

**Fabrication and Characterization of Bio-Based Hybrid Poly
(Vinyl Alcohol)/Carboxymethyl Cellulose Polymer Films,
Reinforced with Graphene Oxide Nanofiller for Packaging
Applications**

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CONCLUSIONS AND SCOPE OF FUTUTE WORK

7.1 Conclusions

The present research work aims to improve the properties of polyvinyl alcohol (PVA) films by adding graphene oxide (GO) nanofiller and explore the influence of different concentrations of GO in PVA/GO nanocomposite films. Using solution casting method, the films were fabricated and thoroughly characterized for their physicochemical, mechanical, morphological, thermal, barrier, antimicrobial, and biodegradation properties. Furthermore, the study introduced carboxymethyl cellulose (CMC), a natural biopolymer, to blend with PVA, to improve PVA/CMC film characteristics while accessing the sustainability aspects of the developed material, such as biodegradability and the use of renewable resources. The research also explored fabrication of nanofiber mats from PVA, PVA/CMC, and PVA/CMC/GO polymer solutions by optimizing key electrospinning parameters, including solution concentration, applied voltage, and flow rate, to achieve uniform, and bead-free nanofiber mats. This emphasizes the influence of incorporating CMC biopolymer and GO nanofiller on the solution properties of PVA blended matrix and the structural characteristics of the resulting PVA/CMC and PVA/CMC/GO nanofiber mats. Thus, the study demonstrated a significant potential of developed nanocomposites for its use in advanced eco-friendly packaging applications. Some of the important findings from the present research work are as follows:

(i) Conclusion on PVA/GO nanocomposite films

- The tensile strength (TS) of PVA films has improved from 1.40 ± 0.02 MPa to 1.99 ± 0.02 MPa with the incorporation of GO from 0.1 wt.% to 0.7 wt. %. Meanwhile, the % elongation at break (%EAB) of the nanocomposite (NC) films rose from $201.02 \pm 5.10\%$ to $268.64 \pm 5.83\%$ with GO concentrations between 0.1 wt.% and 0.3 wt.%, but showed a reduction in %EAB in higher concentrations of GO.
- The scanning electron microscope (SEM) micrographs of PVA/GO nanocomposite film showed uniform dispersion of GO with minimum surface defect and less

nanofiller agglomeration in the film.

- The water vapor permeability (WVP) of hybrid PVA/GO film was reduced from $8.06 \pm 0.21 \times 10^{-5} \text{ g/m}\cdot\text{hr}\cdot\text{Pa}$ to $6.88 \pm 0.04 \times 10^{-5} \text{ g/m}\cdot\text{hr}\cdot\text{Pa}$ at 0.3 wt.% of GO concentration, showing a 18.01% reduction compared to PVA film. However, at higher concentrations of GO, the WVP was increased due to nanofiller agglomeration, thus indicating 0.3 wt.% of GO as the optimal concentration for improved barrier properties. Moreover, the moisture retention capacity (MRC) of the developed PVA/GO hybrid films ranged from 79.33% to 82.06%, falling within the recommended range for food packaging (75% to 95%), indicating its potential to retain moisture and preserve food quality.
- The UV-Vis spectra showed that PVA/GO films had strong UV light absorption, around 300 nm wavelength, attributed to C=O transitions. Moreover, the opacity of NC films increased significantly from 0.30 to 3.21 ($P \leq 0.05$), rising by 181.57% to 967.10% as GO concentration increased from 0.1 wt.% to 0.7 wt.%. The improvement indicates that addition of GO nanofiller greatly enhances the light barrier properties of PVA, overcoming the barrier limitations and supporting its potential for packaging applications.
- Differential scanning calorimetry (DSC) analysis showed an increase in the glass transition temperature from 72.03 °C to 95.62 °C and enthalpy of 50.28 J/g at a 0.3 wt.% GO concentration. Additionally, thermogravimetric analysis (TGA) demonstrated reduced mass degradation of the PVA/GO films at higher temperatures in comparison to the pure PVA film.
- FTIR spectra confirmed that incorporation of GO leads to strong H-bond within the PVA polymer blend that significantly enhances the amorphousness and thermal stability of the nanocomposite films.
- Antimicrobial analysis showed PVA/GO films had excellent antibacterial properties against *S. aureus* bacteria compared to neat PVA film. However, there was no antibacterial activity observed for neat PVA and PVA/GO films for *E. coli* bacteria.
- The soil burial test revealed that PVA/GO films had 46.5% lower degradation rate than neat PVA films after 20 days of soil burial. Additionally, the study revealed that incorporating GO alters the degradation behavior of the PVA polymer, potentially enhancing its durability and stability for specific applications
- Microbial degradation tests using *B. subtilis* and *P. putida* strains showed efficient breakdown of the developed PVA and PVA/GO films. The growth of these

microorganisms indicated that the bioplastic served as a carbon source, thus facilitating its degradation.

(ii) Conclusion on PVA/CMC polymer composite films

- Among the various the developed PVA/CMC hybrid films, film containing 0.5% CMC demonstrated highest TS and improved flexibility compared to other CMC concentrations.
- The addition of CMC led to improvements in WVP and MRC also, with a notable 38.73% enhancement in WVP and an MRC of 78.37% at the 0.5% CMC concentration compared to pure PVA films
- The incorporation of CMC into PVA films significantly altered the color parameter, with the L^* value decreasing from 88.38 to 77.26, and the b^* value increasing from 2.04 to 3.94, indicating a shift toward yellowish tint as CMC concentration was increased. Moreover, the opacity of the hybrid PVA/CMC films was also improved from 218.83% to 371.86% as CMC concentration increased from 0.5 wt.% to 1.5 wt.%, compared to pure PVA films. Thus, the enhancements in color and opacity parameters demonstrate the potential of hybrid PVA/CMC films for packaging applications, offering better light barrier properties than single-polymer PVA films.
- TGA showed a significant enhancement in the decomposition temperature of the hybrid PVA/CMC films, resulting in reduced mass loss compared to the PVA film. This improvement suggests that CMC integration enhances the thermal stability of the hybrid films, making it more suitable for high-temperature applications.
- FTIR spectra confirmed the interaction between CMC and PVA polymers, as indicated by narrowing and shifting the -OH absorption band to a lower wavenumber from 3431 cm^{-1} to 3425 cm^{-1} , suggesting intramolecular forces between carboxylate and hydroxyl groups. This indicates that the addition of CMC to the PVA matrix forms strong interactions, enhancing the amorphous structure and thermal stability of the hybrid films.
- The developed PVA and PVA/CMC film did not exhibit antibacterial properties, as evidenced by the absence of inhibition zones against *S. aureus* and *E. coli* bacteria.
- The soil burial test revealed that PVA/CMC films exhibited a 40% higher degradation rate than PVA films, with weight loss increasing from 10.25% for PVA and 12.37%–14.26% for PVA/CMC after 30 days of soil burial. The biodegradation process was

accelerated by the presence of CMC, enhancing the film's susceptibility to microbial attack. These results emphasize the potential of PVA/CMC bioplastics as more biodegradable alternatives to conventional plastics.

- The microbial biodegradability test against *P. putida* and *B. subtilis* bacteria strains demonstrated that PVA, PVA/GO and PVA/CMC, undergo microbial degradation, unlike synthetic plastics, which showed no growth. These findings highlight the potential of hybrid PVA/GO and PVA/CMC bioplastics for environmentally friendly applications, particularly in packaging and biomedical fields.

(iii) Conclusion on PVA/CMC/GO nanofiber mats

- The addition of 0.5 wt.% CMC significantly enhanced solution conductivity from 24.91×10^{-3} S/m to 102.58×10^{-3} S/m, resulting in a reduction of nanofiber diameter from 116.27 ± 37.64 nm to 90.51 ± 17.56 nm. Incorporating GO from 0.1 wt.% to 0.3 wt.% further improved conductivity and increased viscosity from 85 to 93 mPa.s, leading to larger fiber diameters between 134.81 ± 31.10 nm and 169.22 ± 73.54 nm.
- Morphological analysis showed that incorporating CMC resulted in the formation of smooth, bead-free nanofiber with an average diameter of 90.51 ± 17.56 nm, showcasing 28.46% reduction compared to PVA nanofiber (116.27 ± 37.64 nm). Furthermore, incorporating 0.1 wt.% to 0.3 wt.% of GO into the PVA/CMC matrix also showed minimal bead formation and nanofiller agglomeration, indicating homogeneous GO dispersion, with fiber diameters increasing from 134.81 ± 31.10 nm to 169.22 ± 73.54 nm.
- The dispersion of GO within the PVA/CMC matrix improved the structural integrity, enhancing the mechanical strength and functionality of the nanofiber mats, as confirmed by both FESEM and TEM images.
- As evidenced by rheological analysis, the PVA based nanofiber solutions revealed distinct viscoelastic characteristics, where PVA and PVA/CMC solutions exhibited shear thickening behavior, and PVA/CMC/GO solutions showed shear thinning behavior. Moreover, addition of GO in PVA/CMC matrix resulted in a significant increase in storage modulus and shear stress compared to PVA and PVA/CMC polymer, thus reflecting homogeneous mixing and strong molecular interactions of GO nanofiller with PVA/CMC matrix.
- The TS of PVA-based nanofiber mats has improved with the addition of CMC and GO. Addition of 0.5 wt.% of CMC led to an 18.696% increase in TS compared to

pure PVA mats, while incorporating 0.1 wt.% to 0.3 wt.% of GO further enhanced the TS, ranging from 25.59% to 46.41%.

- The presence of oxygen containing functional group in GO, and carboxyl, and hydroxyl functional groups in CMC, and PVA increases the wettability of PVA/CMC and PVA/CMC/GO nanofiber mats, as indicated by reduced water contact angles from 51.32° to 45.92°. The oxygen-rich structure of GO enhances the barrier properties of hybrid nanofiber mats, resulting in reduced WVP from 1.049 g/m.h. Pa to 0.980 g/m.h. Pa and MRC from 95.68% to 90.854%. Moreover, the MRC of the developed nanofiber mats falls within the recommended range (75%-95%) for food packaging, indicating its ability to effectively retain moisture and prevent its loss.
- The thermal characteristics showed improvement in the decomposition temperature of PVA/CMC/GO nanofiber mats, accompanied by minimal mass loss compared to PVA and PVA/CMC mats. Moreover, within 200 °C, the mass loss of GO-based nanofiber mats was approximately 5% to 10% lower compared to PVA and PVA/CMC mats, thus showcasing the potential of GO based nanofiber mats in thermal packaging applications.
- Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy revealed interactions between the hydroxyl groups of PVA and carboxylate groups of CMCs, with increased intensity in -OH and C-H absorption bands. Addition of GO into the hybrid polymer solution resulted in the dissociation of H-bonds in the OH group of the PVA/CMC matrix, forming additional H-bonds with the functional groups of GO containing oxygen. This is the characteristic indicating that the incorporation of GO fosters strong interactions, thereby improving the material's amorphous nature and thermal stability.

In summary, the successful integration of GO into PVA films offers a promising avenue for industrial applications, especially in the packaging sector, where the combination of enhanced physiochemical, mechanical, barrier, and antibacterial and biodegradability properties provide significant benefits. Moreover, blending PVA with natural biopolymer CMC showed enhanced material characteristics and enhanced biodegradation, making it more environmentally friendly compared to conventional plastics. At last, the drive to investigate the use of advanced electrospinning techniques for developing novel PVA/CMC/GO nanofiber mats highlights its enhanced structural integrity and functional performance. This method offers precise control over the structural and morphological

characteristics of the nanofibers, which is essential for optimizing their effectiveness in packaging applications.

Finally, the research aspires to contribute development, characterization and potential perspective of multifunctional hybrid materials with improved durability, functionality, and environmental sustainability by systematically examining the impact of GO nanofiller, and CMC biopolymer. Thus, the vision and mission of the research provides a sustainable alternative to conventional plastic packaging materials, thereby reducing environmental harm and fostering innovation in the domain of bio-based nanocomposites.

7.2. Scope of future work

The present research focuses on enhancing the properties of PVA by reinforcing it with GO nanofillers and blending it with the natural biopolymer CMC. The aim is to address the inherent limitations of PVA by developing nanocomposite materials with superior mechanical, thermal, barrier, and antimicrobial properties, while simultaneously improving their sustainability through biodegradability and the use of bio-based resources. Furthermore, the fabrication of novel PVA/CMC/GO nanofiber mats through electrospinning was explored, highlighting the impact of CMC and GO on solution behaviour and the structural characteristics of nanofiber mats, broadening the scope for packaging material. The research conducted in this thesis and its findings highlight several potential areas for future investigation, are outlined below:

- Incorporating additional bioactive agents into the PVA/CMC/GO polymer system to develop smart packaging (pH, temperature, and strain sensor) or wound healing applications.
- Investigating the degradation behavior under various environmental conditions (e.g., marine, soil, compost) to assess environmental impact comprehensively.
- Exploring the industrial-scale production of the developed material while maintaining material performance and economic feasibility, transition from laboratory research to practical applications.
- Development of cellulose-based metal matrix composite membranes for gas separation which includes enhanced selectivity, permeability, and stability for specific industrial and bio-medical applications.