CHAPTER: II

LITERATURE REVIEW

This chapter explores research conducted in the field of graphene oxide-based polymer nanocomposites (NC) and its primary goal is to identify existing research gaps. Moreover, the chapter concludes by outlining the scope of the research work presented in this thesis.

2.1 Literature survey on mechanical properties of GO based polymer nanocomposites

The mechanical properties of polymer NC films are important as it determine material's functionality, longevity, and suitability for diverse applications. It is mainly influenced by nanofiller content, geometry and its dispersion within the polymer matrix. The enhancement of these properties is due to the strong interaction between nanofillers and the polymer at their interfaces, along with tailored aspect ratio of dispersed nanofillers [1]. As reported, at 2.0 wt.% GO in glycerol-plasticized starch/GO NC films, the tensile strength (TS) increased from 4.56 MPa to 13.79 MPa, Young's modulus (YM) from 0.11 GPa to 1.05 GPa, while elongation at break (EAB) decreased from 36.06% to 12.11% [2]. Adding 0.3 wt.% and 2.0 wt.% GO in PVA matrix enhanced the TS by 49% and failure strain by 13%–22%, while 2.0 wt.% GO led to a remarkable 144% increase in elastic modulus [3]. Similarly, an enhancement of 62% and 76% in TS and YM was observed for PVA/GO NC film by incorporating 0.7 wt.% GO compared to pure PVA film [4]. PVA/GO NC films fabricated via vacuum filtration with 3 wt.% GO film showed a 128% higher YM and 70% greater tensile yield strength than pure PVA [5]. Adding 0.5 wt.% and 1 wt.% of GO nanoparticles reduces the stress at break of PVA, while incorporating 5 wt.% GO increases it by 25%, from 64 to 80 MPa [6]. According to Halpin-Tsai micromechanical simulations, PVA NC exhibited progressive enhancements in stiffness and elastic modulus when incorporating GO nanofillers with increasing aspect ratios corresponding to lateral dimensions of 0.5 μm, 1.5 μm, and 3 μm [7]. The addition of graphene nanoplatelets (GNP) enhanced the YM and storage modulus of epoxy NC, particularly in the rubbery state, but reduced TS and toughness due to GNP aggregation [8]. The mechanical properties of Gr-based polymer NC are significantly influenced by the reinforcement efficiency, which depends on the filler aspect ratio (α), filler modulus (E_f), filler weight fraction (W_f), and interfacial adhesion with the polymer matrix [9]. With optimal filler-polymer interactions, the TS increased from 42.3 MPa to 50.8 MPa, while YM showed a significant rise from 1477 MPa to 2123 MPa with the addition of 0.04 wt.% GO [10]. Adding 0.5 wt.% of GO in glycerol/nanocellulose/GO film significantly increase the TS from 18.4 MPa to 25 MPa, highlighting the synergistic effect between GO and the biopolymer matrix [11]. In starch/gelatin/GO film, the TS increased from 57.97 MPa to 76.09 MPa, and YM rose from 20.59 MPa to 35.91 MPa, while the EAB decreased from 6.6% to 3.13% at 0.85 wt.% GO concentration [12]. Addition of GO enhanced the TS and EAB of NC films, increasing from 1.40 MPa to 1.51 MPa and from 201.02% to 268.64%, respectively, at a GO concentration from 0.1 wt.% to 0.3 wt.%. However, higher GO concentrations led to a decline in mechanical properties [13]. As reported nanofiber mat developed from PVA/CMC/GO via electrospinning process showed 5.81% increase in TS compared to PVA/CMC nanofibers, while the EAB rose from 6.67% to 42.02% [14]. As reported, agglomeration of nanofillers was observed, particularly at higher nanofiller concentrations, in the two-phase nanocomposites, which subsequently decreases the overall efficiency of the system [15]. Additionally, to achieve notable improvements in the overall effectiveness of nanofiller, it is essential to develop stronger interfacial bonding with uniform dispersion throughout the polymer matrix. Thus, the advancement of polymeric NC incorporating GO offers new opportunities for the food packaging industry with improved properties. This innovation enhances packaging by making it lighter and more durable, expanding its wide range of applications.

2.2 Literature survey on thermal and barrier properties of GO based polymer nanocomposites

Understanding the thermal properties of polymers is crucial for analysing the physical and chemical changes that occur in NC structures as temperature varies. Numerous researchers have utilized GO in the fabrication of graphene NC to investigate thermal properties [16]. Key parameters like glass transition temperature (T_g), melting temperature (T_m) melting enthalpy (ΔH), onset temperature (beginning of the melting event), and end-point temperature (completion of melting) are analysed in differential scanning calorimetry

(DSC) analysis. In contrast, the decomposition temperature, thermal mass loss of material is typically assessed using thermogravimetric analysis (TGA) [17]. With the addition of GO in chitosan/GO nanocomposite film, there is an increase in DSC endotherm peak indicating stronger polymer interactions due to enhanced chitosan hydroxyl bonding [18]. For the CMC/GO nanocomposite film, 7 wt.% GO concentration elevates the T_g of the CMC matrix from 71.68 °C, increasing it by up to 128 °C [19]. Adding 0.1 wt.% to 0.3 wt.% of GO nanofiller into the PVA/CMC/GO polymer matrix significantly enhanced the thermal stability of the nanofiber mats, reducing mass degradation by approximately 10% compared to PVA and PVA/CMC nanofiber mats [14]. DSC thermogram showed that the T_m increased from 220.04 °C to 275.54 °C at 0.3 wt.% of GO, due to the thermal insulating properties of the uniformly distributed graphene fillers within the polymer chain [13]. Comparable studies have shown that adding 3 wt.% GO to PVA improves the T_m and increases the thermal degradation temperature of the PVA/GO film by 8%, raising it from 238 °C to 257 °C compared to PVA film [6]. Addition of GO nanofiller altered the onset decomposition temperatures in different stages of mass loss of PVA film, indicating strong interfacial H bonding between PVA and GO [20]. DSC analysis showed notable increases in melting, T_g, and crystallization temperatures in the NCs due to nucleating effect of GO, with thermal stability progressively improving as GO content was increased [21]. A study demonstrated that adding 5 wt.% GO to PP significantly enhanced its thermal stability, and raising onset degradation temperature by 150 °C [22]. Similarly, the thermal stability of polymethylmethacrylate/polycaprolactone polymer blends improved by 50 °C with the addition of 0.6 wt.% of GO [23]. Thus, integrating graphene-based nanofillers into polymer matrix enhances the thermal stability, reduces dehydration processes, and mass degradation of polmer during calcination. This indicates that GO improves the polymer's ability to withstand high temperatures by increasing its onset temperature and heat resistance.

The barrier properties of polymer films are crucial for maintaining the quality and extending the shelf life of packaged food by preventing moisture migration from the films over time. Biodegradable polymers exhibit a diverse range of permeability rates for small molecules like oxygen and water vapor, varying from high to low permeability [24]. The hydrophilicity of GO, resulting from its oxygenated functional groups, led to a sharp decline in water vapor permeability at the lowest filler loading of 5 wt.% in the polystyrene matrix [25]. The WVP of GO/PVA NCs significantly decreases, from 3.0×10^{-12} g /(cm.s.Pa) to 0.66×10^{-12} g /(cm.s.Pa) upon the addition of 0.04 wt.% GO, resulting in a

78% reduction compared to neat PVA [10]. Addition of 0.3 wt.% GO led to a notable decrease in WVP by 5.22% as compared to PVA/CMC nanofiber mats. This is attributed to the formation of H-bonds between GO and the PVA/CMC polymer chains thus limiting the availability of OH groups and restricts the mobility of the polymer chains [14]. Study showed a significant reduction in WVP from 11.15% to 18.01% at 0.1 wt.% to 0.5 wt.% of GO in PVA/GO films, but further increasing GO from 0.5% to 0.7% raised the WVP of NC film by 2.84%. This shows that exceeding the optimal GO concentration causes nanofiller agglomeration, leading to increased permeability [13]. The high aspect ratio of GO sheets and their self-organization within the polymer matrix effectively hindered the diffusion of water molecules, which significantly improves the WVP at low nanofiller concentrations [26]. Experiment results revealed that incorporating 0.5 vol% graphene into the PVA film significantly reduced the water vapor transmission rate from 19 g/m^2/day to 1.22 g/m^2/day and the oxygen transmission rate from 10 cm/m^2/day/bar to 0.5 cm/m^2/day/bar [27]. Incorporation of GO-ODA (modified by chemically grafting octadecylamine) significantly improves water barrier properties of regenerated cellulose film, leading to 20% reduction WVP from 1.71×10^{-12} to 1.35×10^{-12} g cm^{-1} s^{-1} Pa^{-1} at 2 wt.% GO-ODA loading [28]. As outlined in another research, pure starch/gelatin film lacked water vapor barrier properties, whereas crosslinked NC exhibited improved permeability at 0.85 wt.% of GO [12]. Thus, exceeding the optimal concentration of nanofiller results in agglomeration, which in turn increases permeability. Therefore, it is essential to maintain the optimal nanofiller concentration in the polymer matrix to ensure uniform dispersion, leading to improved permeability required for packaging applications.

2.3 Literature survey on antimicrobial and degradation properties of GO based polymer nanocomposite

The antimicrobial property of packing material is an important feature that need to be considered in order to minimise the growth of microorganisms in food. According to a research report, PVA/GO/Ag nanocomposites demonstrated strong antibacterial activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria, as indicated by prominent inhibition zones, whereas pure PVA showed no antibacterial effect [29]. GO based Poly(3-Hydroxybutyrate-co-3-Hydroxyhexanoate) NCs exhibit strong biocidal effects against both Gram-positive *B. subtilis* and *S. aureus* and Gram-negative *B. cepacia* and *E. coli* bacterias, with antimicrobial activity increasing with GO concentration

[30]. At 1 vol.% oregano oil (OEA) concentration, PVA/OEA/GO NC films exhibited effective antibacterial activity on *L. monocytogenes* and *E. coli* making it highly promising for antimicrobial packaging applications [31]. An early study on GO's antibacterial properties found that the sharp edges of GO nanowalls caused membrane damage of bacteria, inactivating *S. aureus* and *E. coli*. A systematic evaluation against *E. coli* compared the bactericidal effectiveness of graphite (Gt), graphite oxide (GtO), GO, and rGO, revealing GO dispersion as the most effective, followed by rGO, Gt, and GtO [32]. GO effectively hindered the growth of bacterial and fungal pathogens, eliminating approximately 90% of the bacteria and preventing the germination of 80% of macroconidia [33]. GO-ZnO nanoparticle-loaded NC films, prepared by blending with PLA via the solution-blending method, demonstrated strong UV resistance and antimicrobial activity even at low GO-ZnO concentrations, as confirmed by UV-visible spectroscopy and antibacterial tests [34]. Addition of GO/Ag hybrids as nanofillers in a PLA matrix using in situ polymerization and direct mechanical blending, shows that antibacterial efficiency increased from 0 to 99% with at 2 wt.% loading. With in-situ polymerization yielding, superior results were found due to enhanced Ag-cell wall interactions, improved Ag distribution on GO surfaces, and better dispersibility of the hybrids [35]. A recent study showed that neat PVA film lacked antibacterial properties, showing no inhibition against gram-positive *S. aureus* and gram-negative *E. coli* bacteria, while PVA/GO films were ineffective against *E. coli* but exhibited significant antibacterial activity against *S. aureus* in disk diffusion method [13].

Plastics and microplastics, also called polymers and polymeric materials, are widely studied today due to its versatile applications. Their biodegradation is increasingly studied due to their resistance to decomposition, large-scale disposal, and accumulation in ecosystems, but progress in understanding biodegradation processes remains limited [36]. The biodegradability of polymer blends and polymer NCs can be assessed using various methods, including enzymatic, microbiological, and soil burial techniques [37]. The degradation process is influenced by factors such as chemical structure, molecular weight, microbial presence, and environmental conditions [38]. Some polymers degrade faster, such as natural polymers like cellulose and starch, along with biodegradable petroleum-based polymers like polyglycolide and polycaprolactone etc, while, conventional petroleum-based plastics like PE, PS, and PVC degrade at a much slower rate [39]. Various microorganisms are responsible for biodegradation thrive under specific optimal conditions. The process involves two strategies: enzyme-catalyzed hydrolysis and nonenzymatic hydrolysis. As reported, with the addition of CMC, the degradation rate of the PVA/CMC film was increased approximately to 40% on the 30th day of soil burial [40]. Increasing the starch content in PVA/starch films from 0 to 20 wt.% improved the biodegradation rate by 32.45% as evidenced by soil burial analysis over 45 days [41]. In another soil degradation report of blended starch-PVA (7:3 ratio) crosslinked with 10% formaldehyde, 50% weight loss was seen after 50 days of exposure [42]. Similarly, after 20 days of soil burial, PVA/GO films showed a 46.5% lower degradation rate than neat PVA. However, effective microorganism degradation was observed in *Bacillus subtilis* and *Pseudomonas putida* bacteria strains [13]. As reported starch/gelatin film showed the highest degradation, losing 50% of its weight in 6 weeks due to its natural biodegradability. In contrast, crosslinked NC showed 20% less degradation than pure films, as GO nanosheets enhanced stability and slowed degradation [12].

2.4 Literature survey on electrospinning and nanofiber

Technological advancements, product innovation, and system design have significantly revolutionized human lifestyles. However, continuous progress is essential for sustaining a growing society. Nanotechnology holds great promise in food packaging, particularly through the application of nanofibers derived from synthetic polymers, biopolymers, and their composites [43]. Numerous methods for fabricating nanofibers have been developed, including techniques such as splitting bicomponent fibers, melt blowing, physical drawing, dry-wet spinning, phase separation, self-assembly, centrifugal spinning, and electrospinning [44]. Electrospinning (ES) is one of the most versatile, and efficient technologies when compared to template polymerization and melt spraying. Additionally, it is capable of producing continuous nanofibers on an industrial scale [45]. Electrospinning offers several advantages, including a broad selection of raw materials, ultra-fine fiber diameters, and high porosity. ES has successfully produced over 100 types of polymer nanofibers and blends, with diameters varying from a few nanometres to several hundred microns [46]. The ES apparatus primarily comprises four key components: a high-voltage power supply, a syringe pump with nozzles, a spinneret, and a conductive collector [47]. During operation, a polymer solution is extruded through the spinneret, forming a suspended droplet due to surface tension. When high voltage is applied, electrostatic forces charge the polymer droplet, creating repulsion that overcomes surface tension and deforms it into a Taylor cone (a critical precursor to jet formation) which undergoes stretching and thinning of polymer solution as it travels toward the collector, solidifying into ultrafine fibers upon solvent evaporation or cooling (for melts) [48,49]. Additionally, achieving uniform and ultrafine nanofibers requires careful optimization of factors such as type of polymer, polymer solution viscosity, concentration, electrical conductivity, surface tension, type of solvent, and the distance between the spinneret and collector is necessary [50]. As the concentration and viscosity of the polymer solution increase, the entanglement of polymer chains also rises, while surface tension decreases. This leads to the formation of an increasing number of fibers, ultimately resulting in uniform and smooth nanofibers without bead defects [51]. However, at optimal concentration, fiber formation is most effective and, if the solution concentration exceeds the ideal level, it may cause clogging of the spinneret, leading to the production of coarse and irregular ribbon-like fibers [52]. The applied voltage plays a crucial role in determining the morphology and diameter of nanofibers. If the voltage is either too high or too low, bead formation may occur. As the applied voltage increases, the diameter of the nanofibers decreases due to the stronger electrostatic forces, which cause the droplets to stretch further [53]. As reported in an article, the diameter of nanofibers initially decreased and then increased as the applied voltage increased, and they explained this phenomenon by mechanical analysis [54]. Additionally, other researchers reported that higher voltage levels led to greater inconsistencies in nanofiber diameter distribution. The influence of applied voltage on nanofiber diameter can also be affected by factors such as the polymer solution concentration and the distance between the jet device and the collection device [55]. At low solution viscosity, the flow rate has minimal impact on the diameter of nanofibers. However, as the applied voltage is increased, the influence of flow rate becomes more pronounced which significantly alters the nanofiber diameter [56]. A successful fabrication of PLA/ZnO nanofiber mats using the electrospinning technique was performed where optimal morphology, mechanical properties, thermal stability, and antimicrobial activity was observed at 0.5 wt.% of ZnO concentration [57]. As reported Chitosan (CS)/PVA/Antioxidant peptide (AOP) electrospun nanofiber mats exhibit excellent miscibility at the nanoscale, forming uniform and bead-free structure, making it a promising material for biodegradable bioactive packaging [58]. Nanofibers fabricated from PVA, polyvinylpyrrolidone (PVP), and CMC using electrospinning displayed a uniform structure and demonstrated enhanced mechanical properties, with TS exceeding 10 MPa, as well as improved hydrophobicity resulting from improved cross-linking interactions among polymers [59]. Study highlights that recycled PET/GO nanofibers with low GO concentrations ensure well-dispersion of nanosheets, while higher loadings lead to agglomeration. Additionally, increasing GO content results in thicker fibers, likely due to viscosity changes and potential aggregation [60]. As outlined, nanofiber mats developed by grafting N-halamine molecules onto PVA was applied as food pads to enhance food shelf life [61]. Likewise, core–shell nanofibers produced through emulsion electrospinning of gelatin-stabilized corn oil-in-water emulsions effectively encapsulated corn oil and demonstrated exceptional thermal and storage stability, ideal for heat-sensitive and bioactive compounds [62]. The TS of PVA/CMC/GO nanofiber mats increased by 25.59% to 46.41% with the addition of 0.1 wt.% to 0.3 wt.% GO compared to PVA/CMC mats, attributed to enhanced interactions between the hydroxyl (-OH) groups of PVA and the carboxyl (-COOH) groups of CMCs [14]. A review highlighted the application of PVA based electrospun nanofiber mats in drug delivery systems, emphasizing the effectiveness of electrospinning across diverse biomedical fields. Ongoing research is further expected to expand in its use, due to its versatility, affordability, and accessibility [63]. Similarly, a review focused on the growing demand for biodegradable food packaging has led to the development of PVA-based electrospun nanofibrous films, which offer enhanced properties through blends with biopolymers, functional materials, and nanoparticles [64].

Thus, ES technique has achieved significant progress and innovations in food packaging applications. As, it offers limitless potential for creating high-performance food packaging systems that enhance the effectiveness of bioactive compounds while reducing adverse effects. However, the choice of biopolymers and active compounds plays a crucial role in ensuring suitability for specific food preservation applications.

Based on the review of existing literature, the following research gaps have been identified for the present thesis research work.

I. There is a lack of systematic analysis on how varying concentrations of GO nanofiller influence the overall performance of PVA/GO nanocomposite films, particularly in packaging applications.

II. Incorporation of natural biopolymers CMC with synthetic polymer PVA remains insufficiently investigated in packaging applications, especially for the attainment of both performance and environmental sustainability.

III. Limited studies are present on the biodegradation characteristics and long-term effects on the environment, especially concerning the use of nanofillers and biopolymers.

IV. Limited studies on electrospinning for fabricating nanofiber mats from sustainable biopolymer-based PVA/CMC blends incorporating GO nanofillers remains largely unexplored.

V. Lack of studies on how polymer solution properties and electrospinning process parameters affect the structure, morphology, and functional performance of nanofiber mats.

VI. Comprehensive, application-oriented development and characterization of novel PVA/CMC/GO based nanofiber mats for sustainable packaging and biomedical uses are still limited.

Based on stated research gaps, the following key objectives have been outlined for the proposed research.

Objective 1. Development, characterization and potential perspective of poly(vinyl alcohol)/graphene oxide nanocomposite films.

Objective 2. Development and characterization of biodegradable poly(vinyl alcohol)/carboxymethyl cellulose composite films

Objective 3. Synergistic effect of graphene oxide on the properties of poly(vinyl alcohol)/carboxymethyl cellulose electrospun nanofiber mats

2.5 Scope of the present study

The scope of this research is to utilize GO nanofiller as a reinforcing agent in PVA polymer-based composites to address the limitations of polymer matrices and to develop advanced materials with enhanced properties for packaging applications. Additionally, the study is also focused on incorporating natural biopolymer CMC for blending, offering a promising approach to improve material characteristics while accessing the sustainability aspects of the developed material, considering factors such as the use of natural of the bio-based polymers, biodegradability, and reduced environmental impact compared to conventional packaging materials.

Thus, the initial stage of the research work was focused on investigating the potential use of PVA/GO nanocomposite films to overcome the limitation of PVA film. This was accomplished by fabricating PVA/GO nanocomposite films by solution casting method. Different concentrations of GO were incorporated in PVA matrix to analyse the impact of GO concentration in PVA/GO films. This includes evaluating their physicochemical, mechanical, morphological, thermal, barrier, antimicrobial, and biodegradation properties.

The following section of this research focuses on blending PVA polymer with natural biopolymer CMC to develop hybrid PVA/CMC polymeric film. The hybrid films were fabricated using the solution casting method by introducing different concentrations of

CMC into the PVA matrix. The resulting films were then characterized to assess the impact of CMC on the physicochemical, mechanical, morphological, thermal, barrier, antimicrobial, and biodegradation properties of PVA-based films. This study aims to enhance the durability, functionality, and environmental benefits of hybrid films for sustainable packaging applications.

Finally, the research is also focused on the development of novel PVA/CMC/GO nanocomposite films using advanced electrospinning technique, one of the most versatile and efficient methods for producing nanofiber mats. In this process, nanofiber mats were fabricated from polymer solutions of PVA, PVA/CMC, and PVA/CMC/GO by optimizing key electrospinning parameters, including solution concentration, applied voltage, and flow rate, to achieve uniform, bead-free nanofiber mats. The study emphasizes the influence of incorporating CMC biopolymer and GO nanofiller on the solution properties and the structural characteristics of the resulting PVA/CMC and PVA/CMC/GO nanofiber mats. Through these investigations, the research aims to contribute the effective use of CMC and GO additives in PVA matrix in producing nanofiber mats that exhibit enhanced physiochemical, mechanical, thermal, and barrier properties suitable for packaging applications.

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