCN and TOCN-PPy, making them less suitable for high-temperature applications. [22] also observed that increasing glycerol concentrations led to a decrease in crystallinity and tensile strength, particularly at elevated temperatures. They also concluded that while glycerol acts as an effective plasticizer enhancing flexibility, it compromises the structural integrity of the material under thermal stress.

3.6. Differential scanning calorimetry (Films)

Differential Scanning Calorimetry (DSC) was conducted to evaluate

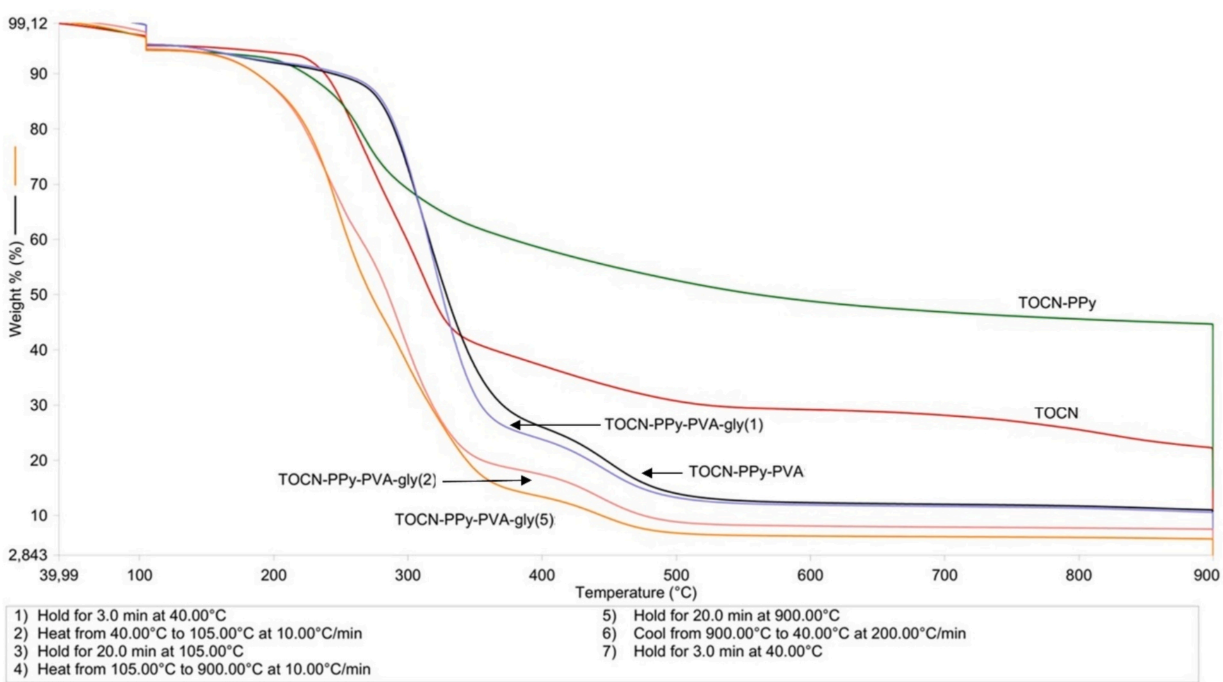

Fig. 5. Thermogravimetric analysis of TOCN-PPy-PVA-Glycerol based paints.

the thermal behavior of TOCN, TOCN-Polypyrrole (TOCN-PPy), TOCN-PPy-PVA, and glycerol-modified composites (TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2, and TOCN-PPy-PVA-Gly5) (Fig. 6). In Fig. 6, the glass transition temperature (Tg) is observed as a subtle deviation in the baseline, indicating molecular mobility changes in the polymer matrix. The pure TOCN sample exhibits a Tg at approximately 135 °C, attributed to the amorphous fraction of cellulose nanofibers. Incorporation of polypyrrole (PPy) into TOCN (TOCN-PPy) results in a slight increase in Tg to ~140 °C, suggesting enhanced thermal stability due to strong interfacial interactions between TOCN and PPy. With the addition of polyvinyl alcohol (PVA), the Tg becomes less defined, indicating a reduction in crystalline fraction and an increase in polymer chain flexibility. The glycerol-modified samples (TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2, and TOCN-PPy-PVA-Gly5) exhibit an even broader Tg transition due to the plasticizing effect of glycerol, which further increases polymer mobility and reduces the rigidity of the composite matrix.

The DSC thermograms of Fig. 6 also reveal significant endothermic peaks in the range of 130 °C to 160 °C, associated with melting or structural relaxation of the composite materials. The pure TOCN sample exhibits a sharp endothermic peak at ~140 °C, corresponding to its degradation point. However, upon incorporating PPy, the transition shifts to a higher temperature (~175 °C), demonstrating improved thermal stability (as in the TGA analysis) due to the presence of polypyrrole. The TOCN-PPy-PVA formulation shows a broader and less distinct endothermic peak (~145–160 °C) compared to TOCN and TOCN-PPy, indicating increased amorphous content and enhanced thermal flexibility. The addition of glycerol further influences the thermal transitions by suppressing sharp melting peaks and broadening the transition region. This behavior is characteristic of plasticized polymer systems, where glycerol disrupts crystalline domains, increasing polymer chain mobility and reducing rigidity. As per [19], incorporating glycerol into PVA films affects their crystallinity. At low glycerol concentrations, glycerol enhances the mobility of molecular chains, promoting ordering and crystallization. However, at higher concentrations, glycerol may aggregate and interact selectively with PVA chains at crystalline interfaces, potentially penetrating the crystals and disrupting molecular order. Interestingly, the TOCN-PPy-PVA-Gly2 and TOCN-PPy-PVA-Gly5 samples exhibit small exothermic peaks (~160–175 °C), suggesting possible molecular rearrangement or secondary crystallization before decomposition. These events may be attributed to 1- a structural Relaxation Phase as the presence of PVA and glycerol leads to weak crystalline reordering, causing an exothermic response, 2- weak Crosslinking or Secondary Crystallization – The polymer matrix, influenced by hydrogen bonding interactions, may undergo localized structural reorganization in response to heating or 3-, reorientation of Hydrogen Bonds – The hydroxyl groups in TOCN, PVA, and glycerol may undergo dynamic rearrangements, leading to minor exothermic energy release.

The polymer matrix, influenced by hydrogen bonding interactions, may undergo localized structural reorganization upon heating. [19] have shown that the addition of glycerol to PVA films affects the crystalline structure, leading to changes in thermal transitions.

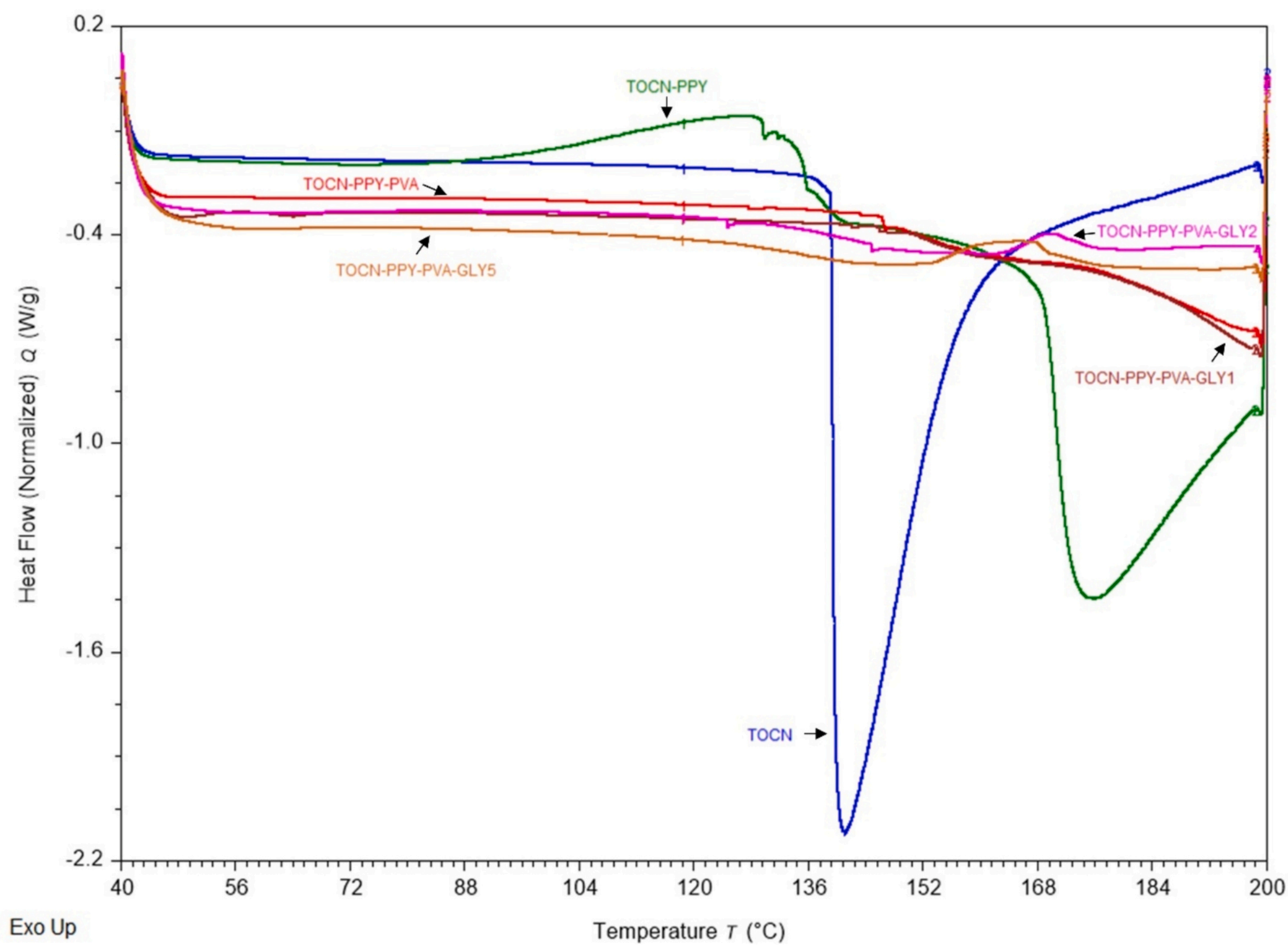

Fig. 6. Differential scanning calorimetry analysis of TOCN-PPy-PVA-Glycerol based paints.

3.7. Qualitative conductivity analysis (Films)

In order to evaluate the electrical conductivity of the samples and confirm the continuous structure of the paints, a qualitative test was conducted using a basic electrical circuit. As explained in the methodology, the sample (in film factor) are used to close the circuit and evaluate the LED intensity (Fig. 7). The aluminum disk was used as a control due to its well-established electrical conductivity and when integrated into the circuit, the bulb glowed brightly, indicating efficient current flow and confirming the material's high conductivity (Fig. 7a). As expected, when the circuit was open (Fig. 7b), the bulb did not illuminate, demonstrating the interruption of the electrical pathway. When TOCN-PPy-PVA-based composites, including TOCN-PPy-PVA, TOCN-PPy-PVA-Gly1, TOCN-PPy-PVA-Gly2, and TOCN-PPy-PVA-Gly5 (Fig. 7c to f), were introduced into the circuit, the bulb emitted a faint but noticeable glow. Although the brightness was significantly lower than that observed with the aluminum disk, the consistent illumination across all samples indicated the presence of measurable electrical conductivity. The faint glow does confirm that the TOCN-PPy-PVA composites possess some level of electrical conductivity, which can be attributed to the incorporation of polypyrrole (PPy) within the matrix [17]. As a conductive polymer, PPy forms pathways that enable charge transport within the otherwise non-conductive TOCN, PVA, and glycerol-based network. The lower intensity of the bulb's glow compared to the aluminum disk underscores the fact that the conductivity of these polymer-based composites is considerably weaker than that of metals, which is expected for conductive polymers. Furthermore, the inclusion of glycerol in the modified samples (Gly1, Gly2, and Gly5) did not significantly hinder conductivity, as evidenced by the consistent bulb illumination. However, we acknowledge that these qualitative tests do not provide a rigorous quantification of electrical conductivity.

3.8. Proposed structure of TOCN-PPY, TOCN-PPy-PVA and TOCN-PPy-PVA-Gly

With the given analysis, we can make hypothesis on the structure of TOCN-PPY, TOCN-PPy-PVA and TOCN-PPy-PVA-Gly paints. Fig. 8(a), (b), (c), (d) illustrates the basic molecules while Fig. 8(e) present a proposed structure of TOCN-PPy.

The TOCN-PPy structure is primarily driven by electrostatic interactions between negatively charged carboxyl (-COO$^-$) groups of TOCN and partially positively charged nitrogen (N$^+$-H) sites in PPy, ensuring strong adhesion of PPy onto the TOCN surface. Raman spectroscopy did confirm polaronic and bipolaronic charge states, reinforcing this interaction. Additionally, hydrogen bonding between residual hydroxyl (-OH) groups in TOCN and N—H sites in PPy provides further stabilization, enhancing dispersion and uniformity. The addition of glycerol (Gly) as a plasticizer induces further changes in the thermal degradation profiles, reflecting its plasticizing effect that enhances flexibility while reducing thermal stability. Together, the TGA and DSC analyses support the proposed structural model, emphasizing the distinct and synergistic interactions among TOCN, PPy, PVA, and Gly. These interactions modulate the composite paints' thermal transitions and residual stability, balancing flexibility with char-forming capacity depending on the formulation. As demonstrated by [21], glycerol disrupts hydrogen bonding within PVA, leading to enhanced flexibility (Fig. 9). In the TOCN-PPy-PVA-Gly composite, this effect improves polymer chain mobility while maintaining the structural integrity provided by TOCN and PPy interactions.

The TOCN-PPy-PVA structure is stabilized by electrostatic interactions and hydrogen bonding. The carboxyl (-COO$^-$) groups of TOCN strongly bind to the N$^+$-H sites of PPy, ensuring uniform deposition. Polyvinyl alcohol (PVA) integrates through hydrogen bonding, primarily interacting with TOCN's hydroxyl (-OH) and carboxyl (-COO$^-$) groups, reinforcing structural stability. Additional PVA (-OH) to PPy (N—H) hydrogen bonding improves dispersion and prevents phase separation. This results in a well-integrated composite, where TOCN provides reinforcement, PPy imparts conductivity, and PVA enhances film uniformity, adhesion, and mechanical performance.

On the other hand, TOCN-PPy-PVA-Gly structure incorporates plasticization effects, in addition to electrostatic interactions and hydrogen bonding. While TOCN and PPy interact electrostatically, PVA binds through hydrogen bonding, stabilizing the matrix. Glycerol acts as a plasticizer, forming hydrogen bonds with PVA (-OH) groups, disrupting PVA's internal network, increasing polymer flexibility, and reducing crystallinity. A minor glycerol (-OH) interaction with TOCN (-OH) may enhance hydrophilicity, modifying the composite's wettability. This well-integrated structure enables TOCN to provide reinforcement, PPy to impart conductivity, PVA to enhance cohesion, and glycerol to improve flexibility, making the material suitable for coatings and functional applications.

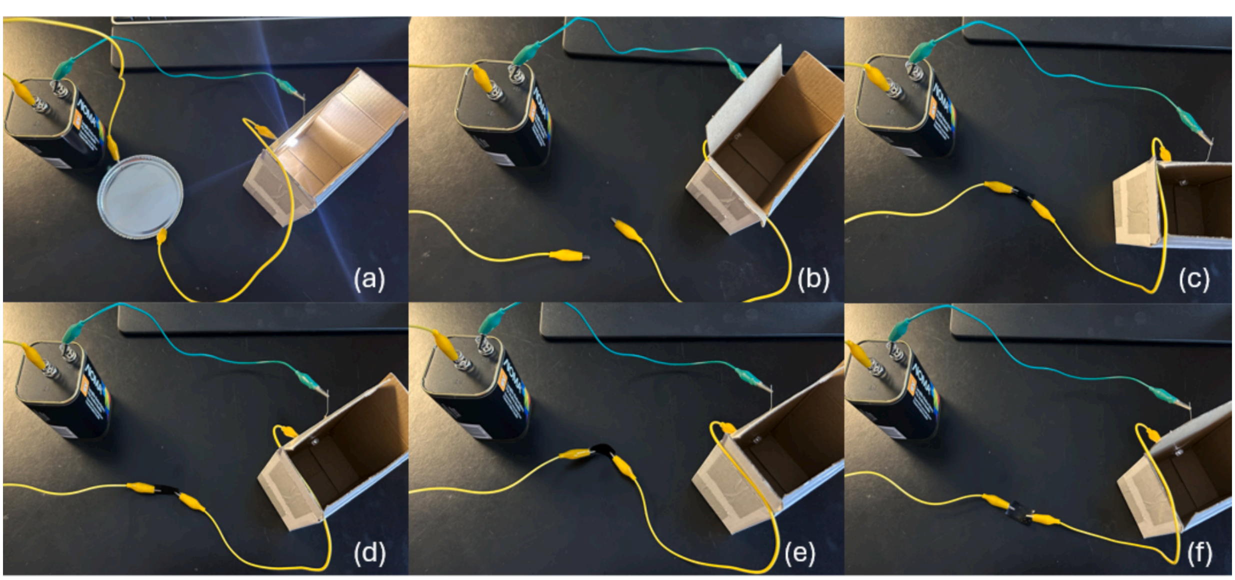

Fig. 7. (a) Circuit with aluminum disk, (b) open circuit, (c) with TOCN-PPy-PVA, (d) with TOCN-PPy-PVA-Gly2, (e) with TOCN-PPy-PVA-Gly2, (f) with TOCN-PPy-PVA-Gly5.

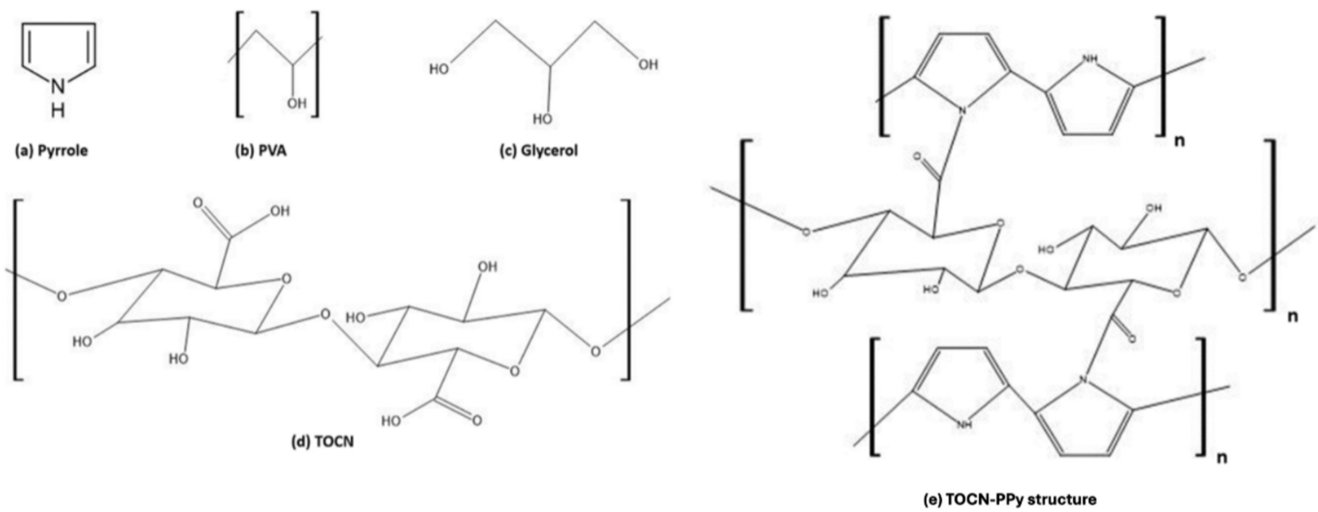

Fig. 8. (a) Pyrrole, (b) Polyvinyl alcohol, (c) Glycerol, (d) TOCN, (e) Proposed TOCN-PPy structure.

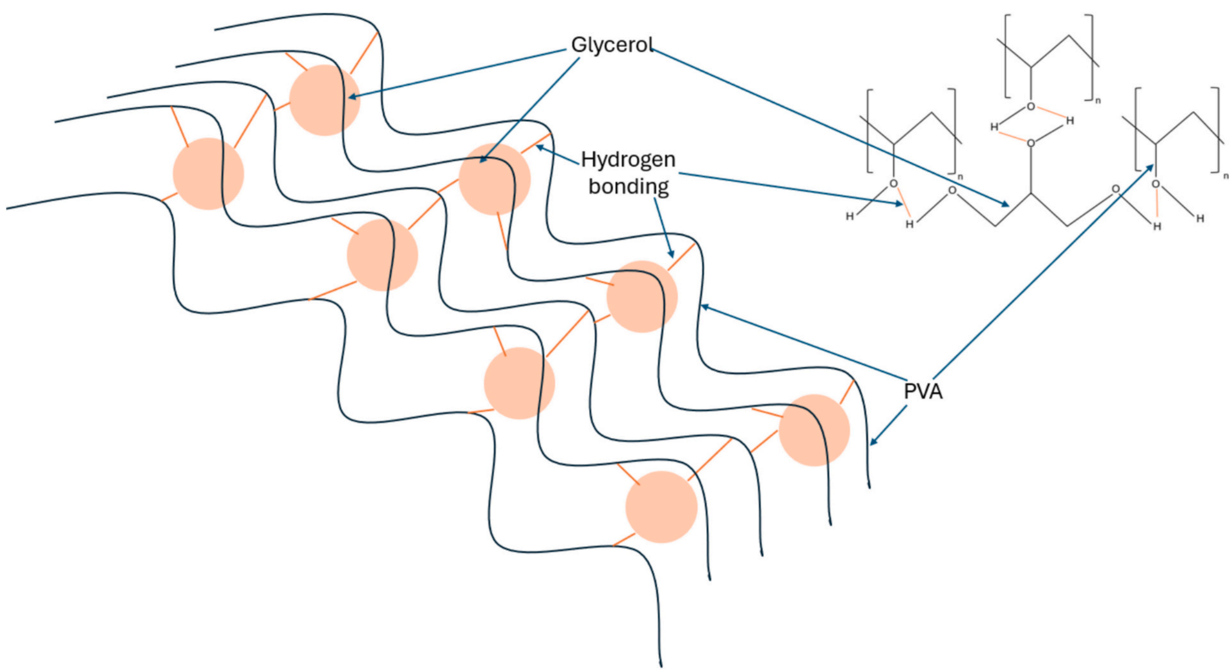

Fig. 9. PVA-Glycerol interaction.

4. Conclusion

This study successfully developed a biobased paint and coating formulation by integrating TOCN with polypyrrole (PPy) in a matrix of polyvinyl alcohol (PVA) and glycerol. The observed nonlinear rheological behavior underscores glycerol's dual functionality: at low concentrations, it enhances network cohesion through hydrogen bonding, leading to increased viscosity; at higher concentrations, it acts as a plasticizer, disrupting interpolymeric interactions and reducing viscosity. Morphological analysis through SEM revealed a well-dispersed, cohesive structure, with glycerol contributing to flexibility and improved internal cohesion. Raman spectroscopy has verified polypyrrole integration by identifying its characteristic vibrational modes. The spectral analysis further validated molecular interactions within the composite, reinforcing its cohesive and stable structure. Additionally, qualitative conductivity testing demonstrated that the material exhibits measurable electrical conductivity, confirming the presence of polypyrrole within the composite. Contact angle measurements demonstrated that increasing glycerol content reduced hydrophobicity and enhanced wettability, indicating the tunability of surface properties for specific applications. Thermogravimetric analysis (TGA) revealed multi-stage thermal degradation, where polypyrrole improved thermal stability, and glycerol contributed to flexibility (which was further confirmed via DSC) by lowering the decomposition temperature. The proposed structure highlights the interaction between PVA and glycerol through hydrogen bonding, which contributes to the flexibility and integrity of the matrix. TOCN-PPy is incorporated into this network, where TOCN interacts with PVA and glycerol via hydrogen bonding, and PPy is expected to be well-dispersed within the matrix, supporting the overall stability and performance of the formulation. While earlier studies primarily explored TOCN-PPy composites as conductive films or coatings, they often lacked formulation strategies suitable for practical, paint-like applications. In contrast, our work advances this field by developing a fully water-based system that combines TOCN and polypyrrole (PPy) with polyvinyl alcohol (PVA) as a binder and glycerol as a plasticizer, thus offering a more application-ready coating formulation. These findings underscore the balance between structural integrity, thermal performance, and adaptability, making the material suitable for diverse industrial and protective coating applications. Furthermore, these results highlight the potential of TOCN-PPy-PVA-Gly composites as a sustainable and high-performance paints. Future research should focus on assessing the antibacterial properties, biodegradability, UV resistance, substrate adhesion, humidity resistance, and gas permeation to explore real-world applications. Additionally, future work will include quantitative electrical conductivity testing, mechanical testing to validate the observed improvements in flexibility, and barrier property analysis to establish comprehensive structure–property correlations and confirm the multifunctional performance of these bio-based coatings.

CRediT authorship contribution statement

Aakash Malik: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Simon Barnabé:** Writing – review & editing, Supervision. **Éric Loranger:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) did not used any generative or AI related tools.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Eric Loranger reports financial support was provided by Natural Sciences and Engineering Research Council of Canada. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research project is funded by the Natural Sciences and Engineering Research Council of Canada (Discovery grant RGPIN-2021-02861) and Municipal Research Chair for Sustainable Cities (UQTR – Victoriaville).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2025.109511.

Data availability

Data will be made available on request.

References

[1] Y.W. Chek, D.T.C. Ang, Progress of bio-based coatings in waterborne system: Synthesis routes and monomers from renewable resources, in: Progress in Organic Coatings vol. 188, Elsevier B.V, 2024, https://doi.org/10.1016/j.porgcoat.2023.108190.

[2] A. Samir, F.H. Ashour, A.A.A. Hakim, M. Bassyouni, Recent advances in biodegradable polymers for sustainable applications, in: Npj Materials Degradation vol. 6, Issue 1, Nature Publishing Group, 2022, https://doi.org/10.1038/s41529-022-00277-7.

[3] K. Oesef, E.D. Cranston, Y. Abdin, Current advances in processing and modification of cellulose nanofibrils for high-performance composite applications, Mater. Des. (2024), https://doi.org/10.1016/j.matdes.2024.113417.

[4] Z. Tang, X. Lin, M. Yu, A.K. Mondal, H. Wu, Recent advances in TEMPO-oxidized cellulose nanofibers: oxidation mechanism, characterization, properties and applications, Int. J. Biol. Macromol. 259 (2024), https://doi.org/10.1016/j.ijbiomac.2023.129081.

[5] Q. Zheng, Y. Li, Y. Liang, T. Chen, F. Li, P. Zhu, Y. Tang, In-situ polymerization of pyrrole on cellulose nanofiber film: structure characterization and electrochemical properties, Ind. Crop. Prod. 222 (2024), https://doi.org/10.1016/j.indcrop.2024.120068.

[6] B. Bideau, J. Bras, S. Saini, C. Daneault, E. Loranger, Mechanical and antibacterial properties of a nanocellulose-polypyrrole multilayer composite, Mater. Sci. Eng. C 69 (2016) 977–984, https://doi.org/10.1016/j.msec.2016.08.005.

[7] B. Bideau, E. Loranger, C. Daneault, Comparison of three polypyrrole-cellulose nanocomposites synthesis, J. Adv. Nanomater. 1 (2) (2016), https://doi.org/10.22606/jan.2016.12007.

[8] G.F.V. Ayissi Eyebe, B. Bideau, É. Loranger, F. Domingue, TEMPO-oxidized cellulose nanofibre (TOCN)films and composites with PVOH as sensitive dielectrics for microwave humidity sensing, Sensors Actuators B Chem. 291 (2019) 385–393, https://doi.org/10.1016/j.snb.2019.04.070.

[9] G.A. Eyebe, B. Bideau, E. Loranger, N. Boubekeur, F. Domingue, Novel TOCNPVOH dielectric composite sheets with low ecological footprint for microwave humidity sensing, IEEE Sens. Lett. 2 (4) (2018), https://doi.org/10.1109/LSENS.2018.2869155.

[10] K. Halake, M. Birajdar, B.S. Kim, H. Bae, C.C. Lee, Y.J. Kim, S. Kim, H.J. Kim, S. Ahn, S.Y. An, J. Lee, Recent application developments of water-soluble synthetic polymers, J. Ind. Eng. Chem. 20 (6) (2014) 3913–3918. Korean Society of Industrial Engineering Chemistry, https://doi.org/10.1016/j.jiec.2014.01.006.

[11] J. Xie, X. Jin, H. Cheng, W. Chen, W. Yu, L. Wang, Molecular origin of the plasticizing effect difference of glycerol with other polyols on plasticizing polyvinyl alcohol (PVA) as elucidated by solid-state NMR, Ind. Crop. Prod. 220 (2024), https://doi.org/10.1016/j.indcrop.2024.119246.

[12] G. dePolo, M. Walton, K. Keune, K.R. Shull, After the paint has dried: a review of testing techniques for studying the mechanical properties of artists' paint, Herit. Sci. 9 (1) (2021), https://doi.org/10.1186/s40494-021-00529-w.

[13] B. Bideau, J. Bras, N. Adoui, E. Loranger, C. Daneault, Polypyrrole/nanocellulose composite for food preservation: barrier and antioxidant characterization, Food Packag. Shelf Life 12 (2017) 1–8, https://doi.org/10.1016/j.fpsl.2017.01.007.

[14] B. Bideau, E. Loranger, C. Daneault, Nanocellulose-polypyrrole-coated paperboard for food packaging application, Prog. Org. Coat. 123 (2018) 128–133, https://doi.org/10.1016/j.porgcoat.2018.07.003.

[15] E. Loranger, K. Jradi, C. Daneault, Nanocellulose production by ultrasound-assisted TEMPO oxidation of Kraft pulp on laboratory and pilot scales, in: IEEE International Ultrasonics Symposium, IUS, 2012, pp. 953–956, https://doi.org/10.1109/ULTSYM.2012.0238.

[16] E. Loranger, A.O. Piché, C. Daneault, Influence of high shear dispersion on the production of cellulose nanofibers by ultrasound-assisted tempo-oxidation of Kraft pulp, Nanomaterials 2 (3) (2012) 286–297, https://doi.org/10.3390/nano2030286.

[17] B. Bideau, L. Cherpozat, E. Loranger, C. Daneault, Conductive nanocomposites based on TEMPO-oxidized cellulose and poly(N-3-aminopropylpyrrole-co-pyrrole), Ind. Crop. Prod. 93 (2016) 136–141, https://doi.org/10.1016/j.indcrop.2016.06.003.

[18] A.M. Abdullah, S.B. Aziz, M.A. Brza, S.R. Saeed, B.A. Al-Asbahi, N.M. Sadiq, A.A. A. Ahmed, A.R. Murad, Glycerol as an efficient plasticizer to increase the DC conductivity and improve the ion transport parameters in biopolymer based electrolytes: XRD, FTIR and EIS studies, Arab. J. Chem. 15 (6) (2022), https://doi.org/10.1016/j.arabjc.2022.103791.

[19] G. Kovtun, D. Casas, T. Cuberes, Influence of glycerol on the surface morphology and crystallinity of polyvinyl alcohol films, Polymers 16 (17) (2024), https://doi.org/10.3390/polym16172421.

[20] J. Tathimongkon, A. Chaijaruwanich, W. Nakkiew, W. Wattanutchariya, Effects of PVA, PVP, and glycerol on the viscosity of a transdermal patch, Adv. Sci. Technol. 143 (2024) 27–34, https://doi.org/10.4028/p-ZZvd6u.

[21] S. Shi, X. Peng, T. Liu, Y.N. Chen, C. He, H. Wang, Facile preparation of hydrogen-bonded supramolecular polyvinyl alcohol-glycerol gels with excellent thermoplasticity and mechanical properties, Polymer 111 (2017) 168–176, https://doi.org/10.1016/j.polymer.2017.01.051.

[22] P.A. Sreekumar, M.A. Al-Harthi, S.K. De, Effect of glycerol on thermal and mechanical properties of polyvinyl alcohol/starch blends, J. Appl. Polym. Sci. 123 (1) (2012) 135–142, https://doi.org/10.1002/app.34465.

[23] Ishpal, A. Kaur, Spectroscopic investigations of ammonia gas sensing mechanism in polypyrrole nanotubes/nanorods, J. Appl. Phys. 113 (9) (2013), https://doi.org/10.1063/1.4793994.

[24] M. Šetka, R. Calavia, L. Vojkůvka, E. Llobet, J. Drbohlavová, S. Vallejos, Raman and XPS studies of ammonia sensitive polypyrrole nanorods and nanoparticles, Sci. Rep. 9 (1) (2019), https://doi.org/10.1038/s41598-019-44900-1.