DESIGN AND FABRICATION OF POLYESTER-BASED BIO-BASED ADHESIVE REINFORCED BY CHITIN NANOWHISKERS

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ABSTRACT

This thesis investigates the potential of chitin nanowhiskers (CNWs), a renewable bio-based nanomaterial, to enhance a commercial polyester (PE) resin (Bondo® Fibreglass Resin). Compared to epoxy systems, which are associated with sensitization, respiratory, and dermatological hazards during processing, polyester resins present comparatively fewer health risks, making them a suitable platform for sustainable adhesive development. The influence of CNW content, processing conditions, and dispersion methods was studied with respect to mechanical strength, adhesion, and thermal stability. Low CNW loadings (0.25–0.50 wt.%) improved strength, ductility, and heat resistance, while higher amounts led to clustering and reduced performance. Moderate heating improved dispersion and properties, whereas prolonged low-temperature processing weakened them. Among dispersion approaches, ethanol offered the most balanced improvements, while dry mixing gave stability but weaker interfacial bonding. Overall, the findings demonstrate that optimizing CNW incorporation can significantly improve polyester resin adhesives, supporting the development of stronger, tougher, and more sustainable alternatives to conventional materials.

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Abbreviations	**Description**
CNW	Chitin nanowhiskers
NP	Nanoparticle
PE	Polyester
PR	Polyester resin
UPR	Unsaturated polyester resin
SPR	Saturated polyester resin
MEK	Methyl ethyl ketone
MEKP	Methyl ethyl ketone peroxide
FTIR	Fourier transform infrared
ATR	Attenuated total reflectance
SEM	Scanning electron microscopy
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
T_g	Glass transition temperature

CHAPTER 1 – INTRODUCTION

1.1 Background and Motivation

Adhesives play an important role in a wide spectrum of industrial and commercial applications by providing reliable bonding of substrates, enabling products and systems to achieve their intended functions and performance. They are omnipresent in modern manufacturing processes, being utilized across almost every industry. The global adhesive market was valued at approximately USD $68.88 billion in 2024, with projections indicating growth to USD $87.04 billion by 2028 [1]. Adhesives can be classified in different ways, with a common method based on structure, including categories such as hot melt adhesives, reactive hot melt adhesives, thermosetting adhesives, pressure-sensitive adhesives, or contact adhesives [2]. Due to their extensive use in demanding sectors such as aerospace and automotive, adhesives are often required to possess exceptional thermomechanical properties to ensure durability and maintain optimal performance under extreme operating conditions. In addition to industrial applications, adhesives are integral to many consumer products, including footwear, furniture, containers, and non-woven fabrics [3]. Among all classes of adhesives, epoxy resins are the most widely used type, with a global market value estimated at USD $12.84 billion in 2022 [4]. Epoxy adhesives have various benefits, including outstanding mechanical properties, excellent adhesion to fibres in composites, superior chemical resistance, high hydrophobicity, and low shrinkage during curing [5-6]. Although cured epoxy was found to have a maximum yield tensile strength of 2900 MPa, a maximum compressive strength of 1690 MPa [7] and was considered an industry standard adhesive, epoxy resins or cured epoxy in the form of dust pose great health risks, which include irritation, skin allergies, and asthma [8]. Sanding and machining epoxy are common operations in

the manufacturing of related products. Inhalation of uncured epoxy vapours or sanded epoxy dust may have led to accumulation of harmful chemicals or particles in the mucosal lining of the respiratory system, posing health hazards in manufacturing facilities [8-9].

1.1.1 Polyester adhesives/resins

In various industrial and commercial applications, polyester (PE) adhesives, also commonly known as polyester resins (PRs), are widely used in adhesive-related applications due to their desirable properties, such as reasonable mechanical properties, good chemical resistance, and high curing efficiency. PRs are typically classified into two categories: saturated polyester resins (SPRs) and unsaturated polyester resins (UPRs). UPRs are formed in a condensation reaction (i.e., esterification) between unsaturated dicarboxylic acids (or anhydrides) and diols [10]. UPRs contain double bonds on the main polymer chain that require cross-linkers, typically styrene, to complete the polymerization process. Depending on the primary saturated acid within the PRs, they can be further subdivided into orthophthalic-, isophthalic-, or terephthalic-type resins. PRs with phthalic anhydride as the primary saturated acid are classified as orthophthalic (o-type / Ortho resins), PRs with terephthalic acid as the primary saturated acid are classified as terephthalic (t-type / Tere resins), and PRs with isophthalic acid as the primary saturated acid are classified as isophthalic (i-type / Iso resins).

Unlike UPRs, SPRs have no double or triple bonds within the polymer backbone and therefore exhibit different operating conditions as adhesives. SPRs can be synthesized using UPR monomers (acids and glycols) in the presence of an excess of glycol during the polymerization [11]. While UPRs are thermosetting resins, SPRs are thermoplastic resins and are often formulated as hot-melt adhesives (e.g., polyethylene terephthalate (PET) used for 3D printing). SPRs may be classified

based on their applications, physical state (solid or liquid), chemical structure (branched or linear), functional groups (carboxylated or hydroxylated), or aliphatic versus aromatic nature [12]. The synthesis of SPRs occurs through a polyesterification process, also commonly known as Fischer Esterification, identified in Figure 1.1, in which carboxylic acids react with glycol to form ester linkages. The reaction must be conducted under excess amounts of acids (acidic conditions) to avoid decarboxylation (loss of active reactants) [10-11]. The diol functional groups in glycol are used in the formulation of both UPRs and SPRs, with a key distinction in the monomer backbone. UPRs contain double or triple bonds, compared to SPRs being fully saturated. To prevent the reverse reaction of esterification (i.e. hydrolysis), the water produced as a by-product must be continuously removed, typically through azeotropic distillation. In this process, an organic solvent (e.g., benzene, toluene, or xylene) forms an azeotrope with the water by-product and sinks to the bottom of the reaction chamber due to its higher density than the reactants. Consequently, they are filtered out using a Dean-Stark trap, thereby minimizing the loss of reactants due to ester hydrolysis [10-11].

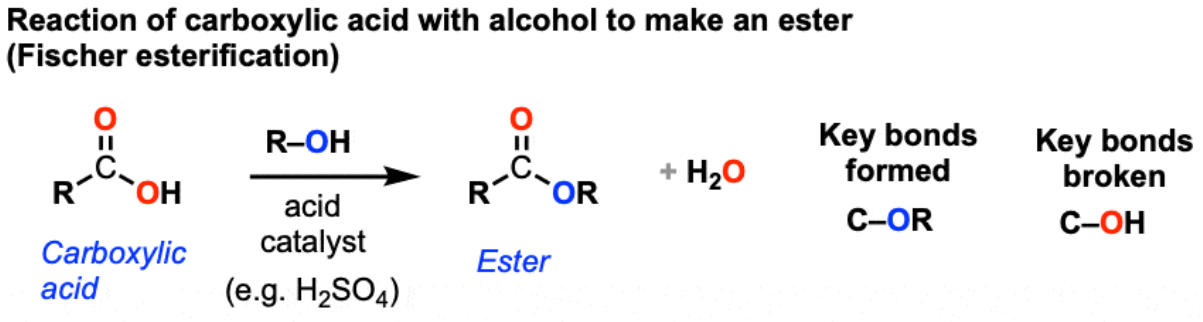


Figure 1.1 Ashenhurst, James. Fisher esterification. 2024.

While PRs are generally considered less hazardous than epoxy resins, which rely on derivatives of bisphenol A (DGEBA), they still present health concerns that need to be addressed. In

conventional PE adhesives, styrene is widely used as a comonomer to alter the properties of the PRs depending on the composition [13]. According to toxicological overviews conducted by the United Kingdom government and an assessment report by the Government of Canada (Environment Canada and Health Canada), styrene exposure can cause respiratory and dermatological irritation, wheezing, coughing, pulmonary edema, cardiac arrhythmias, coma, CNS depression, headache, nausea, vomiting, fatigue, dizziness, and ataxia [14-15]. At lower concentrations, styrene may cause sickness, whereas at higher concentrations it can be fatal. Data from the United States Centers for Disease Control and Prevention and the National Institute for Occupational Safety and Health indicate that occupational exposure to styrene-containing resins is associated with reproductive toxicity, including fertility problems, miscarriage, stillbirth, and birth defects [16]. For instance, two case studies reported in 1974 and 1976 documented adverse pregnancy outcomes in two women who had exposure to styrene, PR, and organic peroxides. One baby died during birth due to anencephaly and the other baby was born with multiple congenital anomalies, including hydrocephalus, ear deformities, and thoracic malformations [17].

Compared to epoxy, which poses potentially severe and even fatal health complications, neat PRs are primarily associated with irritative health hazards. Nevertheless, the severity of health concerns (e.g., genetic / DNA-damage) related to styrene and other additives results in the need to push for more sustainable and bio-based alternatives that are biocompatible and safe for human use. PE-based adhesives provide a promising alternative to epoxy, particularly by incorporating nanoparticles (NPs) into the PE matrices, which can mitigate inferior thermomechanical properties to epoxy and widen the possible applications. The resultant PE nanocomposite resins can be applied in water purification [18], cosmetic additives [19], waste removal [20], and biomedical applications [21]. For applications requiring low-stress or low-performing adhesives, PRs are often

preferred due to their lower cost despite their moderate mechanical properties. Cured UPR typically exhibits a tensile strength of 33 ± 1.5 MPa [22] and a compressive strength of 109 MPa [23]. Table 1.1 compares the properties of polyester resin to epoxy, indicating that the tensile strength and flexural strength of UPR are approximately 80% and 30% of epoxy, respectively [24]. These shortcomings highlight the need for innovative solutions to promote PRs' mechanical properties and make them a more viable alternative to epoxy-based adhesives in both industrial and advanced functional applications.

Table 1.1 Properties of epoxy and polyester resins [24].

Property	**Epoxy**	**Polyester**
Viscosity at 25°C μ (cP)	12000 - 13000	250 - 350
Density ρ ($g.cm^{-3}$)	1.16	1.09
Heat Distortion Temperature HDT (°C)	50	54
Modulus of elasticity E (GPa)	5.0	3.3
Flexural strength (MPa)	60	45
Tensile strength (MPa)	73	40
Maximum elongation (%)	4	1

1.2 Incorporating Nanoparticles in Resins

The incorporation of nanoparticles (NPs) into the matrix of polyester-based adhesives has emerged as a potential strategy to address, and potentially close, the mechanical property gap between them and epoxy resins. The choice of a polyester-based resin as the focus for nanoparticle reinforcement is motivated by its balance of moderate mechanical properties, good chemical

resistance, and high curing efficiency. However, they generally underperform relative to epoxy resins in terms of mechanical strength. The incorporation of nanoparticles provides a pathway to overcome the shortcomings, supported by extensive evidence of utilizing NPs to enhance the thermomechanical properties of adhesives.

The reinforcement mechanisms by NPs are two-fold: (i) NPs with reactive functional groups compatible with those in adhesive resins and epoxy promote crosslinking within the polymer chain, thereby increasing intermolecular interactions; and (ii) well-dispersed NPs, which have a rigid polymetric structure, will form a reinforcing network that enables uniform stress transfer throughout the matrix [5]. Previous studies, particularly involving epoxy adhesives, have shown substantial improvements in both toughness and thermal stability with the addition of NPs. For example, Rahman *et al.* reported that ferric oxide, titanium oxide, and synthesized nickel ferrite nanoparticles in UPR with improvements of 21.62% in tensile strength and 6.56% in Young's modulus, respectively [25]. Chu *et al.* incorporated ramie fabric in unsaturated polyester resin (UPR) and were able to improve the tensile strength of the UPR from 46.8 MPa to 74.1 MPa, an improvement of 27.3 MPa [26]. Furthermore, the incorporation of halloysite nanotube / nanosilica core/shell NPs with steel-epoxy / carbon fibre promoted the lap-shear strength by 130% [5, 27].

Despite these promising outcomes, there remains a critical need to narrow the performance gap between polyester resins (PRs) and epoxy resins. This would, in turn, allow PRs to serve as viable alternatives in high-performance applications, rather than being confined to low-stress or cost-driven uses. Moreover, the use of bio-based or bio-derived NPs would also open pathways for the development of bio-based and environmentally friendly adhesive systems, providing safer and more sustainable options while maintaining the performance standards required in different engineering applications.

1.2.1 Dispersion

One of the greatest challenges in enhancing the thermomechanical properties of adhesive resins through the incorporation of NPs lies in the uniform dispersion of the NPs in the matrix. Particle characteristics such as diameter, shape, and aspect ratio strongly influence their reinforcement performance. This is also true for polysaccharide microcrystals such as chitin [28-29]. Smaller NPs, while offering a higher surface area-to-volume ratio and thereby stronger interaction, are more difficult for uniform dispersion. The loadings of NPs are also crucial for improving the mechanical properties of the material system. Insufficient loading yields limited reinforcement, while excessive loading may result in aggregation. Furthermore, compatibility of NPs with the polymer matrix is another governing factor for the use of NPs as reinforcement filler. Incompatible NPs tend to self-associate and form undesired agglomeration, leading to clusters and voids that weaken the resultant nanocomposites. In contrast, NPs with functional groups chemically compatible with the matrix promote interfacial bonding between them and the matrix, thereby improving structural integrity.

To uniformly disperse NPs into resins, NPs are often suspended in a liquid medium before their incorporation into the resins [30]. This is particularly important for fine particles or NPs produced by mechanical grinding, which may become airborne as aerosols or particulates [30]; however, not all solvents are suitable for this purpose. For instance, water is typically not suitable as a suspension medium for chitin nanowhiskers (CNWs) due to its hydrophobic nature. This promotes film formation upon evaporation of water [31]. Ethanol is a more commonly used suspension medium. It not only serves as a dispersing medium but also penetrates biological membranes, destabilizing and dissolving residual proteins in raw chitinous material [32-33]. This aids in the isolation of CNWs. Despite these advantages, the use of suspension mediums such as ethanol and water must

be thoroughly removed before resin curing because they can potentially trigger undesired reactions with the resins and cause degradation. Furthermore, the residual moisture can also be absorbed by natural fibres. Even small amounts of retained water or ethanol can generate voids and bubbles during curing, compromising the mechanical properties of the resultant composites. [34]. Overall, it remains a significant technical hurdle to uniformly disperse NPs in resins such as polyester resins. Therefore, developing reliable and industrially viable processing methods that maximize the dispersion efficiency continues to be a central challenge in advancing NP-reinforced adhesive systems.

1.3 Chitin and Chitin Nanofibers / Nanowhiskers (CNWs)

According to the *2022 Food and Agriculture Organization of the United Nations: The State of World Fisheries and Aquaculture* report, approximately 5.83 million tonnes of live crustaceans are harvested annually, generating up to 35% waste by weight, or about 2.04 million tonnes of crustacean shell byproducts [35]. Sachindra *et al.* suggested that the percentage of produced waste varied by species. For instance, shrimp processing can yield up to 48% discarded shell waste [36]. Such byproducts represent a significant environmental and economic challenge if left unused. The United Nations Sustainable Development Goals (SDG) 12: Responsible Consumption and Production emphasizes the need to "transition to a circular economy, involving practices such as reusing, refurbishing, and recycling products to minimize waste and resource depletion" [37]. Efficient utilization of seafood byproducts aligns directly with this objective by fostering value-added recycling streams that reduce environmental burden and extend the useful lifecycle of harvested biomass. In this context, converting crustacean shell waste into functional materials such as reinforcement nanoparticles (NPs) offers both ecological, economical, and industrial benefits.

The derived biobased NPs can reinforce adhesives that have lower performance but are more environmentally sustainable. These adhesives with enhanced mechanical properties can be used in a wide spectrum of consumer and industrial products, ranging from footwear and furniture to vehicles, containers, non-woven fabrics, etc. [38]. The improved durability and performance of adhesives can thereby reduce overall material consumption and waste across multiple sectors, resulting in product longevity.

Chitin, the second most abundant naturally occurring polymer after cellulose, is a primary constituent of crustaceans and arthropods' exoskeleton [28, 39]. This polysaccharide has attracted extensive research attention because it is nontoxic, biodegradable, biocompatible, antioxidative, antimicrobial, and thermally stable" [41]. Moreover, it originates from a major biomass resource, making it both abundant and renewable [42]. These positive attributes make chitin particularly attractive to be used as a reinforcing filler in bio-based and environmentally sustainable composites and nanocomposites. By converting crustacean shell waste into functional chitin-based materials, researchers can simultaneously address the global challenge caused by seafood byproduct disposal and contribute to the development of high-performance yet environmentally sustainable adhesive systems.

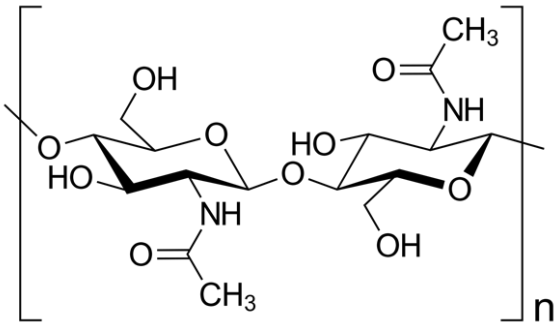


Figure 1.2 Chitin molecular structure.

1.3.1 Crystalline forms of chitin

Chitin exists in three main crystalline polymorphs (i.e., α-chitin, β-chitin, or γ-chitin) depending on the species of origin [28, 43]. Among these, α-chitin is the most commonly occurring form of chitin and is typically found in the shells of crustaceans such as krill, shrimp, lobster, and crab, as well as in insect cuticles, fungal, and yeast cell walls [39, 44]. In α-chitin, the polymer chains are aligned in layers [46]. β-chitin, in contrast, is typically found in squid pens and tube worms [44, 46]. In this polymorph, the polymer chains are oriented in a parallel fashion, which results in weaker intermolecular interactions [28]. While this makes β-chitin more flexible and easier to swell or dissolve in certain solvents, it is weaker mechanically and less stable than α-chitin. The third form, γ-chitin, contains a similar form with chitin molecules in a parallel and anti-parallel arrangement [28] and is found in the cocoons of insects [47]. In shrimp shells, chitin occurs in α-chitin polymorph. The molecules are assembled into chitin nanowhiskers (CNWs), which represent thin fibrillar NPs approximately 3 nm in diameter. They are bundled with organic proteins into fibres that make up the multilayered cuticle plane [39], as illustrated in Figure 1.3. This structural arrangement provides high strength, making α-chitin particularly attractive as a source of reinforcing NPs in nanocomposites. As a result, research has largely focused on α-chitin NPs and their nanostructures because β-chitin is generally considered to be weaker, prone to dissolution, and more reactive in some solvents [28].

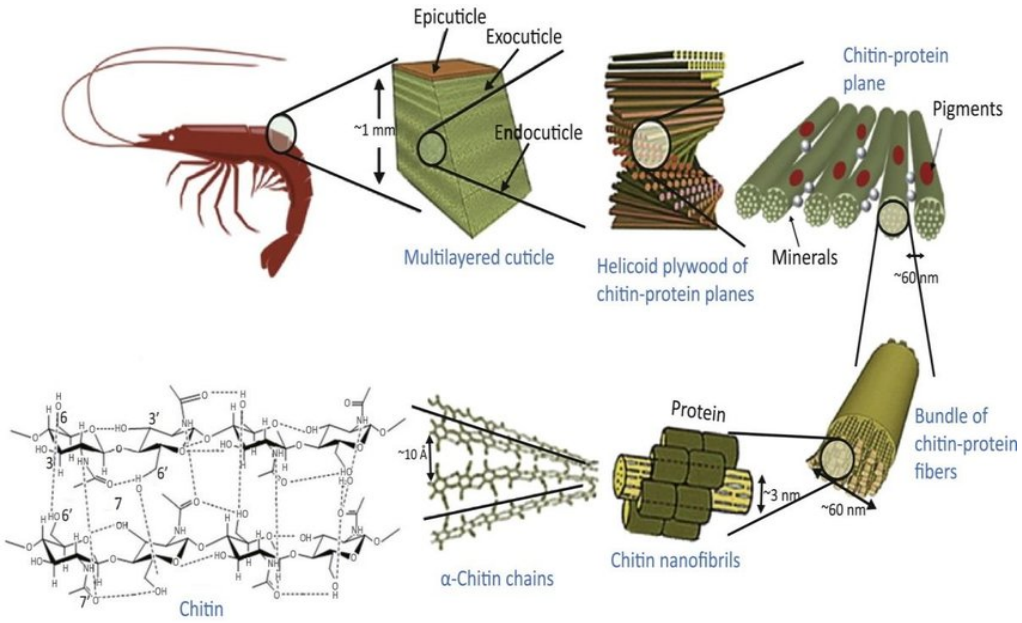
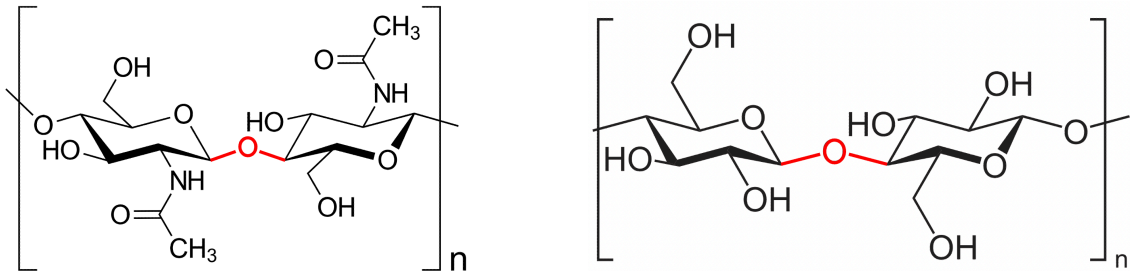


Figure 1.3 Composition of chitin within shrimp shells [39].

1.3.2 Processing methods to obtain chitin

Figure 1.3 shows that chitin exists as α-chitin molecular polymer chains bundled together with organic proteins and inorganic compounds. It is a positively charged polysaccharide and requires processing to remove the proteins and minerals to obtain CNWs. This extraction process is critical because the removal of proteins and minerals not only increases purity but also enhances the degree of polymerization and crystallinity of CNWs, both are crucial to enhance reinforcement performance. However, chitin is highly hydrophobic and insoluble in most organic solvents, making the extraction process technically challenging [39, 48]. Over the years, a range of methods has been developed to prepare CNWs to maximize chitin extraction from proteins and other compounds and to tailor their particle size. NPs' characteristics (i.e., functionality, aspect ratio, and dimension) are crucial because the performance of CNWs as reinforcing filler strongly depends on their morphology and compatibility with the matrix. Well-dispersed CNWs that are

capable of crosslinking among themselves as well as with the adhesive matrix can establish a rigid nanoscale reinforcing network that improves stress transfer and significantly enhances the thermomechanical properties of the adhesive. Among various processing methods, mechanical grinding has been widely studied. This method was originally applied to reduce the crystallinity of cellulose [49], and it has proven viable to handle chitin due to its structural similarities with cellulose. Both chitin and cellulose are polysaccharides that consist of repeating units linked by glycosidic bonds, as identified in Figure 1.4 [48]. Consequently, mechanical grinding can be adapted to break down the hierarchical structure of chitin.



(a) Chitin. *(b) Cellulose.*

Figure 1.4 Glycosidic bond between polysaccharides in (a) chitin and (b) cellulose.

One of the major challenges to fabricating natural fibre-reinforced resin nanocomposites is caused by the hydrophilicity of organic fibres and the hydrophobic nature of unsaturated polyester resins (UPRs) and epoxies [34]. Such interfacial incompatibility hinders effective stress transfer and weakens the performance of the nanocomposites. To address this, a wide range of chemical and physical treatments have been developed to facilitate bonding and / or interactions between fibres and resins; however, research revealed that extensive treatment can degrade the structural integrity of natural fibres, weaken intermolecular interactions and ultimately reduce their adhesion

to the resin [5, 21, 49, 34]. Table 1.2 highlights a drastic percolation threshold, at which the average diameter of CNWs decreases when subject to a duration of ultrasonication. After 30 minutes of ultrasonication, the CNWs tend to agglomerate significantly. The optimization of treatment is critical to promote compatibility while suppressing compromised fibre strength.

Table 1.2 Diameter sizes of CNWs after ultrasonication processing [50].

Ultrasonication time (min)	**Average Diameter (µm)**
0	64.2
30	59.4
90	17.7
150	9.1
210	35.4
270	20

A combination of treatments, such as acid hydrolysis, TEMPO-mediated oxidation, ultrasonication, and electrospinning, has been used to alter the properties of chitin and to remove unwanted proteins and organic solvents from the raw chitin material [21, 49]. For acid hydrolysis, hydrochloric acid has been shown to effectively isolate oligosaccharides from chitin [34]. Calcium chloride [51] or sodium hydroxide [52] is often used in combination with mechanical grinding to improve yield [21, 49]. (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl oxidation or TEMPO-mediated oxidation was found to be effective at dissolving chitin from remnant proteins and other organic compounds. It is done by replacing the C6 hydroxyl groups with carboxylate functional

groups after at least 60 minutes of oxidation [21, 53-57]. This will allow the dissolved chitin to be filtered out to repolymerize to the desired aspect ratios.

In addition to chemical treatment, electrospinning offers a physical approach to fabricating chitin-based nanofibers. In this method, a polymer solution is extruded from a syringe under a strong applied voltage, which overcomes surface tension and draws ultrafine fibres toward a collector such as a rotating drum [21, 58-61]. Altogether, these methods allow researchers to maximize the purity, tailor the dimensions, and improve the surface chemistry of CNWs obtained from raw chitinous material. When dispersed as NPs into PR matrices, CNWs can establish strong interfacial interactions and provide a nanoscale reinforcement network, which in turn improves the thermomechanical properties of PR-based adhesives.

1.4 Objectives

1.4.1 Scientific and technological gap

The incorporation of chitin nanowhiskers (CNWs) in polyester (PE)-based adhesives represents a promising strategy for enhancing thermomechanical properties and promoting the development of sustainable, bio-derived adhesives. However, several scientific and technological gaps remain and must be addressed before CNW-reinforced polyester systems can be fully realized as viable alternatives to traditional epoxy adhesives. One of the most significant challenges lies in achieving uniform dispersion of CNWs within the resin matrix. The reinforcing efficiency of nanoparticles (NPs) is strongly dependent on their size, loading, aspect ratio, and distribution. In polysaccharide-derived microcrystals such as chitin, these parameters play a crucial role in reinforcement properties. Poor dispersion suppresses the overall performance of the adhesive. As demonstrated by Anwer *et al.*, increasing CNW loadings often leads to self-polymerization and crosslinking,

causing aggregation, clumping, and ultimately deterioration of the performance of the resultant nanocomposites. Therefore, developing new strategies to optimize NP loading and achieve uniform dispersion remains an unresolved issue.

A second challenge for uniform dispersion of CNWs in resin matrices is related to the choice of suspension media for chitin NPs. High concentrations of ethanol are commonly used to facilitate processing and protein removal from raw chitinous material; however, complete solvent removal before resin curing is critical, particularly given the absorbency of natural fibres. The presence of residual ethanol or water in fibres can generate bubbles, voids, or interfacial weaknesses in the polymer matrix, severely compromising mechanical integrity. In this context, developing strategies to balance the abilities of some suspension media for CNWs dispersion with the ease of their removal before resin curing is an important area for further study.

Chitin is highly hydrophobic and insoluble in most solvents. These characteristics lead to the need for complex procedures for CNW extraction. Extraction techniques such as mechanical grinding, acid hydrolysis, TEMPO-mediated oxidation, ultrasonication, and electrospinning have shown promise in tailoring CNW morphology, functionality, and purity; however, these processes often suffer from low yields, scalability issues, high energy demands, or incomplete removal of residual impurities. As a result, continued improvement on these approaches is essential to establish reproducible, cost-effective and industrially scalable production of CNWs for adhesive applications. Furthermore, most existing studies focus on α-chitin derived from crustaceans, given its abundance. Yet other crystalline polymorphs, such as β-chitin (e.g., from squid pens) and γ-chitin (e.g., from insect cocoons), possess distinct crystalline structures that may yield different reinforcement performance or compatibility with resin matrices. Further research in this area could

help elucidate processing-structure-property relationships and provide a more comprehensive understanding.

Finally, while there is growing evidence of chitin's positive impact on the thermomechanical properties of epoxy, there remains a lack of investigation into CNW-reinforced polyester adhesives. In particular, systematic studies quantifying the impact of CNW loading on key thermomechanical properties, such as tensile strength modulus, ductility, and glass transition temperature, are still limited. Closing this knowledge gap will be critical in determining whether CNW-reinforced polyester adhesive systems can bridge the performance gap with epoxy adhesives, while offering potential to improve safety and sustainability.

1.4.2 Goals

The overarching goal of this research is to conduct comprehensive parametric studies to investigate the effects of different material and processing parameters on the thermomechanical properties of the CNW-reinforced polyester adhesive systems. This goal is motivated by the need to develop bio-based, high-performance adhesive systems that can serve as sustainable alternatives to conventional epoxy resins. To achieve this overarching goal, this thesis research is guided by the following specific objectives:

1. Optimize CNW dispersion by systematically investigating different dispersion media and dispersion techniques to ensure uniform distribution of CNWs within resin matrices. Particular attention will be given to elucidate the interactions between solvents, CNWs, and the polyester matrix in both the resin and curing phases.

2. Evaluate the influence of solvent selection on curing behaviour and resin performance, to identify suspension media that promote NP dispersion. Furthermore, it is important to avoid

detrimental effects caused by incomplete solvent removal, which may result in degradation of polyester resin during processing.

3. Characterize the impact of CNW incorporation on the thermomechanical properties of polyester adhesives. This will systematically assess tensile strength, elastic modulus, elongation at break, adhesive strength, glass transition temperature, and thermal stability across a range of CNW loadings.

Through these objectives, this thesis research aims to provide a comprehensive elucidation of the role of CNWs in polyester-based adhesives and to establish industrially viable processing strategies. In this context, this work aims to bridge the current performance gap between polyester and epoxy adhesives, while advancing the broader adoption of sustainable nanocomposite materials in industrial applications.

1.4.3 Structure of Thesis

The thesis is organized into five chapters, each addressing a distinct stage of the research and collectively achieving the overarching goal of designing and fabricating polyester-based bio-based adhesive reinforced by chitin nanowhiskers.

Chapter 1 provides an introduction to the research, highlighting the critical role of adhesives across a wide spectrum of industries and the associated health and environmental concerns of conventional adhesive systems. It establishes the motivation for exploring safer and more sustainable alternatives, with particular emphasis on the potential of NPs to enhance thermomechanical properties. In this context, chitin is introduced as a renewable and biocompatible source of reinforcement, positioning it as a promising candidate for the design and fabrication of a bio-based adhesive system.

Chapter 2 presents a comprehensive literature review. This includes various processing strategies to improve compatibility and dispersion of CNWs, an overview of polyester resin adhesives & mechanical reinforcement, nanoparticle reinforcement and nanofiller dispersion strategies, the fundamental challenges of incorporating CNWs into resin matrices, and an overview of the sustainability of utilizing NPs / CNWs. The literature review also identifies existing knowledge gaps and research opportunities, thereby describing the motivation for the thesis research.

Chapter 3 describes the materials and experimental methodology used in this thesis research. It outlines the preparation of CNW suspensions and the protocol of resin casting and curing. The chapter further summarizes the approaches to characterize chemical interactions, morphological properties, thermal behaviour, and mechanical performance of CNW-reinforced PE adhesives.

Chapter 4 presents the results and discussion. Spectroscopic, microscopic, thermal, and mechanical data are analyzed to elucidate the processing-structure-property relationships of the nanocomposites. The chapter also discusses the effects of CNW loading and residual suspension medium on the adhesive performance and thermomechanical properties. The trends in glass transition temperature, degradation onset, tensile strength, elongation at break, and adhesive performance of the CNW-reinforced PE nanocomposite are systematically analyzed.

Chapter 5 concludes the thesis with a summary of the key findings and their implications for sustainable adhesive design. The chapter also outlines limitations of the present work and proposes directions for future research, including strategies for improving solvent removal, exploring CNW surface modifications, and developing scalable methodologies for industrial applications.

CHAPTER 2 – LITERATURE REVIEW

As chitin is nontoxic, biodegradable, biocompatible, antioxidative, antimicrobial, and thermally stable [41], there has been ongoing research on using chitin as a nanoparticle (NP) for adhesives. To maximize the strength of the NP addition, they must be well dispersed in appropriate amounts to create a backbone structure that supports the adhesive matrix. The dispersion of NPs is difficult as they tend to polymerize and agglomerate. Inorganic and ceramic NPs that clump together fuse "friable but extensive networks that cannot be eliminated by chemical or physical means" [62]. This may lead to issues that affect the improvement of the thermomechanical properties of the matrix. The following is a review of processing methodologies used, along with the associated effects of thermomechanical properties:

2.1 Processing - Freeze Drying

Freeze drying is a popular processing method that may remove the water / suspension medium from the chitin, while preventing agglomeration / clumping. Wu and Meredith used freeze drying to create a porous biomimetic structure by controlling the concentration and freezing direction [63]. This was accomplished by altering the freezing rate (freezing temperature and heat transfer variables) to create a variety of targeted structures on a micrometre scale. The chitin nanowhiskers (CNWs) were dispersed in water at pH 4 (to minimize electrostatic repulsion) and cooled at −20 °C to allow the CNWs to align and orient into a developed network structure, whereas a lower cooling temperature would lead to faster aggregation as illustrated in Figure 2.1 [63]. Freeze drying would allow the CNW structure to align and create high aspect ratio chains and minimize agglomeration. The freeze-dried CNW network structure was able to mimic the organic structure

cuticle of a beetle, with improved porosity from 30% to over 95% [64]. Once the CNWs have been freeze-dried, they theoretically may be incorporated with the PRs via compounding or solvent mixing with better compatibility due to the increased porosity. The incorporation and effect of the thermomechanical properties of freeze-dried chitin as an NP in polymers should be investigated further; however, de-agglomeration is dependent on the rate of freezing (which is difficult to control) and is an extremely time-consuming process [64-67]. From a report by Choi *et al.*, 48 hours were required to completely freeze-dry at −20 °C [67]. The NP size was found to be largely dependent on the freezing rate, with freeze-drying was also found to break the NPs (assumed to be by the oil solidification, and not water crystallization) [66-67].

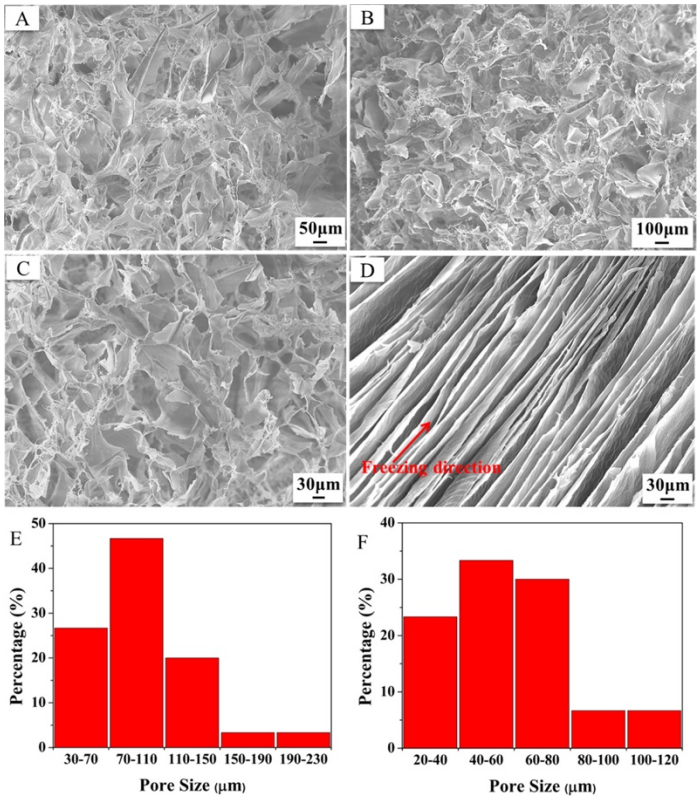


Figure 2.1 SEM images of freeze-dried chitin: (a) top and (b) cross section of samples [63].

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2.2 Processing - Pretreatments

Pretreatment of chitin NPs has been widely investigated as a strategy to improve their compatibility and reinforcing effect when incorporated into polymer matrices. Li *et al.* utilized chitin to reinforce polylactic acid (a renewable resource-derived thermoplastic bio-based monomer) using extrusion moulding. The preparation of the chitin from crab shells was done using the Gopalan and Dufresne 2003 methodology [68], and underwent water, polyethylene glycol, and polyethylene oxide pretreatments [69]. The highest bending modulus and bending strength were found to be 40 wt.% NP using water pretreatment, with 41.2 MPa (bending modulus) and 4153 MPa (bending strength), with an increase by 182.2 and 165.9% from the neat polylactic acid [69]. It was found that the fibre content had a significant effect on the impact toughness of polylactic acid, with increases of 316.3% using water pretreatment, 256.9% using polyethylene glycol pretreatment, 230.2% using polyethylene oxide pretreatment, and 88.4% using compounding [69]. Although the pretreatment methods are effective and eco-friendly, they reduced the aspect ratio, leading to a subdued reinforcing effect of the chitin NP addition [70]. While pretreatments can significantly enhance mechanical properties and toughness, they may also reduce the aspect ratio of chitin, which can limit the full reinforcing potential in composite systems.

2.3 Dispersion Techniques - Compounding

Various compounding techniques have been employed to incorporate chitin into polymer matrices, with processing methods playing a critical role in determining dispersion quality and composite performance. Anwer *et al.* incorporated 0.25 wt.%, 0.50 wt.%, and 0.75 wt.% of chitin into bisphenol A diglycidyl ether (BADGE or DGEBA) epoxy. A modified slurry micro compounding method was used to combine 2.6 parts ethanol: 1 part DGEBA epoxy to dissolve

CNWs, then mechanically stirred at 60 °C to evaporate the ethanol and water, and then cured using triethylenetetramine (TETA) curing agent (13 TETA:100 DGEBA by weight) [64]. From the experimental results, an increase of approximately 12% in the tensile strength, from approximately 70 MPa to 80 MPa, was found with the incorporation of 0.25 wt.% CNW [64]. From an increase in CNW wt.% content, tensile modulus and strength were noted to decrease as there was an increased amount of CNW clustering, as confirmed through scanning electron microscopy (SEM) and transmission electron microscopy imaging [64]. Chitin is noted to have considerable improvement to the thermomechanical properties of epoxy. There is, however, no investigation conducted to develop CNW-reinforced PE adhesives. Rizvi *et al.* incorporated chitin into polylactide hot-melt foams with various amounts of chitin [70]. The chitin was incorporated in the polylactide foams using the Paillet and Dufresne methodology (two cycles of 3N HCl hydrolysis and 3200 rpm centrifuge, followed by dialysis) [71] along with the use of a micro compounder. Although it was expected that the elastic storage modulus should increase with the increase in chitin content, a decrease in storage modulus was found due to the aggregation / self-polymerization of the chitin along with the hydrolytic degradation of the polylactide melt [70]. Before incorporating the chitin, it was not fully dried when mixed with the polylactide and had a gel-like consistency. The amount of moisture in the suspension could have degraded the polylactide and / or introduced voids that would lower the elastic modulus [70]. The elastic storage modulus and the strength of the chitin-polylactide foam was found to have decreased but resulted in an increase in stiffness [70], similar to the results found by Anwer *et al.* A more volatile solvent that would evaporate further or a more complete drying process should be investigated further, however, it may lead to negative effects on dispersion as it may polymerize with the decrease in suspension medium volume. These findings highlight that optimized compounding is essential to

achieve uniform chitin distribution, as inadequate processing can lead to aggregation, reduced mechanical properties, and inconsistent thermomechanical behaviour.

2.4 Dispersion - Coagulation

Coagulation and wet spinning techniques have been widely applied to process chitin / chitosan into matrices, enabling control over fibre morphology and interfacial interactions. Nguyen conducted a processing method that used a coagulation bath at various temperatures (5 °C, 20 °C, and 60 °C). At an increase of 1% chitin concentration to 2%, the chitin hydrophilicity was reduced and resulting in improved mechanical properties, with the tensile strength increased from 79.6 MPa at 5 °C to 182 MPa at 60 °C [72]. Yudin *et al.* utilized a coagulation method by Tamura *et al.* to incorporate CNW into a chitosan matrix, using two coagulation baths followed by a stretching and rolling [73] and feeding the solution (chitin, 10% sodium hydroxide and 10% ethanol solution) through a 0.6 mm die hole at 5.5 mm / s [74]. It was found by Yudin *et al.* that incorporating CNW in a small quantity (0.05 wt.% – 0.3 wt.%) increased the strength of the CNW / chitosan composite by up to approximately 20% as the solution is drawn out by 120% [74]. Watthanaphanit *et al.* utilized wet spinning by mixing CNW suspensions with an alginate solution, and later degassing and extruding into two coagulation baths [75]. It was found that 1-ethyl-3-methyl-imidazolium acetate ionic liquid can dissolve raw crustacean shells, resulting in a high-purity chitin fibre that is able to be used directly from the solution [75]. CNWs that were wet spun using 1-ethyl-3-methyl-imidazolium acetate ionic liquid improved the tensile modulus from 12 GPa to 13 GPa, and the tensile strength from 223 MPa to 237 MPa [76]. Overall, these studies demonstrate that coagulation-based methods can significantly enhance the mechanical

performance of chitin-containing composites, though outcomes are influenced by processing conditions, filler concentration, and solvent systems.

2.5 Dispersion - Electrospinning

Electrospinning has been widely explored as a technique to incorporate CNWs into polymer matrices to enhance their structural and thermal properties. Zhu *et al.* employed an electrospinning methodology to incorporate CNWs into a biodegradable polydioxanone matrix. CNW powder was sonicated in deionized water for 30 minutes, centrifuged in acetone, and suspended in 2,2,2-trifluoroethanol [77]. It was later sonicated and maintained a 9 wt.% of CNW and polydioxanone, and dispensed at 1 cubic cm / h using an 18-gauge blunt tip needle [77]. This was done with an applied potential of 20 kV from 15 cm away at 400 rpm [77]. The peak stress of the CNW-polydioxanone nanocomposite was found to have an increased peak stress from 5 MPa (neat matrix) to 13 MPa (with a 10 wt.% CNW), along with an increased modulus from 18 MPa to 61 MPa (with a 15 wt.% CNW) addition, but with a decrease in the fracture strain from 80-100% compared to 250% of neat polydioxanone [77]. The addition of 15 wt.% CNW improved the decomposition temperature of polydioxanone matrix from 217 °C to 262 °C, along with an increased transition region temperature [77]. These results highlight the effectiveness of electrospinning CNWs for producing nanocomposites with improved strength and stability, while also revealing trade-offs in ductility.

2.6 Polyester Resin Adhesives & Mechanical Reinforcement

Unsaturated polyester resins (UPRs) and saturated polyester resins (SPRs) are synthesized using polycondensation reactions but vary depending on structural and functional requirements.

Commercial UPRs are produced by reacting unsaturated acids, glycols, and styrene monomers [78]. Commercial SPRs involve reacting saturated diacids and diols, forming stable polymer chains with only single bonds. SPRs are inert and used in applications such as construction materials or coil coatings [79]. Polyester resins are used compared to epoxy due to their cost-effectiveness, processing advantages, properties for specific applications and versatility. However, epoxy offers higher performance in mechanical properties, water resistance and lower shrinkage. Mani *et al.* evaluated polyester resin and epoxy as polymer binders for concretes with an analysis on compressive, split-tensile, flexural and impact strengths, abrasion resistance, skid resistance, resistance to various chemicals, water absorption, cavitation resistance and setting shrinkage [80]. Results from compressive, split-tensile, flexural and impact strengths indicate both polyester and epoxy concretes had higher performance compared to cement concretes; however, epoxy was observed to have higher performance compared to polyester resins. However, due to the hydrophilic nature of polyester resin to induce hydrolysis, it was found that the polyester concrete had a significantly higher water absorption at both ambient and boiling temperatures [80]. It is also important to note that the setting shrinkage of polyester concrete was much larger compared to epoxy. As the polymer chains pull together, this results in voids, high internal stresses, instability, and poor interfacial bonding, which can result in lower dimensional accuracy. Cavalcanti *et al.* formulated natural fibre-reinforced composites using polyester and epoxy resins to investigate the compatibility of the resins with combinations of jute, curaua, and sisal. Results indicate that epoxy provided the natural fibres with higher tensile strength and thermal stability; however, polyester composites demonstrated higher tensile stiffness, flexural stiffness and impact energy [81]. While polyester resins remain ideal for cost, processability, and versatility, their higher water absorption, greater setting shrinkage, and comparatively lower mechanical performance than epoxy highlight

the need for reinforcement strategies to overcome these limitations and expand their applicability in structural and adhesive systems.

2.7 Nanoparticle Reinforcement & Dispersion Techniques

Nanoparticles (NPs) improve the mechanical properties, including adhesive performance, through reinforcement and interfacial effects. For NPs with high stiffness and high aspect ratio (e.g. CNWs), they can sustain partial amounts of the applied load. When NPs are well dispersed, they can transfer stress from the polymer matrix to the stiffer NPs. They are also able to increase the fracture surface area as more energy is required to propagate cracks around or through the NPs, therefore increasing toughness. Figure 2.2 illustrates well-dispersed NPs that force cracks to deflect in a direction or branch, requiring more fracture energy [82]. Certain NPs that can chemically bond with the matrix through compatible functional groups would also create regions in the polymeric chains to restrict chain mobility, leading to higher stiffness and improved thermal stability. For NPs that cannot chemically bond with the matrix (or have poor interfacial adhesion), NPs may be pulled out during fracture. This indicates weak bonding but still absorbs energy and contributes to toughness on a macroscopic scale. NPs are also able to fill microscopic voids, reducing defect density. A challenge in utilizing NPs is that they tend to agglomerate due to thermodynamic driving forces. When NPs attract to each other, they form dense agglomerates and disperse when repelled from each other. Vollath determined that the size and distribution of agglomerates can be predicted using entropy-based models, where the enthalpy of interaction between the NPs determines the sizes of agglomeration [83]. If the enthalpy of interaction between nanoparticles is lower than that with the surrounding resin, the particles preferentially attract each other, leading to agglomeration rather than stable dispersion [83]. In adhesives, uncontrolled

agglomeration produces large clusters that serve as stress concentrators and reduce mechanical reinforcement efficiency.

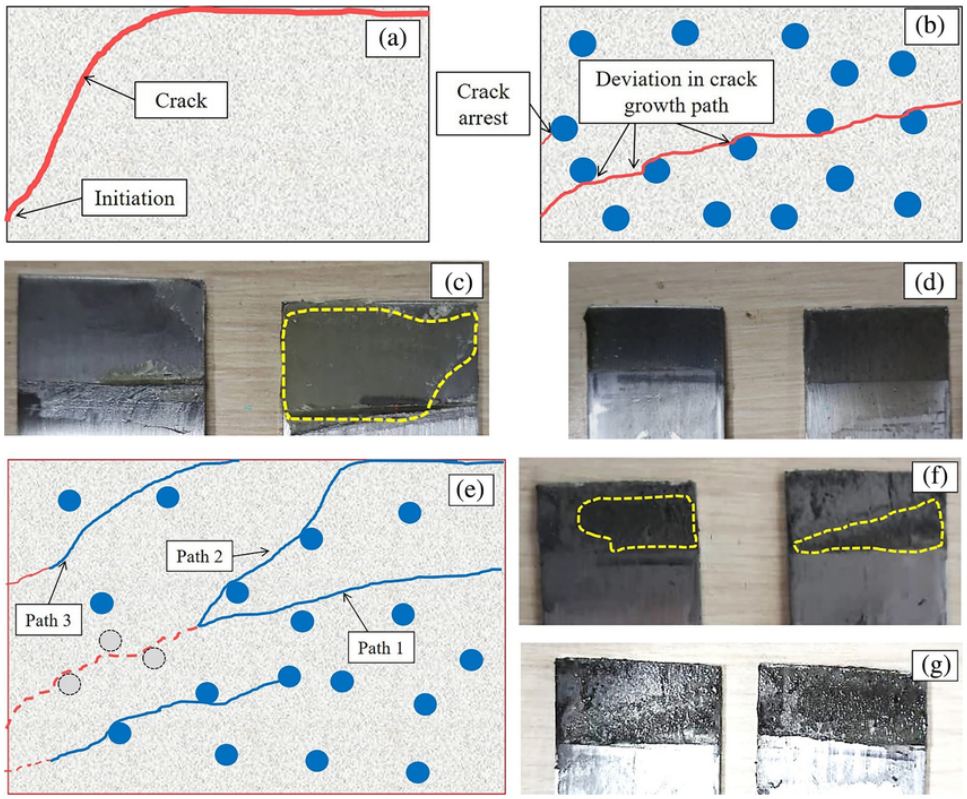

Figure 2.2 SEM images of freeze-dried chitin: (a) top and (b) cross section of samples [81].

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A method of improving NP dispersion is to utilize solvents. Solvent-assisted dispersion mitigates this effect by lowering interparticle attraction, breaking up aggregates, and enabling a more uniform distribution of nanoparticles, which is essential for effective stress transfer and improved fracture resistance. Solvent-assisted dispersion is often utilized to break up NP agglomerates and to stabilize them in a liquid medium. The solvent used and the energy input to disperse the NPs, often sonication or stirring, are critical to ensure stable and well-dispersed NPs.

Careful consideration must be given depending on the NP incorporated. Qamar *et al.* note that physical methods without chemical reactions (i.e. stirring, ball milling, high shear mixing, and sonication) to disperse graphene lower the dispersion rate and damage the chain structure of graphene, leading to increased defects [84]. When using an organic NP such as CNW, solvent-assisted approaches may help bridge this risk of damaging the CNW structure by temporarily stabilizing CNWs in a medium that can interact with both the particles and the resin, thereby improving their dispersion before curing. The presence of CNWs in solvent(s), to form a slurry, allows excessive energy input during sonication or stirring to dissipate into the solvent. This may reduce the risk of damaging the CNW structure and assist in maximizing the reinforcing potential.

2.8 Sustainability

The growing demand for sustainable materials has driven interest in bio-based NPs as alternatives to traditional synthetic NPs. Although conventional reinforcements such as carbon nanotubes, graphene, and silica can significantly enhance polymer performance, they have a high cost and energy-intensive production, creating environmental concerns. In contrast, bio-based NPs such as cellulose nanocrystals and CNWs are renewable, biodegradable and sourced from abundant waste products. When compared to alternative bio-based NPs, Tardy *et al.* discussed how CNWs are more energy intensive to extract compared to plant-based materials; however, they can be obtained at a smaller NP size / scale [85]. For example, CNWs are more optimal as a reinforcement filler in composites due to their positive surface charge and greater hydrophobicity. A common organic filler, such as starch, is more hydrophilic and possesses higher surface area and absorption, which is optimal for improving film properties, such as water resistance [86]. A high amount of energy to process CNWs (in relation to alternative plant-based NPs) largely arises

from the need to remove minerals and pigments, as well as to separate the tightly bound chitin-protein fibres and the associated proteins [39, 85]. Although CNW production requires significant energy input for demineralization, depigmentation, and protein removal, this process allows the conversion of discarded waste into high-value nanomaterials, thereby reducing environmental impact and providing a sustainable alternative to conventionally processed NPs. Berroci *et al.* reported a life-cycle assessment of CNWs, identifying a global warming potential as low as 18.5 kg [CO_2] per 1 kg of CNW produced from fungi [87], whereas Kushnir *et al.* estimated 125 kg [CO_2] per 1 kg of carbon nanotube produced [88]. This contrast highlights the environmental advantage of bio-based NPs like CNWs, reinforcing their potential as a bio-based nanomaterial for polymer reinforcement compared to traditional synthetic options.

CHAPTER 3 – SYNTHESIS AND ANALYSIS METHODOLOGY

3.1 Materials and Methodology

3.1.1 Materials

Chitin (cationic; 80 mesh) was sourced from Qingdao Yuda Century Economy and Trade Co., Ltd (Qingdao City, SD, China) and processed into chitin nanowhisker (CNW) suspensions in pure ethanol (5% wt. of CNW in ethanol) by Neptune Nanotechnologies Inc. (Markham, ON, Canada). Ethanol was initially selected as the primary dispersion medium due to its commercial availability and its compatibility with unsaturated polyester resins (UPRs), as water is unsuitable because of hydrolysis and reverse polymerization concerns. In order to evaluate solvent effects on CNW dispersion and resin performance, additional suspensions were prepared using various solvent systems, including ethanol, acetone, methyl ethyl ketone, as well as a modified powder form. Pure grade acetone and methyl ethyl ketone were purchased from SolvableWorks. The UPRs used throughout this thesis research were 3M Bondo® Fibreglass Resin, which consists of methyl ethyl ketone peroxide; 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TPIB), hydrogen peroxide, and methyl ethyl ketone. The associated curing agent, 3M Bondo® methyl ethyl ketone peroxide (MEKP), was employed to initiate crosslinking during the resin curing process. Despite the commercial designation “Fibreglass Resin,” direct correspondence with the manufacturer confirmed that the formulation contains no fibreglass filler. Instead, the nomenclature reflects its intended application as a matrix resin for fibreglass layup and repair systems.

3.2 Experimental Setup and Procedure

3.2.1 Incorporating CNW into Pure Ethanol and Acetone

CNWs were suspended in various ethanol and acetone solvent systems using rotary evaporation to promote uniform dispersion of CNWs in the suspension medium. For ethanol suspensions, two successive rotary evaporation cycles of 300 g each were performed at 80 °C, with the second round added when the slurry was visibly adhering to the beaker, indicating partial solvent removal and increased particle cohesion. Acetone suspensions were prepared following the same approach, with two evaporation cycles of 300 g each, but performed at 60 °C under the same adhesion criterion. It was crucial to perform two evaporation cycles to prevent excessive solvent retention, which would otherwise become challenging to ensure complete solvent evaporation and increase the likelihood of CNW aggregation due to their polar behaviour. This two-stage approach also minimized the risk of overheating, thereby ensuring efficient solvent removal without flooding the condenser or causing boiling over.

3.2.2 Incorporating CNW into an Ethanol / Acetone Mixture

Suspensions of CNWs in ethanol / acetone mixtures were prepared using a staged mixing and dispersion process to optimize compatibility and minimize aggregation. The CNW-ethanol suspension medium system was first heated to 60 °C until it reached a visibly thickened state. Acetone was then introduced at a 2:1 mass ratio to the CNW while the mixture was subjected to continuous heated stirring. Following this, the suspension underwent ultrasonication at 25 Hz for less than 5 minutes to enhance nanoparticle dispersion. Mild heating at 40 °C was applied immediately afterward to maintain fluidity without promoting premature solvent loss. The partially processed suspension was then allowed to decant for 5 minutes before a second addition of acetone

at a 10:1 mass ratio relative to CNW. This was performed under stirring at 60 °C, followed by a second round of ultrasonication at 25 Hz for less than 5 minutes. The suspension was then heated mildly at 40 °C again. After a final decanting period of 5 minutes, an additional acetone addition at a 10:1 mass ratio was performed under the same stirring and heating conditions until a final CNW-to-suspension medium ratio of 5 wt.% was achieved.

This two-stage solvent addition approach was employed in order to prevent excessive CNW aggregation in the suspension, which would likely occur if a large volume of solvent were introduced at once. By incorporating solvent incrementally and assisted with ultrasonication and controlled heating, it would promote more uniform dispersion through a balance of solvent removal and particle stabilization. This mixing procedure would improve the compatibility of CNWs with the ethanol / acetone suspension medium and enhance the homogeneous dispersion of CNWs into the resin system.

3.2.3 Incorporating CNW into an Ethanol / Acetone / Methyl Ethyl Ketone Mixture

Suspensions of CNWs in ethanol / acetone / methyl ethyl ketone (MEK) mixtures were prepared by extending the procedures outlined in Section 3.2.2. Initially, the CNW-ethanol suspension medium system was heated to 60 °C until visibly thickened. Acetone was then added to the CNW at a 2:1 mass ratio under continuous stirring at elevated temperature. After that, the mixture was ultrasonicated at 25 Hz for less than 5 minutes and subsequently subjected to mild heating at 40 °C. Following a 5-minute decant period, acetone was added at a 10:1 mass ratio relative to CNW while stirring at 60 °C. A second ultrasonication at 25 Hz for less than 5 minutes was then applied to the suspension system. The system was undergoing mild heating again at 40 °C and decanted for 5 minutes before a final addition of acetone at a 10:1 mass ratio. This process continued until a 5

wt.% CNW-to-suspension medium ratio was achieved. In order to facilitate incorporation of MEK, the suspension was further heated to evaporate 10 wt.% of the solvent medium, after which MEK was introduced at 15 wt.% and the mixture was reheated to restore the CNW-to-suspension medium ratio to 5 wt.%. This multi-solvent mixing strategy was designed to suppress CNW aggregation while promoting compatibility with the polyester resin. The addition of MEK aimed to enhance CNW's compatibility with UPR curing conditions, thereby increasing the likelihood of achieving a more uniform NP dispersion and potentially strengthening the interfacial bonding between CNW and UPR within the resultant nanocomposite system.

3.2.4 Samples Fabrication using Slurry Compounding and Casting

A 5 wt. % CNW suspension was ultrasonicated for 10 mins at 24.45 kHz to minimize agglomeration and clumping. Weighed amounts of the CNW suspension were then loaded into 3M Bondo® Fibreglass Resin under continuous stirring. In order to remove the suspension medium, the mixtures were subjected to controlled heating. The suspension mediums containing ethanol and / or MEK were heated at 80 °C for approximately 45 minutes, whereas suspension mediums containing only acetone were heated at 60 °C. Throughout this process, the mixtures were repeatedly weighed to monitor and confirm solvent removal. Following solvent evaporation, the CNW-resin mixtures were degassed, cured with methyl ethyl ketone peroxide (MEKP), and casted into molds to prepare samples for subsequent characterization.

3.2.5 Chitin Powder Processing and Manufacturing

A novel method patented by Neptune Nanotechnologies Inc. was employed to obtain processed CNW NPs with a significantly reduced degree of agglomeration from crystalline chitin [89]. In

this process, a non-colloidal mixture of chitin is subjected to hydrolysis by mixing approximately 2.5 to 4 N hydrochloric acid under continuous stirring at 90 to 100 °C for 4 to 5 hours. Once the mixture transitions predominantly into a colloidal state, it is cooled to 25 °C. The resulting membranes are neutralized using a base. Complete neutralization is achieved by diluting the chitin reaction mixture with water at a 1:5 ratio for approximately 78 hours until the pH stabilizes at 7. The mixture is then centrifuged to separate highly crystalline CNWs from the amorphous hydrolyzed chitin. The hydrolyzed chitin slurry is subsequently mixed with water at a 1:5 slurry-to-water ratio to obtain a uniform suspension. Finally, the water is removed using spray drying, yielding well-dispersed CNW nanoparticles.

3.3 Characterization of Commercial PR

3.3.1 Fourier-Transform Infrared (FTIR) Spectroscopy – Chemical Interactions and Functional Groups

Infrared spectra of the synthesized and commercial PRs were obtained using a FTIR spectrometer (VERTEX 70v, from Bruker) by utilizing a transmission mode over a scan range of 4000 to 400 cm^{-1}. The acquired FTIR spectra were used to determine the chemical structures of the samples by analyzing the relative transmission and its corresponding wavenumber. Cured samples were ground into powder and subsequently sieved using a 60-grade mesh. The samples were placed onto a clean attenuated total reflectance (ATR) crystal after nominal calibration and confirmation of the interferogram signal strength. The samples were then pressed against the ATR crystal to obtain the transmission spectra.

3.3.2 Scanning Electron Microscopy (SEM) – Morphology and Dispersion

SEM (Vega 3, from Tescan) was used to examine the surface morphology, nanoparticle dispersion, and fracture characteristics of the commercial PR and CNW samples. Prior to imaging, thin specimens were immersed in liquid nitrogen for 10 seconds to induce embrittlement, then horizontally fractured by securing them in a vice and applying a horizontal impact. The samples were then mounted on aluminum stubs using conductive carbon tape and subsequently sputter-coated with a thin layer of gold (Desk V, from Denton) using plasma deposition under an argon gas atmosphere to enhance conductivity and minimize charging during imaging. A thin layer of conductive carbon paint was applied along the sides of the specimens to facilitate charge dissipation during imaging.

3.3.3 Differential Scanning Calorimetry (DSC) – Thermal Transitions

DSC (Discovery DSC 250, from TA Instruments) was used to characterize the glass transition and characteristic temperatures related to other endothermic reactions. This was done by analyzing the heat flow through the samples as a function of temperature. The samples were ground into powders and sieved using an 80-grade mesh and were placed in a Tzero® aluminum pan that was loaded into the DSC chamber. The samples were equilibrated at 35 °C before heating to 400 °C at a rate of 10 °C / min.

3.3.4 Thermogravimetric Analysis (TGA) – Thermal Degradation

TGA (TGA 55, from TA Instruments) was used to characterize the composition and thermal stability of the synthesized and commercial PRs. This was done by analyzing the weight difference and change of the samples as a function of temperature. The samples were ground into powders

and sieved using an 80-grade mesh and were placed on an aluminum pan. The samples were equilibrated at 35 °C before a heating rate of 20 °C / min was applied to heat the samples to 600 °C while the furnace was purged under a nitrogen medium.

3.3.5 Tensile Test – Elongation at Break, Elastic Modulus, and Tensile Strength

Tensile testing of the samples was performed in accordance with ASTM D638, *Standard Test Method for Tensile Properties of Plastics*, using Type IV specimens designed for small plastic samples. Platinum silicone molds conforming to the ASTM D638 Type IV geometry were procured from MB Prototyping Ltd., and the samples were cast in the molds following the manufacturer's specifications. After curing, the specimens were carefully sanded with 400-grit sandpaper in accordance with specifications and conditioned under standard room conditions (i.e., 23 °C) for 72 hours as per ASTM D618. Mechanical testing was conducted on a linear-torsion dynamic test instrument (ElectroPuls E3000, from INSTRON) at a crosshead speed of 5 mm / min, with eight specimens tested for each composition.

3.3.6 Single-Lap Shear (SLS) Test – Adhesive Strength

Adhesive strength and failure mode were evaluated in accordance with ASTM D1002, *Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)*. Samples were prepared and cured following the specifications and applied to the bonding area under standard laboratory conditions. The samples were then allowed to cure and conditions in accordance with ASTM D618. Cold-rolled 2024 aluminum alloy sheets with T3 temper treatment, procured from McMaster-Carr, served as the substrates and were cut to the required dimensions. The substrates were cleaned of debris using

precision wipes before bonding. The adhesive tests were conducted using a linear-torsion dynamic test instrument (ElectroPuls E3000, from INSTRON). Shims were added to the substrates in the grip area to compensate for grip misalignment, thereby suppressing bending moments caused by eccentric loading and promoting a more uniform shear stress distribution across the bonded area. Figures 3.1 and 3.2 illustrate the single-lap shear test with cohesion failure and adhesive failure, respectively. Cohesion failure indicates that the strength between the adhesive and the substrate (i.e. adhesive strength) is greater than the internal strength of the adhesive itself (i.e. shear strength). On the fracture surface, cohesive failure is typically identified by visible adhesive remnants left on both substrates, indicating that the crack propagated through the bulk of the adhesive rather than at the interface. While this demonstrates strong substrate adhesion, it also emphasizes the need to improve the resin's cohesive strength to resist crack propagation under load. In contrast, adhesion failure occurs when the external bonding between the adhesive and substrate breaks. In this case, the fracture occurs at the adhesive–substrate interface, leaving little to no adhesive residue on one of the surfaces.

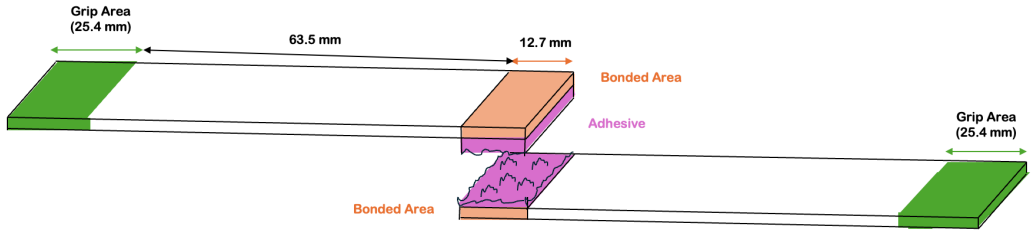

Figure 3.1 Illustration of the single-lap shear test with cohesion failure.

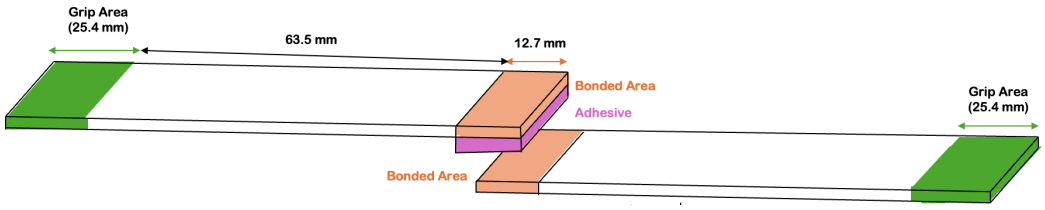

Figure 3.2 Illustration of the single-lap shear test with adhesion failure.

CHAPTER 4 – RESULTS AND DISCUSSION OF THE DESIGN AND FABRICATION OF CNW-REINFORCED POLYESTER ADHESIVE SYSTEMS

4.1 Effects of CNW Loading on CNW-Reinforced Polyester Adhesives

Ethanol was selected as the primary suspension medium to evaluate the effect of increasing chitin nanowhisker (CNW) loading on polyester resin. This choice was guided by both practical and methodological considerations. The commercially supplied CNWs were originally processed in an ethanol-based medium, which has been demonstrated to be an effective CNW suspension system for reinforcing other polymers (e.g., epoxy) through industrially scalable processes. Using ethanol in this study, therefore, ensured consistency with established methods while enabling adaptation to polyester systems, which is more challenging due to its potential hydrolysis during processing. It provided a direct pathway for scaling up the methodology developed herein to large-scale applications.

The study was conducted in which neat commercial polyester resin was subjected to the same thermal treatment as the CNW-reinforced samples to isolate the effect of CNW loadings. This ensured that any observed change in resin performance could be attributed to the loading of CNWs instead of the thermal history during processing. In this context, the analyses revealed the effects of CNW loadings on the thermal, mechanical, and adhesive properties of polyester-based adhesives and their CNW-reinforced nanocomposites.

4.1.1 Effects of CNW Loading on the Chemical Structures of CNW-Reinforced Polyester Nanocomposites

Figure 4.1 illustrates the Fourier Transform Infrared (FTIR) spectra of CNWs suspended in ethanol, the neat polyester resin, and the CNW-reinforced polyester nanocomposites with different CNW loadings. The spectrum of CNW demonstrated a broad absorption band between 3100–3600 cm^{-1}. This is attributed to N–H and O–H stretching vibrations with the presence of aliphatic alcohols such as ethanol. The peaks observed at 2964 cm^{-1} and 877 cm^{-1} are related to C–H stretching and bending vibrations, respectively. The presence of ethanol in the system is confirmed by a strong peak at 1043 cm^{-1} as a result of C–O stretching.

The CNW spectrum displayed a broad absorption region around 3324 cm^{-1}, which is a result of overlapping N–H and O–H stretching vibrations associated with its amino and hydroxyl functional groups. These functional groups are central to the ability of CNW to form hydrogen bonds and to interact with the polyester matrix. As CNW loading increases, the broad absorption band 3324 cm^{-1} gradually increases. At the same time, the relative amount of suspension medium (i.e., ethanol) introduced into the resin also rises with CNW loading. Since ethanol contains free hydroxyl groups, it can facilitate the hydrolysis of the polyester chains during processing. This effect was reflected in the increased intensity of absorption bands at 1419 cm^{-1} and 1579 cm^{-1}, corresponding to the symmetric and asymmetric stretching vibrations of the carboxylate group (COO^{-}). The stronger peaks around these wavenumbers are consistent with hydrolytic cleavage of ester bonds in the polyester. It can be concluded that CNW dispersion not only introduces functional groups from the nanoparticles to facilitate CNW-polyester interaction but also promotes degradation of polyester chains by hydrolysis in the presence of residual ethanol.

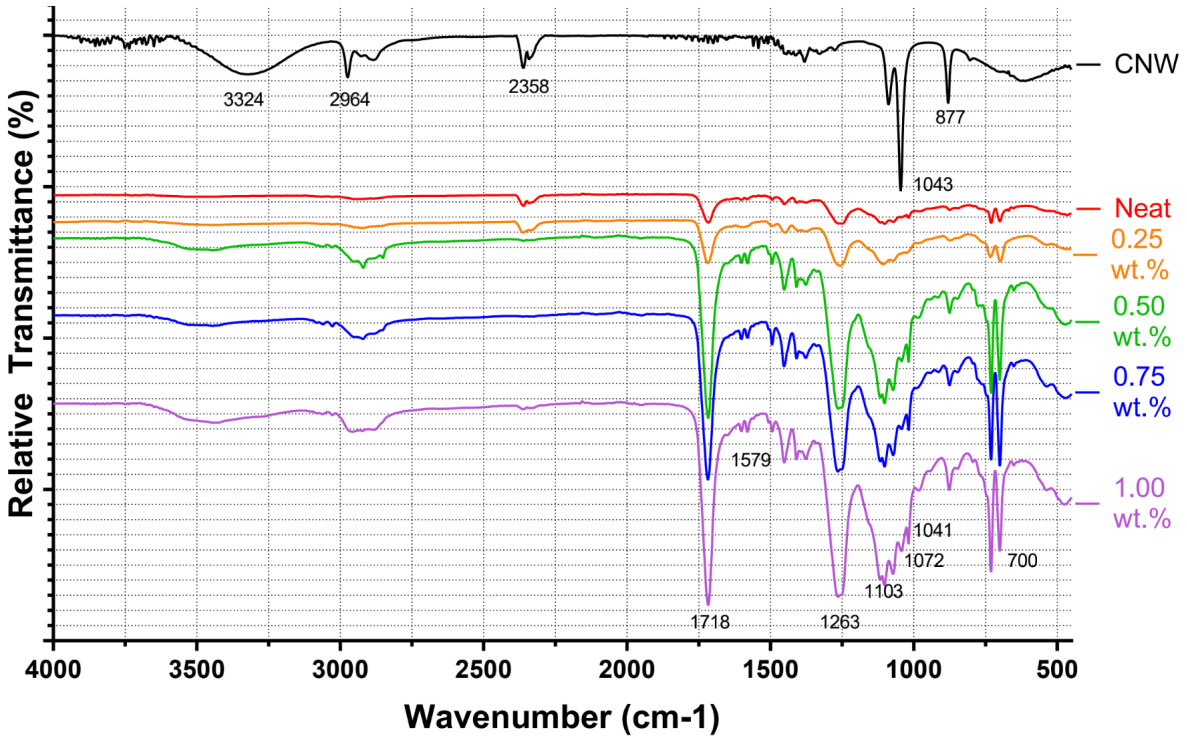

Figure 4.1 FTIR spectra of commercial resin with increasing CNW loadings.

4.1.2 Effects of CNW Loading on the Morphological Properties of CNW-Reinforced Polyester Nanocomposites

Figure 4.2 illustrates the morphology of CNW NPs in their dry state, without the dispersion in a suspension medium. These particles were not uniformly dispersed but instead clustered into agglomerates of varying sizes. This was expected due to the strong hydrogen bonding and interactions among CNW NPs. As a result, individual whisker-like structures were absent, with the CNWs clustering into dense aggregates in dried or powder form. Such agglomeration indicated that the tendency of CNWs to form clusters during processing remains a major challenge, limiting their effectiveness as a reinforcing filler. In order to uniformly disperse CNWs within the polyester matrix, additional processing strategies such as surface modification, ultrasonication, or the use of carefully selected suspension mediums will be needed. The inhomogeneous clustering of CNWs

in varying sizes also suggested the possibility of localized stress concentration. These sites may have acted as initiation points for failure propagation under mechanical loading. Furthermore, agglomeration reduced the effective surface area available for interfacial bonding between CNWs and the polyester resin and thereby suppresses the overall reinforcing capability of the CNWs.

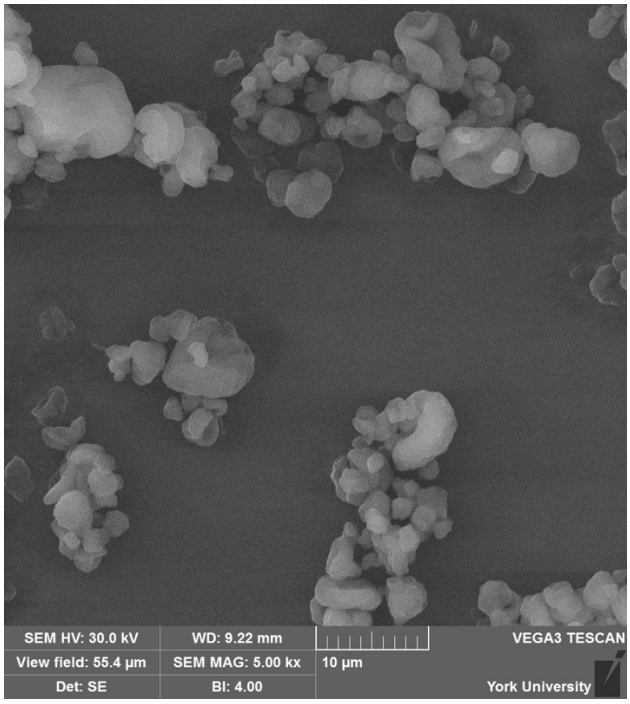

Figure 4.2 SEM micrograph of CNW in dry-powder form.

Figures 4.3 (a) through (e) depict SEM micrographs of cryo-fracture surfaces of CNW-reinforced polyester resin samples at increasing CNW loadings, using ethanol as the suspension medium. The neat resin (Figure 4.3a) exhibited a relatively smooth fracture surface with minimal roughness, which indicated brittle failure. The absence of reinforcing filler particles led to clean fracture surfaces with little evidence of crack deflection or energy absorption, establishing the baseline for comparison with CNW-reinforced polyester systems.

At 0.25 wt.% CNWs (Figure 4.3b), some degrees of CNW clustering are observed across the fracture surface. These agglomerates acted as localized stress concentrator sites and potential crack initiation sites. Despite some degree of CNWs agglomeration being present in the nanocomposites, the SEM micrograph showed a satisfactory dispersion of CNWs, leading to good potential to promote both the thermal and mechanical properties of the adhesive system. Nevertheless, the tendency of CNWs to form can still negatively impact stress transfer efficiency between the filler and resin.

At 0.50 wt.% CNW (Figure 4.3c), the fracture surface showed increased roughness with evidence of microcracks forming around dispersed particles. Moreover, small voids were visible, likely resulting from CNW agglomerates being dislodged during fracture. These features suggested partial reinforcement, as CNWs altered crack paths and promoted greater energy dissipation; however, the microvoids also revealed potentially weak interfacial adhesion between CNWs and polyester resin. Unlike epoxy systems, in which hydroxyl groups can promote hydrogen bonding with CNW, polyester relies on the dipole-dipole force to interact with CNWs. This leads to a higher chance of debonding of CNWs from the matrix and results in interfacial cavities.

At 0.75 wt.% CNWs (Figure 4.3d), larger CNW agglomerates dominated the fracture surface, which confirmed that higher loadings result in significant clustering. While these aggregates may have stiffened the resin locally, they disrupted uniform reinforcement and acted as potential defect sites that compromise mechanical integrity. The further weakening in interfacial bonding caused by larger agglomerates or a smaller surface area-to-volume ratio limited effective stress transfer across the filler-resin interface. This observation indicates that CNW loading beyond a threshold

level may potentially promote significant agglomeration, leading to weaker interfacial bonding and less efficient stress transfer.

At 1.00 wt.% CNWs (Figure 4.3e), a pronounced void is observed where a CNW agglomerate has been lodged. This feature further emphasizes the poor interfacial bonding between the highlights the CNWs and polyester resin when significant clustering occurs. The absence of strong interfacial interaction increases the chance of debonding of CNW from the polyester matrix during fracture. In other words, this may have detrimental effects on both the thermal and mechanical properties of the CNW-reinforced polyester nanocomposites.

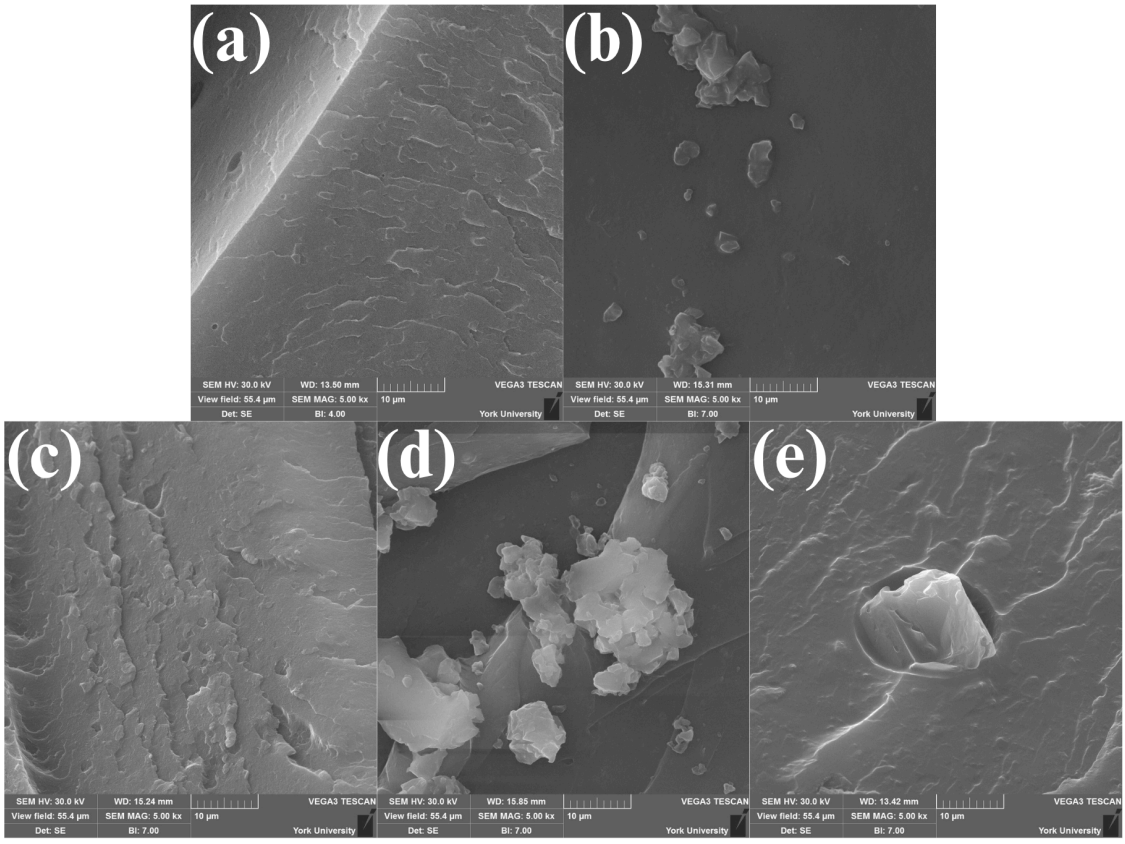

Figure 4.3 SEM micrograph of CNW-reinforced samples containing (a) neat, (b) 0.25 wt.%, (c) 0.50 wt.%, (d) 0.75 wt.%, and (e) 1.00 wt.% CNW loading.

4.1.3 Effects of CNW Loading on the Glass Transition Temperature of CNW-Reinforced Polyester Nanocomposites

Differential scanning calorimetry (DSC) analysis of CNW-reinforced polyester resin revealed a strong dependence of glass transition temperature (T_g) on CNW loadings. Figure 4.4 reveals that the maximum T_g has been achieved with 0.50 wt.% CNW, with a 19.4% improvement over the T_g of the neat sample. In contrast, a further increase in CNW loading suppressed the T_g, with a significant decline at 1.00 wt.% CNW loading. This observation indicated that while the incorporation of CNWs could increase T_g as the interaction between CNW and polyester resin restricts the mobility of polymer chains in the adhesive system, increasing CNW beyond the threshold would lead to a detrimental effect on the thermal properties, indicating hydrolysis due to excessive ethanol introduced in the system. A control study with neat resin subjected to the same thermal history revealed negligible changes in T_g, confirming the observed enhancement is caused by CNW incorporation rather than the thermal history.

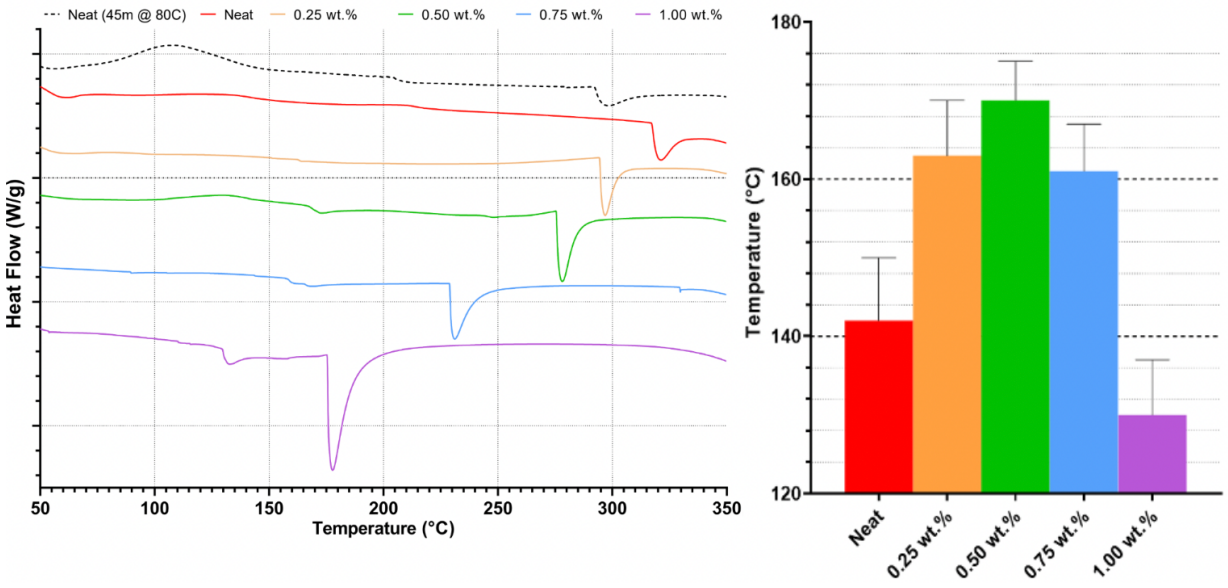

Figure 4.4 DSC thermograms of polyester resin loaded with different CNW loadings (left) and corresponding bar graph of glass transition temperature (right).

In addition to the effect of CNW loading on T_g, DSC scans (Figure 4.4) revealed a distinct endothermic peak associated with the polyester resin (Figure 4.5). The amplitude of this peak increased, and its temperature shifted to lower temperatures with increasing CNW loading. This trend is consistent with ethanol-facilitated hydrolysis of the polyester matrix, as supported by Fourier Transform Infrared (FTIR) analysis. For neat samples, the endothermic peak is likely attributed to chain-scission and initial resin degradation. At higher CNW loadings, residual ethanol from the suspension medium, rich in hydroxyl groups, promoted additional chain cleavage, leading to the formation of lower molecular weight species. The decreasing onset temperature of the endothermic peak is attributed to the lower thermal stability of these shorter chain species, which require less energy to degrade. The simultaneous increase in amplitude suggested that greater quantities of these lower molecular species are produced at higher CNW loadings. This indicated that ethanol-assisted hydrolysis not only altered the resin's molecular structure but also compromised its thermal resistance, with potential consequences for the mechanical integrity of the adhesive. In addition to the influence of ethanol during processing, the observed trend may also be partially attributed to CNW agglomeration and the chemical nature of the chitin surface. At higher loadings, agglomerated CNWs may have created localized regions where hydroxyl and acetamide functional groups are concentrated, increasing the likelihood of hydrolytic interactions with the polyester matrix. These interactions can further catalyze chain scission, resulting in the accelerated formation of low molecular weight species. Therefore, both solvent retention and CWN surface chemistry may act collaboratively to promote hydrolysis and account for shifting and amplification of the endothermic peak. From SEM analysis, it is conclusive that higher CNW loadings led to pronounced agglomeration, which not only caused micro voids or gaps within the resin matrix but also introduced localized sites of thermal instability. These agglomerated regions,

combined with the hydrolytic activity of chitin functional groups, further contributed to the reduced thermal resistance observed in DSC.

The presence of an optimal CNW loading (i.e., 0.50 wt.%) that maximized T_g suggests that there are two competing mechanisms for the incorporation of CNW in polyester resin to influence T_g. On the one hand, the presence of CNW hindered polymer chain mobility in the matrix, leading to higher T_g. On the other hand, increased CNW loading led to excessive residual ethanol, promoting polyester chain cleavage through hydrolysis reaction during processing and thereby reducing T_g. Beyond 0,50 wt.% CNW loading, the excessive ethanol retention and the resultant polyester hydrolysis became a more dominating factor than CNW-polyester interaction to the nanocomposite's thermal properties. As a result, T_g decreased as the CNW loading increased from 0.50 wt.% to 1.00 wt.%.

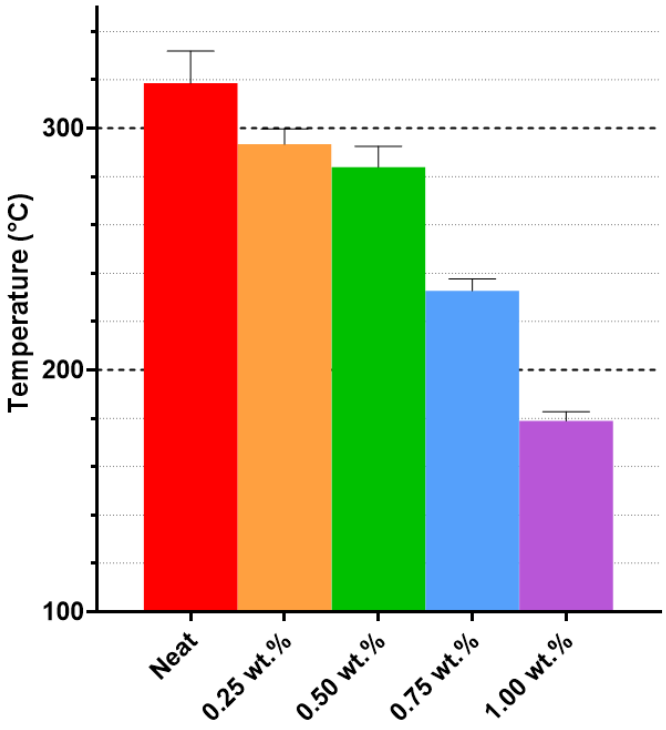

Figure 4.5 DSC bar graphs of onset temperature of characteristic endothermic peak.

A one-way ANOVA confirmed that CNW loading had a statistically significant influence on both T_g and the onset temperature of the endothermic peak. For T_g, the effect was highly significant ($F(5,32) = 33.51$, $p < 0.0001$). For the onset temperature of the endothermic peak, the effect was also highly significant ($F(5,18) = 139.6$, $p < 0.0001$). These results validated the observed thermal trends and confirmed that CNW loading, together with ethanol-facilitated hydrolysis, governs the balance between reinforcement and degradation in CNW-reinforced polyester nanocomposite adhesives.

4.1.4 Effects of CNW Loading on the Thermal Stability of CNW-Reinforced Polyester Nanocomposites

Figure 4.3 illustrates the thermographs of neat polyester resin and its CNW-reinforced nanocomposites obtained by thermogravimetric analysis (TGA) as well as the onset temperature of thermal degradation. It revealed a progressive decrease in the thermal degradation onset temperature as CNW loading increases. The neat polyester resin exhibited the highest onset temperature, at approximately 344 °C, whereas the addition of CNWs reduced the onset temperature to approximately 342 °C at 0.25 wt.% CNW loading and further to about 340 °C at 0.50 wt.% CNW loading. Beyond 0.50 wt.% CNW loading, the decline in the onset temperature with further increase in CNW loading appeared to plateau, with the 0.75 and 1.00 wt.% composites both stabilizing near 338°C and 336°C, respectively. This trend indicated that the addition of CNWs consistently reduced the thermal stability of the polyester resin, with the most pronounced effect occurring at lower CNW loading.

The reduction in thermal degradation onset temperature can be attributed to several potential mechanisms. A larger amount of residual ethanol from suspension medium exists at higher CNW

loadings. Its volatilization during heating lowers the apparent degradation onset. The CNWs are polysaccharide-based nanoparticles with lower intrinsic thermal stability than polyester. Therefore, their early decomposition contributed to additional mass loss. Hydroxyl and amine groups on CNWs may have also catalyzed chain cleavage reactions, weakening the polyester network during heating. Furthermore, at higher CNW loadings, CNWs tend to agglomerate, which creates localized inhomogeneous sites and increased porosity, thereby creating more reactive sites that increase the rate of thermal degradation. In short, these combined effects explain the progressive decline in onset temperature. The plateau beyond 0.50 wt.% CNW loading suggested that once sufficient CNW and residual ethanol are present, further additions did not significantly promote thermal instability.

The TGA findings are strongly supported by the FTIR and DSC results. FTIR analysis revealed the growth of COO^{-} related peaks (i.e., 1419 cm^{-1} and 1579 cm^{-1}) as CNW loading increased. This indicated polyester hydrolysis facilitated by ethanol and surface functionalities of CNWs. This interpretation was further strengthened by the DSC analysis, showing that T_g maximized at 0.50 wt.% CNW loading and declined as CNW loading further increased. The larger endothermic peak was also consistent with the chain cleavage and thereby a larger amount of lower molecular weight species. Finally, the TGA results confirmed that the promoted hydrolysis-driven chain cleavage with higher CNW loading not only reduced T_g but also negatively impacted the thermal stability of the nanocomposites.

Statistical analysis further supported these conclusions. A one-way ANOVA confirmed that CNW loading had a statistically significant effect on the thermal degradation onset temperature ($F(5,22) = 1323$ and $p < 0.0001$). Altogether, the FTIR, DSC, and TGA results presented a coherent

interpretation. A larger amount of residual ethanol and CNW surface functionalities promoted polyester hydrolysis, which in turn suppressed thermal stability.

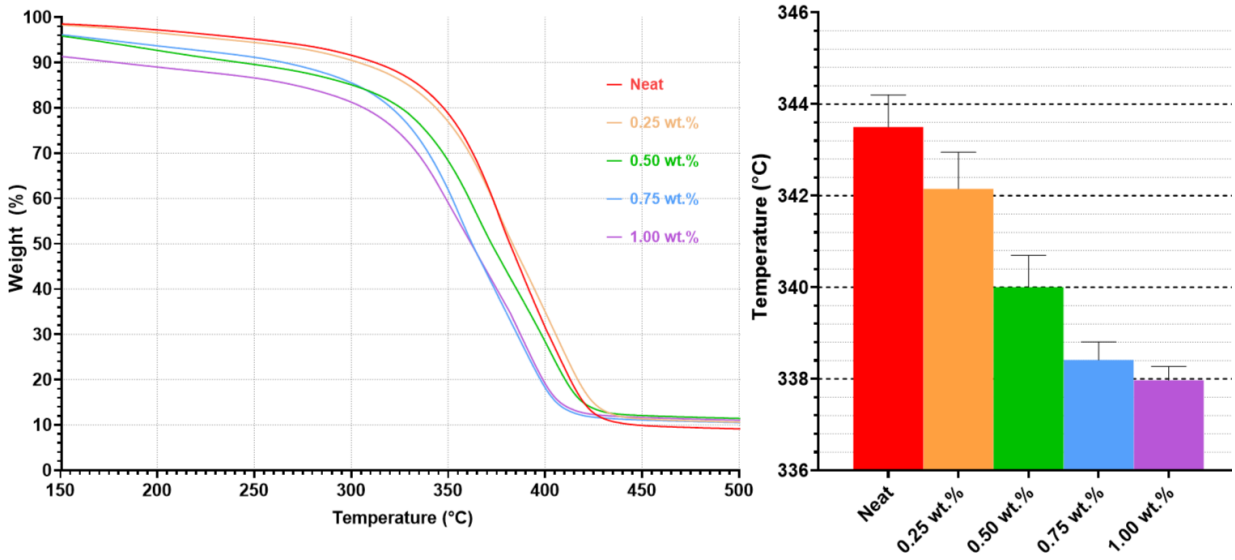

Figure 4.6 TGA thermogram of polyester resin with increasing CNW loadings (left) and corresponding bar graph of degradation onset temperature (right).

4.1.5 Effects of CNW Loading on the Tensile Properties of CNW-Reinforced Polyester Nanocomposites

The stress-strain responses revealed a clear reinforcing effect of CNW addition, particularly at low to moderate loadings (i.e., ≤0.50 wt.%). Figure 4.7 shows the tensile strength and elastic modulus of the reinforced nanocomposites. The addition of 0.25 wt.% CNW loading increased tensile strength by 15.9% and elastic modulus by 40.0% relative to the neat commercial resin subjected to the same thermal history as the nanocomposites. The results demonstrated that even small amounts of CNWs can significantly enhance load-bearing capability. The neat polyester resin exhibited a tensile strength of 43.51 MPa, whereas the composite sample reinforced with

0.50 wt.% CNW achieved a maximum tensile strength of 52.96 MPa. This improvement demonstrates the reinforcing effect of CNWs, which is attributed to the high intrinsic tensile strength of the CNWs (i.e., 1.5 to 3 GPa) and their ability to act as a nanoscale stress distributor to delay the onset of failure; however, beyond 0.50 wt.% of CNW loading, the reinforcing benefits began to diminish. This reduction in tensile properties at higher concentration was most likely due to CNW agglomeration, as shown in the SEM micrographs in Figure 4.3. This non-uniform CNW dispersion introduces stress concentrators and disrupts the continuity of the polyester matrix. These agglomerates hindered efficient stress transfer and reduced the effective surface area available for matrix–filler interactions. Furthermore, the ethanol-driven hydrolysis of the polyester matrix with higher CNW loading also played a significant role in the significantly deteriorated tensile properties. A similar trend was observed in the thermal analysis, where CNW dispersion at moderate loadings contributed to chain restriction, but excessive loadings promoted heterogeneities and hydrolytic degradation.

A one-way ANOVA confirmed that the effect of CNW loading on tensile strength was highly significant ($F(5,35) = 35.04$ and $p < 0.0001$). These results support that low to moderate CNW loadings (i.e., 0.25 to 0.50 wt.%) yield an optimal balance by maximizing dispersion and reinforcing efficiency. In contrast, higher CNW loadings compromised mechanical integrity through filler aggregation and ethanol-driven polyester hydrolysis. These findings emphasized the importance of carefully optimizing CNW loading to leverage their reinforcing potential without suppressing uniform dispersion and structural integrity of the polyester network. It also suggested the need to develop strategies to optimize the thermal processing and suspension medium to minimize the ethanol-driven hydrolysis of polyester during the nanocomposite processing.

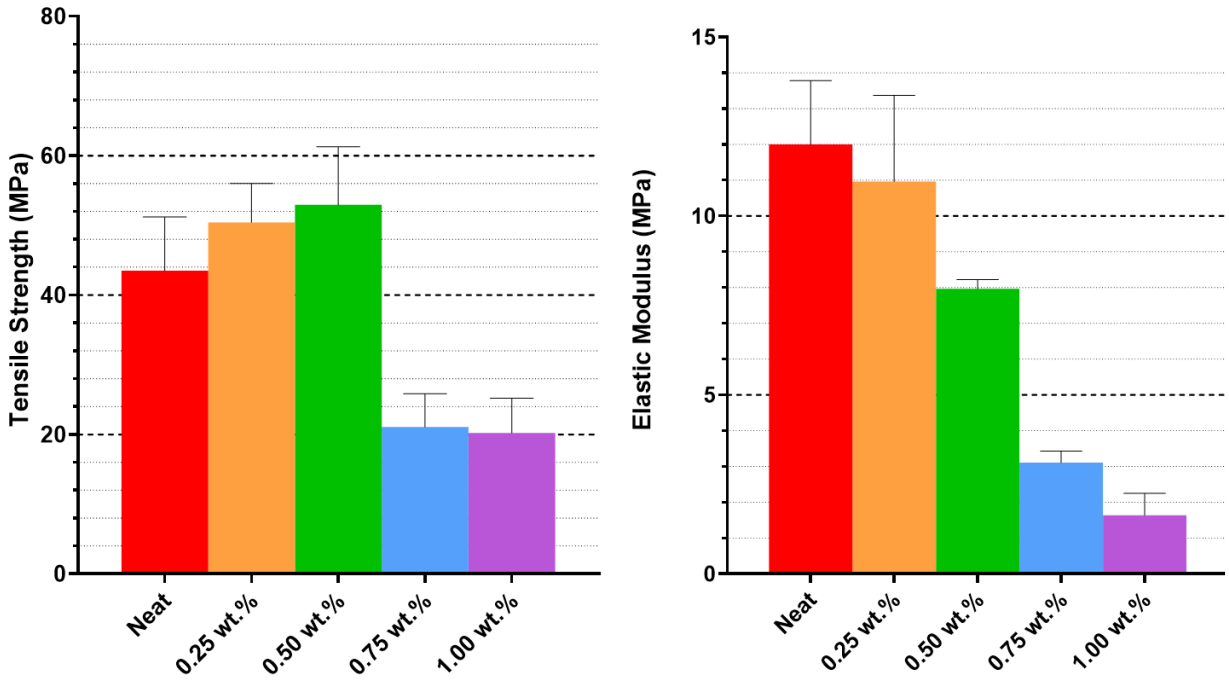

Figure 4.7 Bar graphs of commercial resins with increasing CNW loadings, indicating tensile strength (left), and elastic modulus (right).

Table 4.1 identifies that the incorporation of CNWs leads to a notable increase in elongation at break of the CNW-reinforced polyester resin, indicating improved ductility and strain tolerance compared to the neat resin. The neat resin exhibited an elongation at break of 2.55 mm, while the addition of 0.25 wt.% CNW increased elongation at break to 3.36 mm. A more substantial improvement was observed at 0.50 wt.% CNW, where elongation at break nearly doubled to 5.08 mm. This enhancement reflected the ability of CNWs to act as nanoscale stress-transfer bridges within the polymer matrix, distributing applied loads more evenly and delaying the onset of fracture. Beyond simple stress transfer, CNWs likely contributed to fracture resistance by promoting crack-bridging and crack-deflection mechanisms. The whisker-like morphology of CNWs allowed them to span developing microcracks, hindering crack propagation and forcing

crack paths to deviate. This increased the energy required for crack advancement and allowed the material to sustain greater strain before catastrophic failure. The resulting toughening effect explains the sharp improvement in elongation at break up to 0.50 wt.% CNW.

At higher CNW loadings (0.75 wt.% and 1.00 wt.%), elongation at break plateaued at approximately 5.12 and 5.15 mm, respectively. This plateau suggested that a saturation threshold was reached, beyond which additional CNW content did not significantly enhance ductility. Agglomeration at elevated loadings may have also reduced the number of effective crack-bridging sites, while simultaneously introducing stress concentration points that counteract further gains.

Table 4.1 Elongation at break of tensile samples with increasing CNW loadings.

Sample	**Elongation at Break (mm)**
Neat	2.55
0.25 wt.% CNW	3.36
0.50 wt.% CNW	5.08
0.75 wt.% CNW	5.12
1.00 wt.% CNW	5.15

Together with the tensile strength results, these findings suggested 0.50 wt.% CNW as a potential optimal loading to balance strength and ductility. At this concentration, CNWs provide effective reinforcement by improving stress transfer, promoting crack deflection and bridging microcracks. In contrast, at CNW loading higher than 0.50 wt.%, aggregation and ethanol-driven hydrolysis undermined these mechanisms, leading to diminishing improvements. These results highlight the dual role of CNWs in polyester nanocomposites: not only as reinforcements that

improve strength, but also as ductility enhancers that increase toughness and energy absorption under tensile stress.

4.1.6 Effects of CNW Loading on the Adhesive Strength of CNW-Reinforced Polyester Nanocomposites

Single-lap shear testing revealed a non-linear response of adhesive strength on CNW content within the polyester resin matrix. The neat resin exhibited a baseline adhesive strength of 4.50 MPa. At 0.25 wt.% CNW, a modest increase to 4.97 MPa was observed, suggesting that low CNW loadings can marginally enhance interfacial bonding, potentially by increasing surface energy or mechanical interlocking at the bonded interface. However, this initial improvement was not sustained as CNW loading continued to increase. At 0.50 wt.% and 0.75 wt.% CNW loadings, adhesive strength dropped to 3.74 MPa and 3.12 MPa, respectively, before showing a slight recovery (i.e., 3.56 MPa) at 1.00 wt.% CNW loading. This progressive decline reflects the challenges of NP dispersion at higher loadings, where agglomeration introduced interfacial defects as shown in the SEM micrographs (Figure 4.3). Such interfacial defects reduced substrate wetting and disrupted cohesive interactions within the adhesive layer. Furthermore, residual ethanol from the CNW suspension medium may have contributed to hydrolytic degradation of the polyester matrix, weakening its cohesive strength.

Examining failure modes across all samples revealed a combination of adhesive and cohesive failures. Adhesive failure refers to separation occurring at the interface between the adhesive and the substrate, indicating weaker interfacial bonding. In contrast, cohesive failure occurs within the adhesive layer itself, suggesting the adhesive material was weaker than the bond with the substrate. The coexistence of both failure modes indicates that bonding efficiency is governed not only by

adhesion to the substrate but also by the structural integrity of the nanocomposite adhesive system. As CNW loading increased, the prevalence of cohesive failure suggested that both ethanol-facilitated hydrolysis and CNW agglomeration contributed to the suppressed integrity of the adhesive phase.

A one-way ANOVA confirmed that CNW loading had a statistically significant effect on adhesive strength ($F(5,28) = 15.20$ and $p < 0.0001$). This result validates the observed non-linear trend, where low CNW content slightly improved adhesion, but higher loadings led to a marked reduction due to poor dispersion and matrix degradation. The statistical significance reinforces that these variations are not due to random error but are directly linked to CNW loadings, which are governed by the competition of filler reinforcement, dispersion challenges, and matrix degradation.

More importantly, by comparing the experimental results of adhesive strength to those of the tensile and elongation at break, it clearly demonstrated that CNW reinforcement benefits more on bulk mechanical properties than on interfacial adhesive performance. At 0.50 wt.% CNW loading, tensile strength and ductility revealed maximum improvements because of effective stress transfer and crack deflection within the polymer matrix. In contrast, adhesive strength peaked only at 0.25 wt.% before declining over higher CNW loadings. The difference in optimal CNW loadings suggests that the interface is more sensitive to dispersion quality and ethanol-induced hydrolysis than the bulk material. In other words, optimization of CNW content must account not only for reinforcement of the matrix but also for interfacial bonding in adhesive applications.

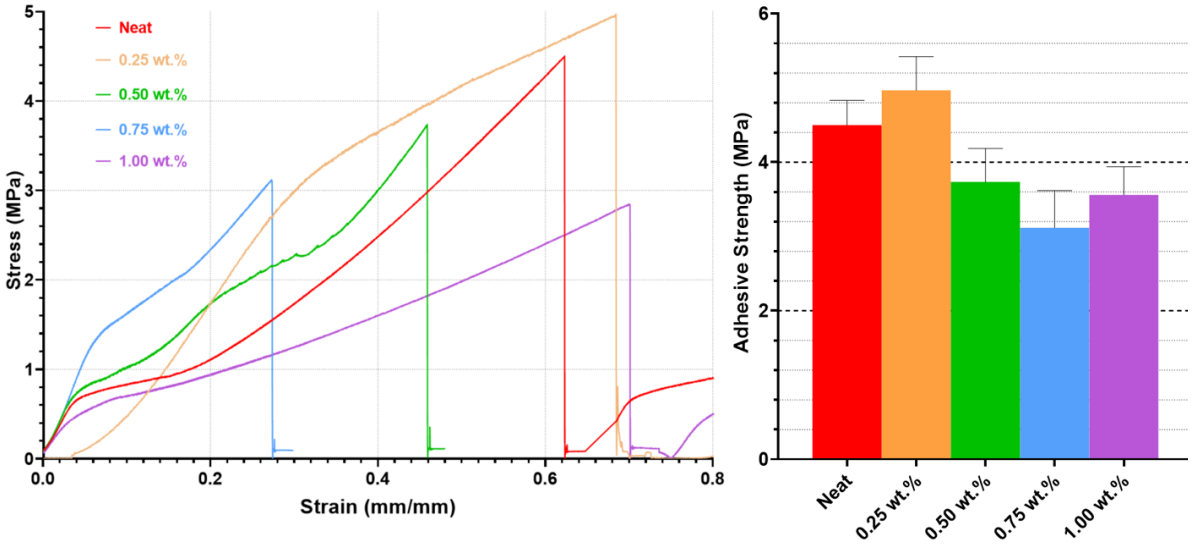

Figure 4.8 Adhesive property curve of commercial resins with increasing CNW loadings (left) and bar graph of adhesive strength (right).

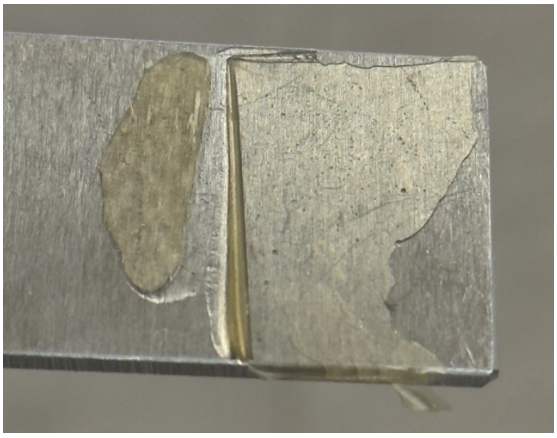

Figure 4.9 Residual resin from single-lap shear test indicating combination of adhesive and cohesive failure of the resin.

4.2 Effects of Thermal History on CNW-Reinforced Polyester Adhesives

To isolate the effects of CNW incorporation from those induced solely by the processing conditions, a thermal history analysis was conducted on the neat commercial polyester resin. This

step was necessary because the introduction of CNWs into the resin system required the use of a solvent-based suspension medium (primarily ethanol), which had to be fully evaporated prior to curing. As CNW loading increased, the volume of suspension medium introduced into the system also increased proportionally. This necessitated greater thermal input to ensure complete solvent removal, due to both the increased solvent mass and the higher cumulative latent heat of vaporization. To understand how this additional heating might have independently influenced the resin's thermal behaviour, a set of neat resin samples was subjected to the same heating protocol as those containing CNWs. These control samples allowed for a direct comparison between thermally conditioned neat resin and CNW-reinforced samples. 0.25 wt.% CNW was selected for a comparative analysis based on preliminary results, which indicated that 0.25 wt.% CNW offered the most balanced enhancement in thermomechanical properties with minimal adverse effects from ethanol retention or thermal degradation. At this concentration, the CNWs demonstrated strong interfacial interaction with the resin matrix, leading to noticeable improvements in thermal stability and mechanical performance, without introducing excessive viscosity or agglomeration during processing. Additionally, 0.25 wt.% CNW served as a conservative yet effective benchmark for comparing the impact of dispersion medium and thermal history on composite behaviour, providing a clear and consistent reference point across all experiments.

4.2.1 Effects of Thermal History on the Chemical Structures of CNW-Reinforced Polyester Nanocomposites

An analysis was conducted on the chemical structure for both neat and CNW-reinforced polyester resin samples (0.25 wt.% CNW), in different conditions, including unheated, heated at 80 °C for 45 minutes, and heated at 60 °C for 90 minutes. FTIR spectroscopy revealed that all neat

samples were nearly identical, showing no notable shifts or changes in peak intensity. This indicated that thermal processing / treatment did not alter the chemical structure of the polyester resin despite chain scission. Similarly, 0.25 wt.% CNW samples under the same heating conditions exhibited insignificant variations in the intensity of ethanol-related peaks, depending on the extent of the heating.

4.2.2 Effects of Thermal History on the Morphological Properties of CNW-Reinforced Polyester Nanocomposites

SEM analysis was not conducted on samples used in the thermal history study, as the primary objective of that investigation was to isolate the effects of thermal exposure on the bulk thermal and mechanical properties of the resin system. Since no changes were made to CNW content or dispersion strategy in these samples, and no additional nanoparticles were introduced, morphological examination was not expected to yield meaningful differences. Therefore, SEM imaging was reserved for samples where dispersion quality, nanoparticle interaction, and microstructural features were directly influenced by processing variables such as suspension medium or CNW concentration.

4.2.3 Effects of Thermal History on the Glass Transition Temperature of CNW-Reinforced Polyester Nanocomposites

DSC was utilized to investigate the effects of thermal processing conditions and their influences on the T_g and other observed thermal behaviours of both neat and 0.25 wt.% CNW-reinforced PR systems, as presented in Figure 4.10. The neat resin samples were subjected to different heating conditions (i.e. unheated, heated at 80 °C for 45 minutes, and heated at 60 °C for 1.5 hours) and

exhibited minimal variation in T_g with values of 142.0 °C, 141.2 °C, and 139.9 °C, respectively. A one-way ANOVA confirmed that these differences were statistically significant ($F(2,12) = 15.06$, $p = 0.0005$), though the magnitude of change was small, suggesting that the polyester matrix was thermally stable under the heating durations used. In contrast, 0.25 wt.% CNW-reinforced samples exhibited more substantial changes in T_g, depending on the extent of heating. The unheated sample, which retained ethanol from the suspension medium, demonstrated the highest T_g at 162.0 °C, followed by 163.2 °C for the sample heated at 80 °C for 45 minutes, and a reduced T_g of 150.1 °C after 1.5 hours at 60 °C. These results suggested that the shorter, higher-temperature heating effectively removed more residual ethanol without significantly disrupting the CNW interactions with the PR. Prolonged low-temperature heating may have increased molecular mobility or promoted degradation. A one-way ANOVA confirmed these differences were statistically significant ($F(2,12) = 8.55$, $p = 0.0049$). In addition to T_g, the presence and behaviour of the characteristic endothermic peak varied significantly across conditions. The endothermic peak, which was associated with chain relaxation, residual solvent effects, or hydrolysis-induced changes, was observed in neat samples. The peak shifted from 321.0 °C in the unheated sample to 254.8 °C and 256.1 °C after heating at 80 °C and 60 °C, respectively. The decline in peak temperature reflected a loss of residual ethanol and potentially chain scission within the PR. A one-way ANOVA confirmed this difference was highly significant ($F(2,12) = 106.7$, $p < 0.0001$). Among the 0.25 wt.% CNW-reinforced samples, an opposite trend was observed. The unheated sample exhibited a lower endothermic peak of 232.6 °C, which increased to 254.4 °C and 276.9 °C with increasing thermal treatment. This suggested that ethanol retained in the unheated sample may have facilitated hydrolysis or disrupted polymer crosslinking, while the heated sample had reduced solvent content and a more stable composite structure. A

one-way ANOVA confirmed that the differences were statistically significant ($F(2,12) = 55.02$, $p < 0.0001$). These findings demonstrated that thermal history affected not only solvent retention but also the structural and thermal behaviour of CNW-reinforced polyester resins. It is observed that the duration and intensity of heating during processing were sensitive when subjecting PRs to any heating. Controlled thermal processing is therefore critical for optimizing material performance while minimizing solvent and thermal-related degradation effects.

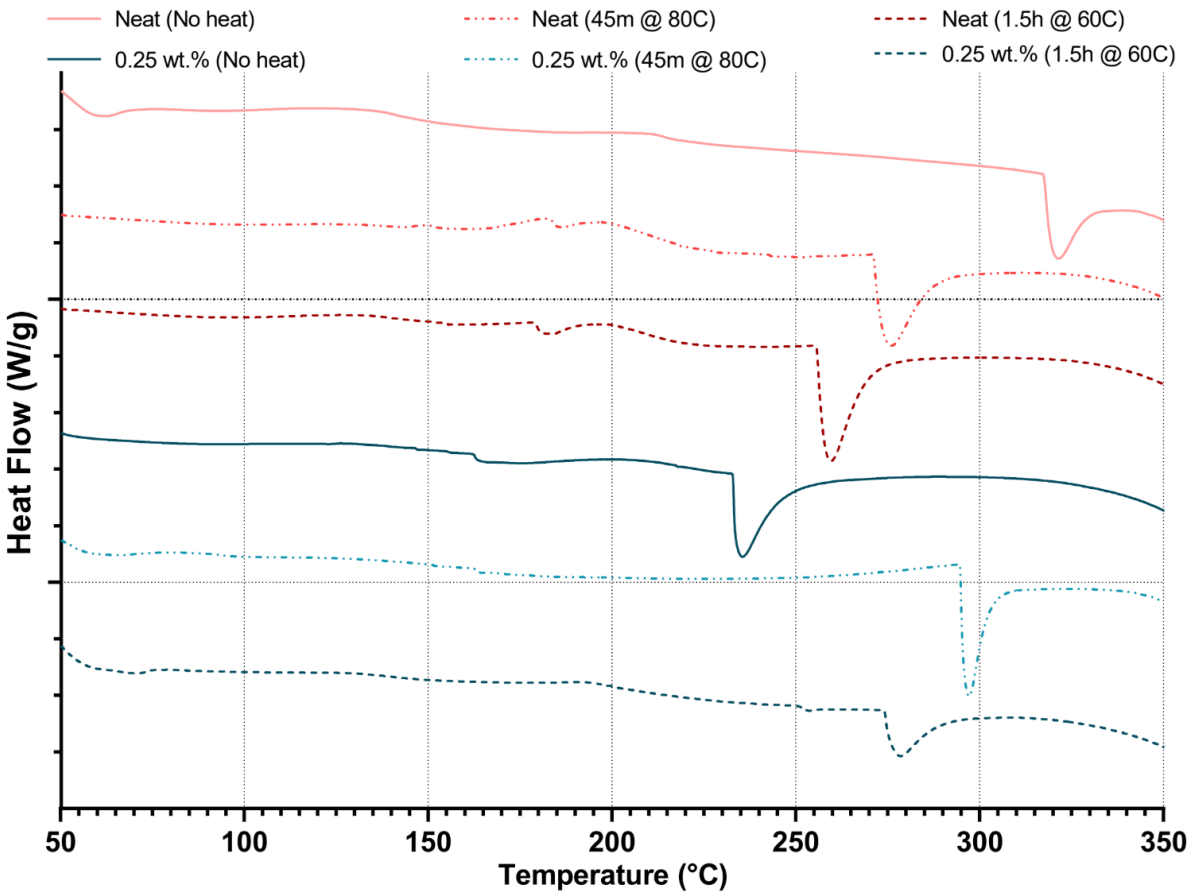

Figure 4.10 DSC thermograms of polyester resin with various thermal history in both neat and 0.25 wt.% CNW loadings.

4.2.4 Effects of Thermal History on the Thermal Stability of CNW-Reinforced Polyester Nanocomposites

Figure 4.11 illustrates TGA results that evaluated how thermal processing influences the degradation onset temperature of both neat and 0.25 wt.% CNW-reinforced PR systems. In the neat resin, the degradation onset temperature decreased from 343.5 °C in the unheated sample to 326.7 °C after heating at 80 °C for 45 minutes and 325.9 °C after 1.5 hours at 60 °C. A one-way ANOVA confirmed that these reductions were statistically significant ($F(2,12) = 35.97$, $p < 0.0001$), indicating that prolonged or elevated thermal exposure may initiate minor degradation that reduces the thermal resistance. For 0.25 wt.% CNW-reinforced samples, the variation in degradation onset temperature was more distinct. The unheated samples containing ethanol degraded at 323.3 °C, while heating at 80 °C for 45 minutes, degraded later at 342.2 °C. The samples that were heated at 60 °C for 1.5 hours led to a further decrease to 315.1 °C. A one-way ANOVA confirmed that these results were statistically significant ($F(2,12) = 20.47$, $p = 0.0001$). The results suggested that moderate heating is effective at removing residual solvent and stabilizing the resin, compared to extended low-temperature heating, which may have promoted hydrolysis and reduced thermal stability. Overall, these findings indicate the importance of optimizing thermal treatment during processing to balance solvent removal while minimizing thermal effects to PRs when incorporating CNW particles.

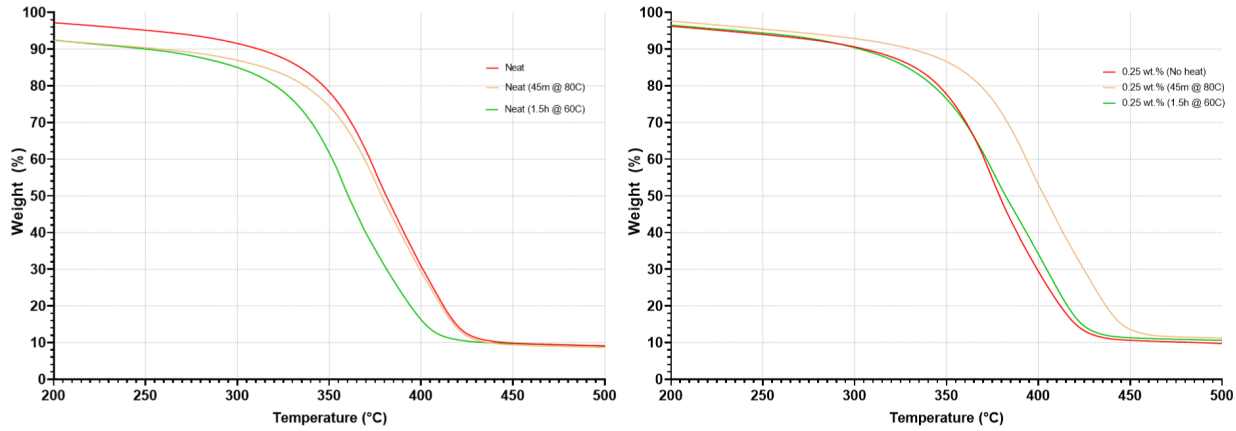

Figure 4.11 TGA thermogram of commercial resin with various thermal history in both neat (left) and 0.25 wt.% CNW loadings (right).

4.2.5 Effects of Thermal History on the Tensile Properties of CNW-Reinforced Polyester Nanocomposites

Tensile testing was conducted to evaluate the influence of thermal processing on the mechanical performance of neat and 0.25 wt.% CNW-reinforced PR systems. Table 4.2 presents the tensile strength, elastic modulus, and elongation at break for both neat and 0.25 wt.% CNW loadings at different processing temperatures and duration. For the neat resin, tensile strength significantly decreased with heating from 43.5 MPa with no heating to 33.0 MPa after 45 minutes at 80 °C and further decreased to 25.9 MPa after 90 minutes at 60 °C. A one-way ANOVA confirmed these differences to be statistically significant ($F(2,14) = 9.02$, $p = 0.0030$), indicating that thermal exposure negatively impacted the load-bearing capacity of the neat resin. Similarly, the elastic modulus decreased from 12.1 MPa to 10.2 MPa under prolonged heating, suggesting reduced stiffness due to potential softening or degradation of the polymer matrix. The elongation at break similarly decreased progressively from 2.55 mm under no heating to 1.66 mm with 1.5 hours of heating at 60 °C, indicating that applying a thermal history reduced ductility and increased

brittleness. In contrast, 0.25 wt.% CNW-reinforced samples demonstrated improved mechanical properties depending on the heating applied. The samples heated for 45 minutes at 80 °C demonstrated the highest tensile strength at 50.4 MPa, compared to 38.6 MPa for the unheated resin with residual ethanol and 36.9 MPa for the samples heated for 1.5 hours at 60 °C. A one-way ANOVA indicated a significant difference between groups ($F(2,12) = 15.01$, $p = 0.0005$). This improvement suggested that moderate heating facilitated improved dispersion without causing significant degradation. It is important to note that the elastic modulus peaked at 11.0 MPa in the samples heated for 45 minutes, while the samples with no heating had the lowest at 10.5 MPa. It is possible to conclude that load transfer or phase interactions between the CNW and polyester resin were affected by the thermal processing and hydrolytic effects. Overall, these results demonstrate that thermal processing can either deteriorate or enhance mechanical performance depending on CNW incorporation. While neat resin becomes more brittle and weaker with heating, CNW-reinforced systems benefit from controlled thermal exposure, particularly short-duration, high-temperature treatments that promote improved tensile strength and dispersion.

Table 4.2 Mechanical properties of tensile test samples with varying thermal history.

Sample		**Tensile Strength (MPa)**	**Elastic Modulus (MPa)**	**Elongation at Break (mm)**
Type	**Heating**			
Neat	No heat applied	43.5	12.1	2.55
	45 mins @ 80 °C	33.0	10.4	2.04
	90 mins @ 60 °C	25.9	10.2	1.66
0.25 wt.% CNW	No heat applied	38.6	10.5	3.12
	45 mins @ 80 °C	50.4	11.0	3.36
	90 mins @ 60 °C	36.9	10.8	3.05

4.2.6 Effects of Thermal History on the Adhesive Strength of CNW-Reinforced Polyester Nanocomposites

The adhesive strength of both neat and 0.25 wt.% CNW-reinforced PRs were evaluated using a single-lap shear test to assess the influence of thermal history. Figure 4.12 identifies the adhesive strength for neat and 0.25 wt.% CNW loadings, respectively. For the neat resin, the adhesive strength decreased from 4.50 MPa to 4.07 MPa when subjected to 45 minutes of heating at 80 °C. The adhesive strength further decreased to 4.02 MPa after heating for 1.5 hours at 60 °C. A one-way ANOVA revealed these differences were statistically significant ($F(2,14) = 62.52$, $p < 0.0001$), indicating that prolonged or elevated heating may reduce cohesive bonding or affect the integrity of the cured adhesive layer. In the 0.25 wt.% CNW systems, the adhesive performance was more sensitive to thermal treatment. The unheated sample, which retained residual ethanol from the suspension medium, demonstrates the lowest adhesive strength at 2.97 MPa, possibly due to a lack of solvent removal and weak interfacial bonding. In contrast, heating the mixture at 80 °C for 45 minutes resulted in a significant improvement to 4.97 MPa. This suggested that moderate thermal heating effectively removed residual solvent and enhanced CNW dispersion, which promoted stronger interfacial adhesion. Heating for 1.5 hours at 60 °C led to a slight reduction in strength to 4.14 MPa, possibly due to overexposure to thermal conditions. A one-way ANOVA confirmed a statistically significant effect of thermal history ($F(2,12) = 15.01$, $p = 0.0005$).

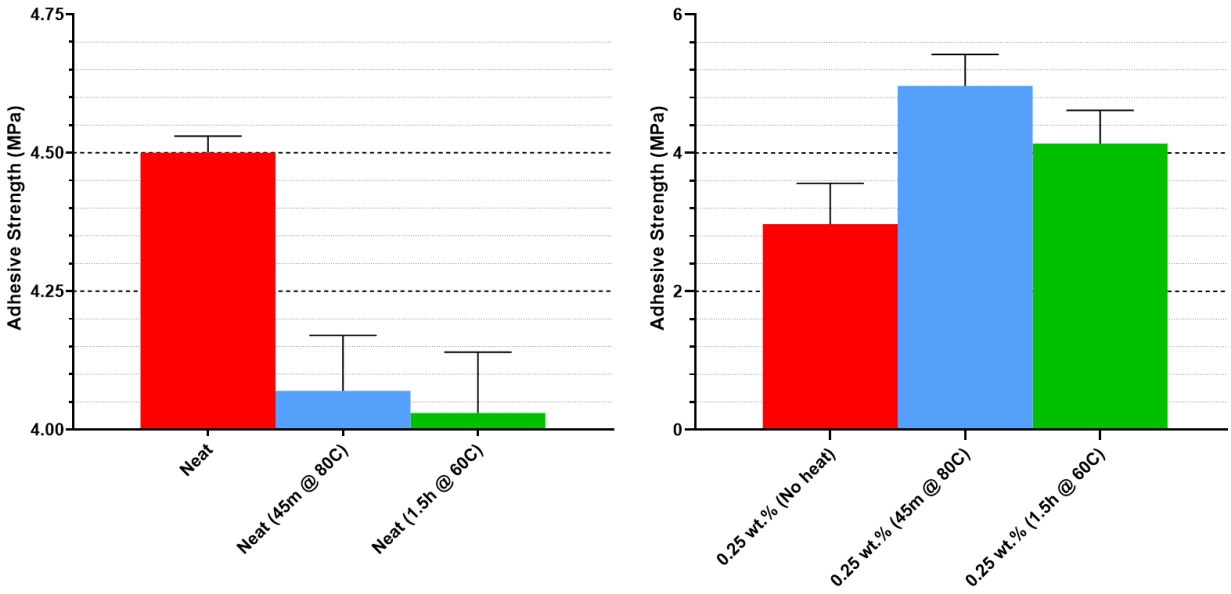

Figure 4.12 Adhesive strength bar graph of commercial resin with various thermal history in both neat (left) and 0.25 wt.% CNW loadings (right).

All thermal history adhesive samples exhibited a similar combination of adhesive and cohesive failure to the loading analysis adhesive samples during single-lap shear testing. This consistent failure pattern across all compositions indicated that while CNW reinforcement and thermal history influenced adhesive strength, the fundamental failure mechanism remained unchanged. The presence of cohesive failure suggested that the internal strength of the resin matrix played a dominant role, while the adhesive component reflected the interfacial interaction between the bonded surfaces and the cured resin. These results underscore the importance of optimized heating protocols for maximizing adhesive performance, particularly in solvent-processed CNW-reinforced systems.

4.3 Effects of Suspension Medium Choice on CNW-Reinforced Polyester Adhesives

To evaluate the effectiveness of various suspension media on CNW dispersion within a polyester resin system, a range of solvent systems was investigated. Each system was used to prepare suspensions at a fixed CNW loading of 0.25 wt.%, selected based on prior findings that indicated it provided the most pronounced enhancement in properties while minimizing the negative effects associated with thermal processing. This approach enabled a comparative analysis of how different solvent environments influenced CNW dispersion and subsequent resin performance. The suspension media included pure ethanol (denoted by 'CE25'), pure acetone (denoted by 'CA25'), an ethanol / acetone mixture (denoted by 'CEA25'), and an ethanol / acetone / methyl ethyl ketone (denoted by 'CEAM25') mixture. The samples prepared by the novel methodology of incorporating CNW nanoparticles, without the use of a suspension medium, are denoted by 'CP25'.

4.3.1 Effects of Suspension Medium Choice on the Chemical Structures of CNW-Reinforced Polyester Nanocomposites

Figure 4.13 shows the FTIR spectra of the commercial polyester resin and the CNW-reinforced resin samples prepared using various suspension media. As discussed in the spectrum of the neat polyester resin displayed prominent peaks in Section 4.1.1, the neat polyester resin displayed prominent peaks in the range of 2950 cm^{-1}, attributed to C–H stretching of aliphatic groups present in both the polyester matrix and styrene diluent. A sharp band near 1718 cm^{-1} corresponded to the stretching vibration of the ester carbonyl group, characteristic of the polyester backbone. The presence of aromatic styrene structures was confirmed by C=C stretching bands observed between 1400 and 1600 cm^{-1}, as well as distinct =C-H bending vibrations near 700-710 cm^{-1} and 730-750

cm^{-1}, indicating monosubstituted benzene and disubstituted benzene rings, respectively. The CNW-incorporated samples utilized different variations of suspension media, demonstrated sharper signals near 1715 cm^{-1}, overlapping with the polyester peak and suggested traces of residual ketone solvents. Additionally, a medium-intensity peak was observed at 1375 cm^{-1} and a broader C-H stretch between 2940-2960 cm^{-1} was observed in the acetone-processed samples, which corroborated with known acetone properties. CEAM25 samples exhibited similar trends, demonstrating a broad band between 2930-2960 cm^{-1}, indicating carbonyl and methyl / ethyl C-H stretching, which is associated with possible incomplete solvent removal or altered resin-CNW interactions. Solvent effects were also observed in the aromatic ring region with styrene-associated peaks near 700-740 cm^{-1} across all formulations, with stronger signals appearing in acetone and MEK samples. Importantly, no peak was detected at 1800 cm^{-1} in any sample, indicating the absence of anhydrides, acid chlorides, or other high-energy carbonyl groups. This suggests that the resin was well cured, and no aggressive degradation or hydrolytic byproducts were introduced during solvent evaporation or CNW incorporation.

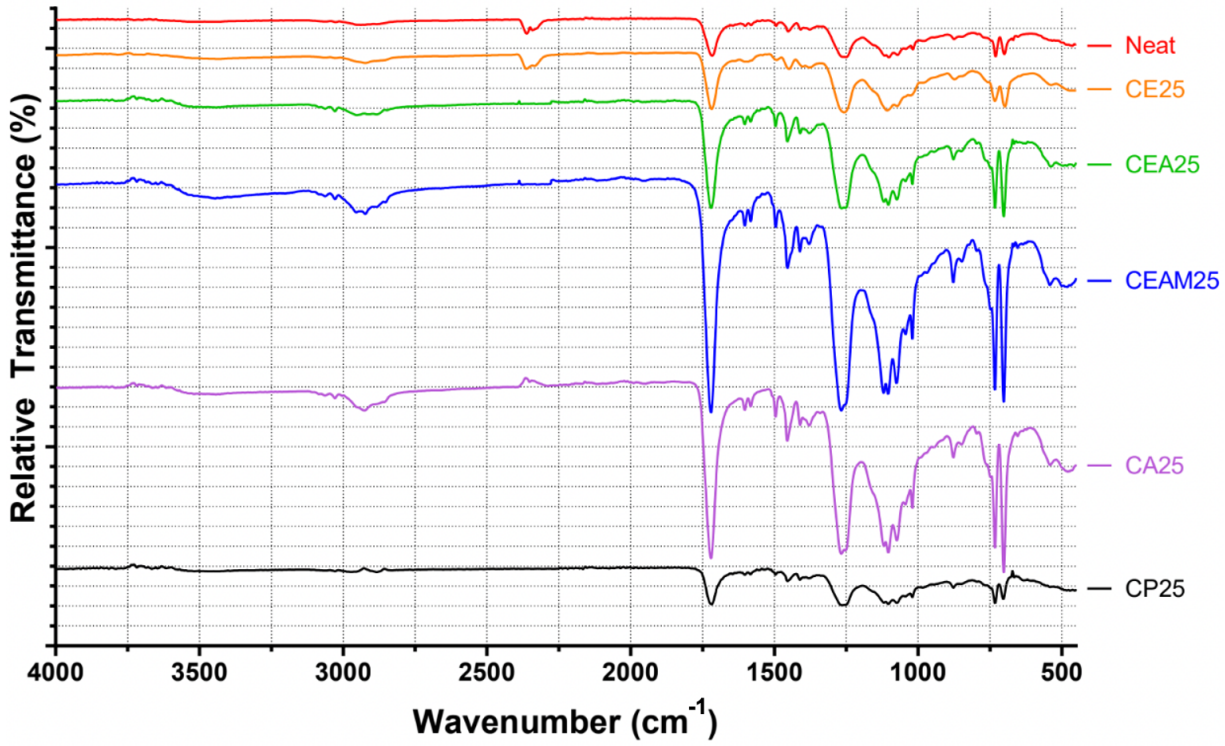

Figure 4.13 FTIR scans of commercial resin with 0.25 wt.% CNW utilizing various suspension media.

4.3.2 Effects of Suspension Medium Choice on the Morphological Properties of CNW-Reinforced Polyester Nanocomposites

Figure 4.14 presents SEM micrographs of polyester resin samples reinforced with 0.25 wt.% CNW using various suspension media. CE25 (Figure 4.14a) exhibits a relatively smooth fracture surface with minimal surface roughness and small CNW agglomerates, indicating partial dispersion as discussed in Section 4.1.2. The small cluster sizes suggested that ethanol provides a reasonable level of dispersion, although full individualization of CNWs is not achieved. The absence of micro voids indicates that most CNW clusters remained embedded in the resin during fracture, however, the smoothness of the fracture surface suggested brittle failure mode with limited crack deflection CEA25 (Figure 4.14b) demonstrated much larger clusters distributed

unevenly across the fracture surface, creating regions of high agglomeration that may have acted as localized stress concentrators during loading when compared to CE25 images. These clusters were unevenly distributed with regions of high CNW agglomeration, demonstrating poor dispersion. The large cluster sizes created potential stress concentration sites, which would facilitate crack initiation under loading. The rougher fracture surface compared to CE25 suggested some energy absorption, but the clustering implied that CNW nanoparticle reinforcement is limited due to the dispersion. CEAM25 (Figure 4.14c) displayed a complex fracture morphology with visible clusters and microvoids. Similar to SEM morphology in Section 4.1.2, these voids are presumed to result from CNW clusters being dislodged during cold fracture, resulting in cavities in the resin. The presence of both microcracks and microvoids indicated that the ethanol / acetone / MEK suspension media combination may have facilitated some degree of dispersion (due to the MEK in the suspension media polymerizing with the MEK in the resin system) but lacked strong interfacial bonding between the CNW and polyester resin. This contrasts with epoxy systems, where CNWs chemically bond and remain embedded within the epoxy matrix system. CA25 (Figure 4.14d) demonstrated apparent agglomeration; however, there were more pronounced ridges and parallel crack paths. This suggested that acetone promoted slightly better dispersion, allowing the CNWs to maintain a fracture path (as the CNW clusters are perpendicular to the fracture path). However, visible clusters remained and indicated that although using acetone has improved the surface morphology, there was a lack of interfacial adhesion. CP25 (Figure 4.14e) demonstrated the most severe agglomeration compared to utilizing suspension media when incorporating CNWs into the polyester resin matrix. The lack of a suspension medium has led to poor dispersion, which resulted in CNWs remaining as compact aggregates rather than being distributed throughout the resin. Several microvoids were visible where large agglomerates were

dislodged during cold fracture, leaving relatively large cavities. These voids acted as defect sites that significantly weakened the composite by accelerating crack propagation. The fracture surface also appeared smoother in regions away from clusters and microvoids, suggesting localized brittle failure around areas without CNWs and stress concentration around agglomerates. These micrographs highlighted that the use and choice of suspension medium strongly influenced both the dispersion quality of CNWs and the resultant surface fracture morphology. CE25 promoted smaller agglomerates but maintained a brittle surface, CEA25 introduced larger clusters but slightly rougher fracture features, CEAM25 showed both clusters and micro voids during the cold fracture, and CP25 produced the poorest dispersion with severe agglomeration and void formation. These results reinforce the importance of solvent-assisted dispersion strategies for improving CNW nanoparticle distribution and minimizing stress concentrators in polyester resin systems.

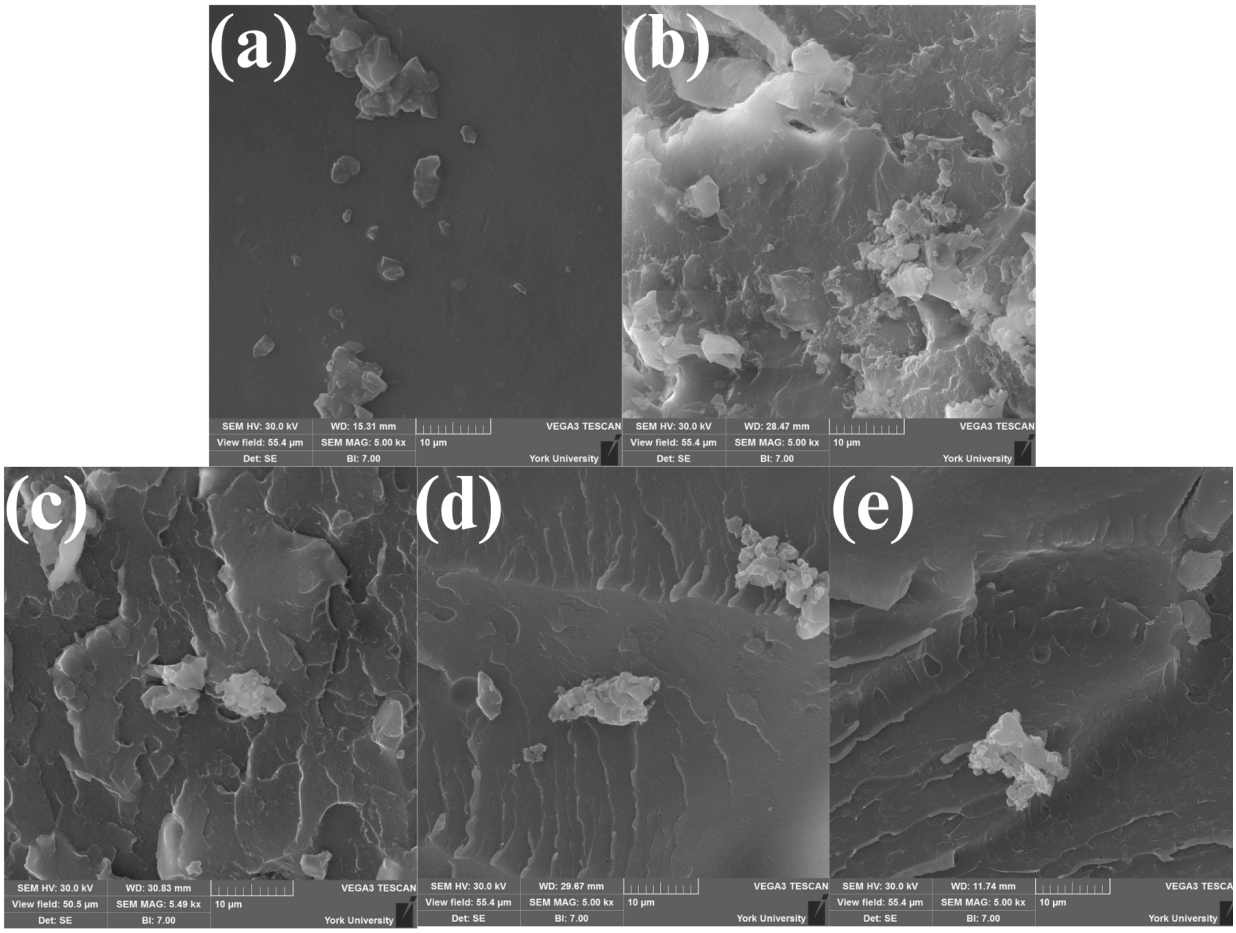

Figure 4.14 SEM micrograph of CNW-reinforced samples utilizing (a) ethanol, (b) ethanol / acetone, (c) ethanol / acetone / MEK, (d) acetone, and (e) dry powder.

4.3.3 Effects of Suspension Medium Choice on the Glass Transition Temperature of CNW-Reinforced Polyester Nanocomposites

Figure 4.15 demonstrates the thermal behaviour of CNW-reinforced PR systems with various suspension media, utilizing DSC. All samples exhibited a $T_{g,}$ with the neat sample showing a T_g of 163.17 °C, followed by CEA25 demonstrating 154.54 °C, CEAM25 demonstrating 153.79°C, CA demonstrating 150.91 °C, and CP25 demonstrating the highest of 181.02 °C. These results suggested that CNW provides greater thermal stability, compared to neat resins, with pure ethanol-

based suspensions promoting stronger polymer-NP interactions or improved dispersion compared to other suspension media. However, by adding the novel CNW NPs directly into the commercial resin mixing no additional heating, the neat resin was not subjected to the deficits of heating and had the thermal stability optimized with the presence of CNW. A one-way ANOVA was conducted to evaluate the effect of suspension medium on the T_g of CNW-reinforced polyester resin systems. The analysis revealed a statistically significant difference among groups ($F(5,21) = 12.88$, $p < 0.0001$), indicating that the choice of medium and processing method significantly influenced T_g values. The characteristic endothermic peak is observed approximately at 300 °C, which may have been related to the residual solvent interactions, extent of dispersion, or hydrolysis-induced molecular changes introduced by the different suspension media during processing. However, similar to initial DSC testing for CNW suspended in pure ethanol, the characteristic endothermic peak can also be observed in CEA25 samples. No endothermic peak is observed in other suspension mediums (i.e. CA25, CEAM25, CP25). Unlike acetone, which evaporates quickly and lacks free radicals for hydrogen bonding, ethanol remained in the slurry and actively interacted with the resin matrix, altering its thermal response. The lack of presence of the endothermic peak in the CEAM25 sample is believed to be attributed to the presence of MEK, which altered the solvent environment and suppressed hydrolytic degradation. CP25 samples did not contain this peak, where this feature is observed and attributed to hydrolysis-induced structural changes or residual solvent effects. The absence of this peak in CP25 supported the conclusion that the peak arises using the compound-casting slurry method and not from the CNWs themselves. As such, CP25 may be used as a reference for the unmodified thermal signature of CNWs and provides secondary evidence that CNWs, when not processed with solvents, contribute significantly to the thermal stability of the resin systems. A separate ANOVA was performed on samples that

exhibited a distinct endothermic peak (neat, CE25, and CEA25), which also showed a significant difference between groups ($F(2,16) = 29.75$, $p < 0.0001$). These results confirm that both thermal transitions were meaningfully affected by CNW incorporation and suspension medium.

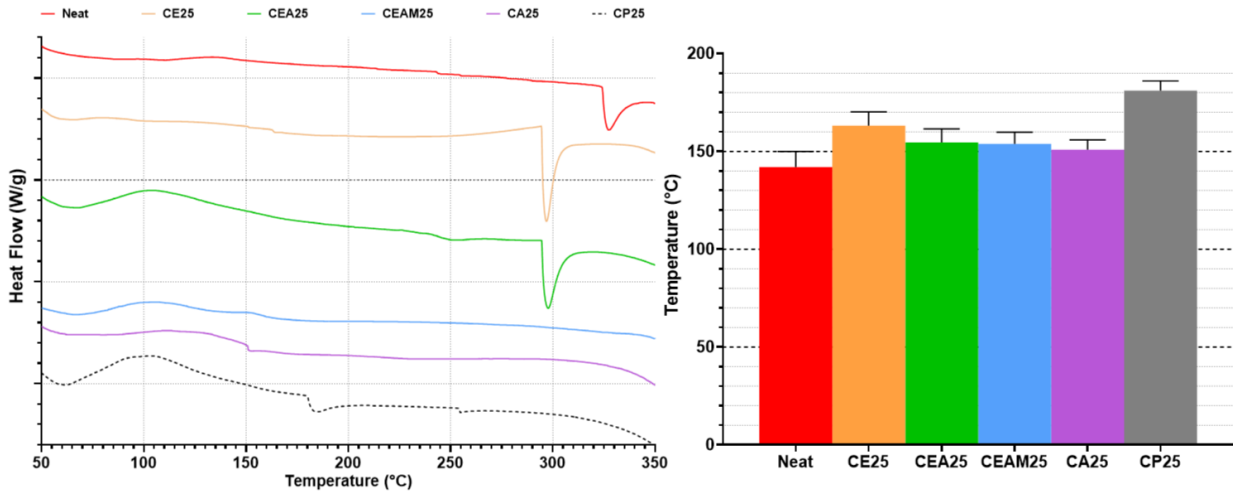

Figure 4.15 DSC thermograms of polyester resin loaded with 0.25 wt.% CNW utilizing various suspension media (left) and corresponding bar graph of glass transition temperature (right).

4.3.4 Effects of Suspension Medium Choice on the Thermal Stability of CNW-Reinforced Polyester Nanocomposites

TGA was performed to assess the thermal stability of the CNW-reinforced PRs, using different suspension media. The degradation onset temperature was used as a comparative measure of the thermal resistance of the different samples. Figure 4.15 presents the thermal degradation behaviour of 0.25 wt.% CNW samples utilizing various suspension media. The CE25 sample demonstrated a slightly reduced onset at 342.15 °C, likely due to residual hydroxyl content or hydrolysis byproducts introduced during processing. In comparison, CEA25 samples and CEAM25 samples demonstrated significantly higher degradation onset temperatures of 358.22 °C and 357.28 °C,

respectively, indicating improved thermal stability. The CA25 sample also exhibited an elevated degradation onset temperature at 353.33 °C. The increase in thermal stability in the acetone-containing systems can be attributed to reduced hydrolysis and better dispersion of CNWs, leading to fewer small-weight molecular species in the cured matrix. The presence of MEK in the CEAM samples appeared to maintain the stabilizing effect of acetone while also suppressing the degradation typically facilitated by ethanol. These results suggested that the choice of suspension medium plays a critical role in influencing the thermal degradation behaviour of CNW-reinforced PRs. CP25 demonstrated the highest degradation onset temperature at 359.18 °C, confirming the intrinsic thermal stability of CNWs in processed powder form. The elevated onset temperature suggested that the CNWs themselves are thermally stable and did not contribute to early-stage degradation. Compared to samples prepared utilizing suspension media, CP25 results further supported the interpretation that residual solvents, hydrolysis byproducts, or chain scissions of the polymers introduced using the compound-casting slurry method may reduce thermal resistance. Using processed CNW powder provided essential reference data that the solvent environment and processing history influenced the thermal degradation behaviour of CNW-reinforced polyester composites. A one-way ANOVA was performed to evaluate the effect of suspension medium on the degradation onset temperature of CNW-reinforced polyester resin samples. The analysis revealed a statistically significant difference between groups ($F(5,21) = 46.10$, $p < 0.0001$), confirming that the choice of suspension medium and processing method significantly influenced thermal degradation behaviour. These findings supported the observed variation in thermal stability, particularly the elevated onset temperature in CP25 and the reduced stability in ethanol-processed samples.

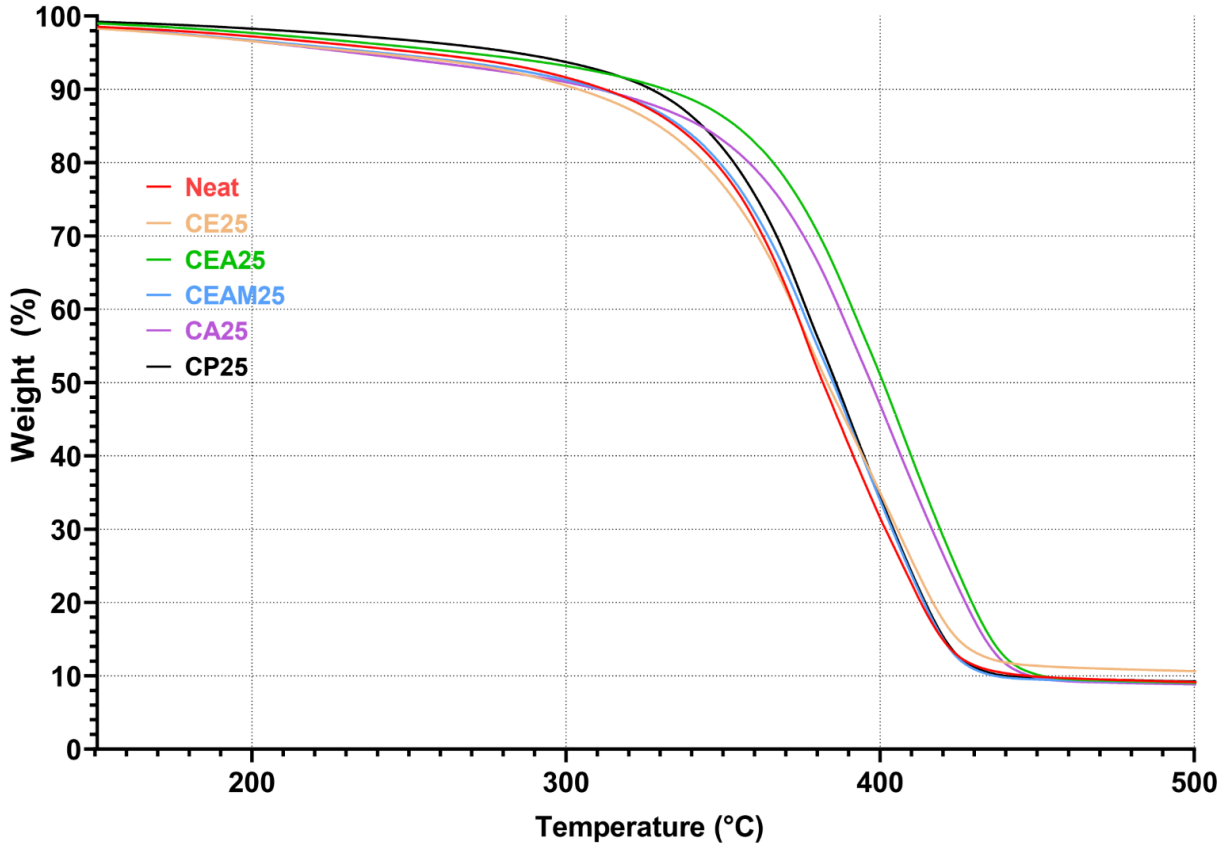

Figure 4.16 TGA thermogram of commercial resin with 0.25 wt.% CNW utilizing various suspension media.

4.3.5 Effects of Suspension Medium Choice on the Tensile Properties of CNW-Reinforced Polyester Nanocomposites

Tensile testing was conducted to evaluate the mechanical performance of CNW-reinforced PR samples prepared using different suspension media. Figure 4.17 illustrates both the measured tensile strength and strain at failure, conducted to assess the combined effects of dispersion quality and interfacial interactions between the CNWs and the resin matrix. The neat resin exhibited a tensile strength of 43.51 MPa with a corresponding strain at failure of 3.5 mm/mm. The incorporation of CNWs using a pure ethanol suspension medium resulted in an improved tensile

strength of 50.43 MPa and a slight increase in strain at failure to 3.7 mm / mm. This suggested an enhanced load transfer and moderately improved ductility. The highest tensile strength observed was the CEAM25 system at 51.68 MPa, along with the highest strain at failure of 4.3 mm / mm, indicating both strong interfacial bonding and more uniform dispersion of CNWs within the resin. In contrast, CEA25 samples exhibited reduced tensile strength of 35.39 MPa despite a moderate increase in strain at failure of 4.0 mm / mm, most likely attributed to incomplete dispersion. CA25 samples showed the weakest performance in tensile strength at 22.63 MPa and a slightly reduced strain at failure of 3.4 mm / mm, indicating poor CNW integration and likely agglomeration within the matrix. These results emphasized the importance of suspension medium selection in achieving optimal mechanical properties. Systems incorporating MEK or ethanol alone provided the most effective reinforcement, while acetone-based systems underperformed due to weaker particle–matrix interactions and less favourable dispersion. CP25 demonstrated 48.80 MPa in tensile strength, which is comparable to both CE25 and CEAM25 systems. However, there was a significant reduction in the strain at failure of the processed CNW powder of 3.6 mm / mm. This indicated that CP25 samples had increased stiffness and higher strength; however, there was reduced toughness. As there was no suspension media used, such as ethanol or acetone, there was less interaction between CNWs and the resin. Weak interfacial adhesion prevented effective stress transfer from the matrix to the CNWs, causing the composite to fracture prematurely under applied strain.

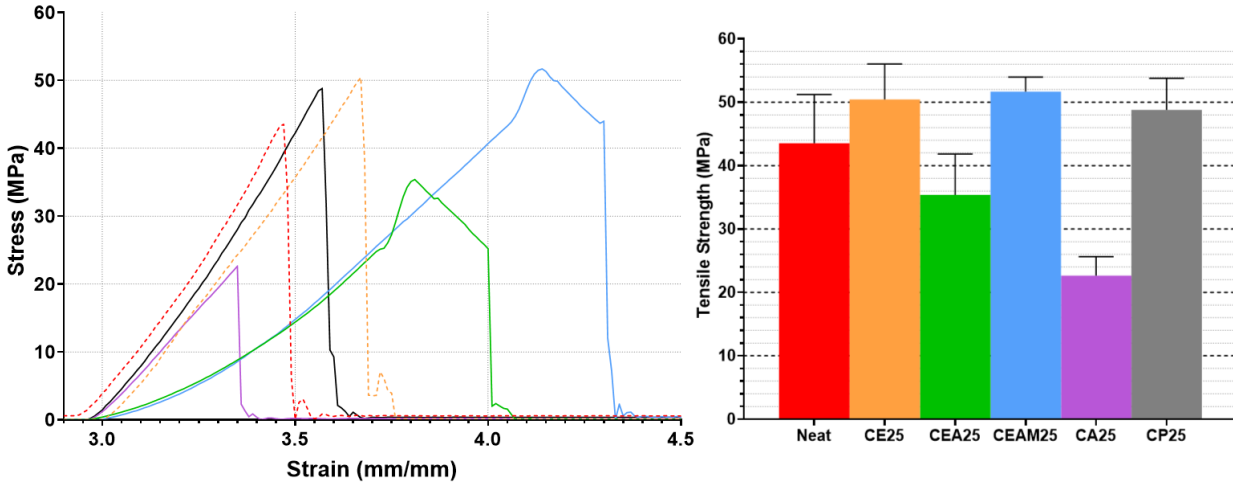

Figure 4.17 Stress-strain property curve of commercial resin tensile samples with 0.25 wt.% CNW utilizing various suspension media (left) and corresponding tensile strength bar graph (right).

The elongation at break, as denoted in Table 4.3, was measured to assess the ductility of the polyester resin samples reinforced with 0.25 wt.% CNW dispersed using different suspension media. As a baseline ductility of the unmodified matrix, the neat resin without CNWs exhibited an elongation at break of 2.55 mm. The addition of CNWs led to a notable increase in elongation across all formulations, which suggested enhanced energy absorption capability and improved strain tolerance. CE25 samples showed moderate improvement, as noted previously, with acetone-containing systems exhibiting higher elongation at break. CA25 had an improvement of 5.08 mm, nearly double the neat baseline samples. CEA25 and CEAM25 had further improvements of 5.12 mm and 5.15 mm, respectively. These findings suggested that while ethanol contributed to strong interfacial bonding (as reflected in tensile strength), the presence of acetone and MEK enhanced matrix flexibility and dispersion uniformity, resulting in an improved elongation behaviour. The increased ductility in these systems may be attributed to improved CNW dispersion and reduced

stress concentrations, which allowed the resin to deform / elongate more before failure. CP25 had a reduced elongation at break, an improvement compared to the neat samples, but less than any other sample utilizing a suspension medium. This confirmed that the lower elongation at break observed in the CP25 sample, compared to solvent-processed composites, suggested insufficient interfacial adhesion between the CNWs and the polyester matrix. This limited interaction hindered stress transfer and led to earlier failure during tensile loading.

Table 4.3 Elongation at break of tensile test samples utilizing various suspension media.

Sample (0.25 wt.% CNW)	**Elongation at Break (mm)**
Neat (no CNW)	2.55
Pure Ethanol (CE25)	3.36
Pure Acetone (CA25)	5.08
Ethanol / Acetone (CEA25)	5.12
Ethanol / Acetone / MEK (CEAM25)	5.15
Powder (CP25)	3.25

4.3.6 Effects of Suspension Medium Choice on the Adhesive Strength of CNW-Reinforced Polyester Nanocomposites

The adhesive strength was evaluated using a single-lap shear test to assess the bonding performance of cured polyester resin. The neat resin exhibited an adhesive strength of 4.5 MPa, which is used as the baseline for comparison. From the reinforced samples, CE25 samples resulted in the highest adhesive strength of 4.97 MPa, indicating that CNWs dispersed using ethanol promoted good interfacial compatibility and dispersion. However, all other suspension media

demonstrated a reduction in adhesive strength. CEA25 demonstrated an adhesive strength of 3.30 MPa, while CA25 achieved 3.67 MPa. The lowest adhesive strength was observed in CEAM25 at 2.52 MPa, suggesting that the inclusion of MEK, despite improving tensile properties and elongation, may have negatively impacted the NP-resin interface or weakened the cohesive bonding in the adhesive layer. These results highlighted the complex trade-offs between suspension medium, dispersion quality, and interfacial adhesion. While certain solvent combinations improve bulk mechanical properties, they may also introduce microstructural or chemical changes that compromise adhesive performance. The ethanol-based system emerged as the most balanced formulation for mechanical strength, offering both improved tensile and adhesive properties. The CP25 samples exhibited an adhesive strength of 2.96 MPa, notably lower than the neat and CE25 samples. This reduction was likely due to poor NP dispersion and weak interfacial adhesion between CNWs and the polyester matrix. Without solvent-assisted mixing or ultrasonication, the CNWs tend to agglomerate, leading to heterogeneous distribution within the resin and the formation of stress concentrations at the bonding interface. These results suggested that direct incorporation of CNWs, without adequate dispersion strategies, not only limited mechanical reinforcement but may have also disrupted the structural integrity of the adhesive bond. Although there was variation in adhesive strength across different suspension media, all suspension medium samples exhibited a similar mixed adhesive / cohesive failure mode observed in the CNW loading analysis samples. This consistent failure behaviour suggested that the type of suspension medium used did not alter the fundamental failure mechanism, even though it influenced interfacial bonding strength and overall adhesion.

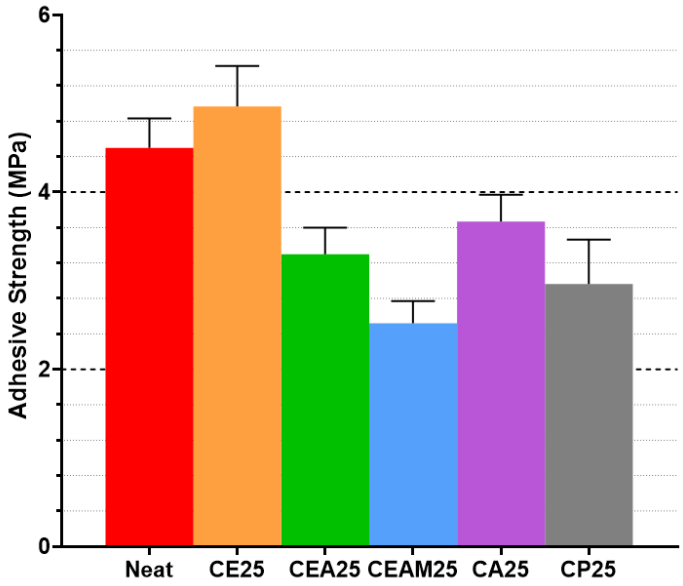

Figure 4.18 Adhesive strength of commercial resin samples with 0.25 wt.% CNW utilizing various suspension media.

CHAPTER 5 – Conclusion, Contributions, and Future Directions

5.1 Conclusion and Contributions

This work set out to address the growing demand for sustainable and high-performance adhesives by exploring the reinforcement of commercial polyester resin with CNWs. Chapter 1 highlighted the limitations of conventional adhesives, particularly epoxies, in terms of cost, mechanical performance, and health and environmental concerns, while positioning polyester resins as a more accessible alternative. The incorporation of nanoparticles (NPs) was introduced as a strategy to improve the mechanical and thermal properties of polymer resins, with bio-based nanomaterials, such as CNWs, offering the advantage of renewability and reduced environmental impact. Chapter 2 reviewed existing processing methodologies for CNWs and dispersion strategies for NP in polymer matrices, with a focus on agglomeration challenges, poor interfacial bonding, and the influence of solvent-assisted processing. The literature review identified CNWs' high aspect ratio and strong hydrogen-bonding, but also highlighted their tendency to form clusters, limiting reinforcement efficiency. Previous work on chitin preparation methods was discussed to establish the critical roles of surface chemistry and processing in order to achieve homogeneous dispersion. These methodologies include compounding, freeze-drying, coagulation, pretreatments, and electrospinning. The background established the need to investigate practical dispersion techniques for CNWs in polyester resins, bridging the gap between sustainability and performance.

Building on the foundation of a comprehensive literature survey and the needs of the industrial partner (Neptune Nanotechnologies Inc.), the experimental methodology focused on incorporating CNWs into commercial UPR (3M Bondo® Fibreglass Resin) to evaluate dispersion, morphological effects, thermal behaviours, and mechanical performance. CNWs were suspended

in ethanol and alternative solvent systems (e.g., acetone, ethanol / acetone, ethanol / acetone / methyl ethyl ketone) to assess the effects of suspension mediums on NP dispersion. Rotary evaporation, staged solvent addition, ultrasonication, and controlled heating were employed to promote homogeneous dispersions while minimizing agglomeration. Samples were fabricated using slurry compounding and casting, followed by solvent removal, degassing, curing with MEKP, and molding. Characterization techniques included FTIR spectroscopy to identify chemical structures, SEM for morphological properties, DSC to evaluate glass transition and thermal chemical behaviours, and TGA for thermal stability. Mechanical performance was tested through ASTM-standard tensile testing (Type IV specimens) to measure tensile strength, modulus, and elongation at break, as well as single-lap shear (ASTM D1002) to evaluate adhesive bonding strength and failure modes. This integrated methodology enabled systematic investigation of processing-structure-property relationships in CNW-reinforced polyester resins.

Experimental results revealed that CNW loading, thermal processing conditions, and suspension media selection collectively governed the performance of PR composites. While ethanol was a practical and scalable suspension medium for dispersing CNWs, its residual presence during processing introduced competing effects on polyester nanocomposites. At low to moderate loadings (≤0.50 wt.%), CNWs improved tensile strength and ductility. The glass transition temperature was also increased due to restricted chain mobility and promoted stress transfer; however, at higher loadings, CNW agglomeration and more severe ethanol-driven hydrolysis reduced thermal stability, decreased adhesive strength while introducing voids at filler-matrix interface, and thereby compromised interfacial integrity. The balance between reinforcement and degradation highlights the impact of CNWs as nanoscale reinforcements that enhance mechanical performance, but also as carriers of ethanol due to the tendency of fibres to

absorb ethanol, and reactive functional groups that can accelerate polyester hydrolysis. Optimal property enhancement was observed with 0.25 – 0.50 wt.% CNW loading, where improved tensile strength, ductility, and glass transition temperature were achieved without severe agglomeration or degradation. Beyond this range, excessive CNW content led to reduced performance due to poor dispersion and hydrolysis-related effects.

Thermal history studies further demonstrated the sensitivity of CNW-polyester adhesive systems to processing conditions. For 0.25 wt.% CNW-reinforced nanocomposites, moderate heating (i.e., 45 minutes at 80 °C) effectively removed residual ethanol while maintaining or enhancing T_g and thermal stability. In contrast, prolonged heating at a lower temperature (i.e., 90 minutes at 60 °C) promoted hydrolysis and reduced thermal stability. These findings underscore the delicate balance between solvent removal and thermal exposure, as both factors significantly influence composite behaviour. Mechanical testing demonstrated that CNW incorporation mitigated the detrimental effects of thermal exposure observed in neat PR. Tensile strength and adhesive performance were maximized under moderate thermal treatment, where CNWs promoted interfacial interaction and load transfer without inducing aggregation or excessive viscosity. Overheating or prolonged exposure, however, reduced these benefits. These emphasized the critical role of thermal history in defining composite performance.

The selection of suspension medium also plays a critical role in determining the dispersion quality, thermal behaviour, mechanical performance, and adhesive properties of 0.25 wt.% CNW-reinforced polyester resin systems. FTIR analysis confirmed that all formulations remained chemically stable with no evidence of aggressive degradation or byproduct formation, although traces of residual solvent were detected in some solvent-processed samples through increasing signal strength. SEM imaging revealed that dispersion quality varied significantly with the ethanol

suspension medium (CE25) promoted smaller CNW agglomerates, acetone-containing systems (CEA25, CEAM25) resulted in larger clusters and micro voids, and direct powder incorporation (CP25) produced the poorest dispersion with severe agglomeration. These morphological differences directly influenced the bulk material properties. Thermal analysis indicated that CNW incorporation generally improved T_g and thermal stability relative to neat resin. CE25 and CEAM25 samples achieved moderate improvements in T_g and degradation onset temperature. In contrast, CP25 displays the highest thermal stability, highlighting the intrinsic contribution of CNWs when solvent effects are eliminated. DSC results also suggested that residual solvent interactions can alter polymer-NP interactions and influence endothermic transitions, emphasizing the balance between solvent use and composite thermal behaviour. Mechanical testing showed that tensile strength and ductility were closely linked to dispersion quality and interfacial adhesion. CEAM25 exhibited the highest tensile strength and strain at failure due to a more uniform CNW distribution, while CE25 provided a balanced combination of strength and adhesion. In contrast, CA25, CEA25, and CP25 samples demonstrated either reduced strength or ductility, largely due to poor particle dispersion or insufficient interfacial bonding. Adhesive testing further reinforced the importance of solvent-assisted dispersion. In particular, CE25 delivered the highest adhesive strength, whereas CP25 and other solvent combinations exhibited reduced bonding performance, highlighting the role of proper NP integration in maintaining cohesive and interfacial integrity.

Overall, the findings highlight the importance of optimizing CNW content, thermal treatment, and dispersion strategy to maximize the reinforcing potential of CNWs in PRs. Most importantly, this study represents the first systematic and comprehensive investigation of CNW-reinforced polyester adhesive systems. It has filled a critical scientific and technological gap in the research community. From a research perspective, the outcomes of this thesis research extend knowledge

on solvent-assisted dispersion, identifying its opportunities and challenges in fabricating CNW-reinforced polyester adhesive systems. From an industrial standpoint, it has been identified that ethanol-based suspension can serve as a scalable processing strategy to formulate CNW-reinforced polyester adhesive, although careful consideration will be needed to optimize the thermal processing conditions. In short, these contributions have established a foundation for future development of sustainable and high-performance bio-based nanocomposite adhesives. The thesis research also represents a novel step towards integrating bio-based CNW into commercially relevant adhesive technologies.

5.2 Future Directions and Methodology for Commercial Applications

This study established the suspension medium as a decisive factor in the performance of CNW-reinforced polyester nanocomposites prepared by slurry compound and casting. Although all systems demonstrated chemical stability, the choice of medium strongly influenced dispersion quality, thermal stability, and mechanical and adhesive properties. Ethanol-based suspensions (CE25) and ethanol / acetone mixed suspensions (CEAM25) yielded the most balanced performance, minimizing CNW agglomeration and enhancing tensile strength, ductility, and adhesive strength. In contrast, other solvent systems (CA25, CEA25) and direct powder incorporation (CP25) introduced larger agglomerates, voids, or reduced toughness, highlighting the importance of suspension medium selection. These findings highlight the need for optimized solvent strategies to harness the reinforcing potential of CNWs in thermosetting resins.

Looking forward, several pathways emerge to advance CNW–polyester nanocomposites toward practical, sustainable adhesive technologies:

1. **Substrate adhesion.** While improvements in tensile strength and bulk cohesion were observed, optimizing interfacial bonding to diverse substrates remains an open challenge. Future research should systematically evaluate adhesion on metals, plastics, composites, and natural fibres, as substrate chemistry will govern interfacial interactions. Further modification of CNWs may promote stronger bonding, while exploring compatibilizers or interfacial coupling agents could bridge chemical mismatches. Strategies for tailoring the interphase must be paired with durability studies under moisture, heat, and cyclic loading to simulate real service environments for commercial-scale implementation.
2. **100% bio-based adhesive systems.** Commercial polyester resins provide a practical baseline, but their petroleum-derived origin limits sustainability. Transitioning toward bio-based polyester systems offers a pathway to fully renewable, green adhesives. Future work should evaluate CNW reinforcement in resins derived from bio-monomers, where compatibility, polymerization kinetics, and crosslink density may differ significantly from commercial PR. The use of a biopolymer matrix with a bio-derived nanofiller like chitin would establish a new class of sustainable structural adhesives.
3. **Dispersion methods.** Despite ethanol's relative success, dispersion uniformity remains a significant restraint. Hydrolysis from residual solvent interactions and CNW aggregation at higher loadings limit reproducibility and performance. Research should prioritize scalable dispersion methods such as high-shear mixing, sonication, or reactive compatibilizers that improve CNW affinity with PR. Exploring monomer-stage incorporation by dispersing CNWs directly into liquid reactants during polymerization offers a promising route to improved integration without relying on residual solvents. Where solvent-free processing is desired, direct powder incorporation of CNWs, such as

those produced by Neptune Nanotechnologies Inc., should be investigated further for industrial scalability.

4. **Industrial feasibility.** For real-world implementation, solvent-assisted dispersion must balance efficiency, cost, and environmental impact. Ethanol, while effective, risks hydrolysis of polyester under prolonged thermal exposure, underscoring the importance of low-temperature or no-heat dispersion strategies. Industrial feasibility studies should compare solvent recycling or optimizing solvent-free powder incorporation to identify the most scalable approach.
5. **AI-driven optimization.** Given the complexity of suspension medium effects and the large experimental design space, artificial intelligence (AI) and machine learning offer powerful tools to accelerate optimization. By combining experimental datasets with predictive algorithms, AI can identify promising nanoparticle-matrix combinations while minimizing trial-and-error experimentation through Design of Experiments. Integrating AI into materials development could drastically reduce the number of physical experiments required, leading to faster innovation cycles and more cost-effective development of CNW-reinforced adhesives.

In summary, ethanol-based suspensions currently provide the best performance balance in CNW–PR composites, but long-term commercial success will depend on strategies that improve substrate adhesion, leverage bio-based resins for sustainability, resolve dispersion challenges, and integrate AI for accelerated optimization. Together, these directions define a roadmap toward scalable, high-performance, and fully sustainable CNW-reinforced polyester adhesives.

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