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School of Engineering and Digital Sciences

Bachelor of Engineering in
Mechanical and Aerospace Engineering

**Multifunctional Coating for Metal/Polymer
Surfaces using Polyurethane/Nanofibre
Composites**

by

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Declaration

We, Nurmerey Aidos, Madina Nurgaziyeva, and Beibars Zhenis, hereby declare that this report, entitled “Multifunctional Coating for Metal/Polymer Surfaces using Polyurethane/Nanofibre Composites” is the result of our own project work except for quotations and citations that have been duly acknowledged. We also declare that it has not been previously or concurrently submitted for any other degree at Nazarbayev University.

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Abstract

Polyurethane coatings are widely used in engineering for their versatility, but polyurethane often lacks mechanical strength and thermal stability in extreme applications, which creates a need for reinforcing fillers. This study investigates the development of high-performance composite coatings by reinforcing polyurethane with Poly-p-phenylene benzobisoxazole (PBO) nanofibers (PNFs). A top-down approach was employed, combining acidic protonation using MSA (methanesulfonic acid) and TFA (trifluoroacetic acid) with mechanical disintegration through planetary ball milling to synthesize PNFs from commercial PBO fibers. This process successfully converted 15 μm microfibers into 10-50 nm nanofibers, achieving approximately 800-fold reduction in fibre thickness and improved surface activity for interfacial bonding.

Composite coatings were fabricated with varying PNFs content and characterized for morphological, mechanical and protective properties. The results demonstrated that PNFs content of 0.1 wt% yielded the most significant performance enhancement, exhibiting 217% improvement in tensile strength (25.66 MPa) and 160% in Young's Modulus (11.43 MPa). Moreover, mechanical properties on adhesive applications revealed a similar trend with the best performing concentration to be 0.05 wt% for lap shear strength (2.39 MPa) and 0.1 wt% for impact resistance (1.83 J). Numerical analysis revealed that neat PU fits well in the Marlow model, while reinforced composites require detailed modelling using RVE. The study confirms that PNFs offer strengthening properties to polyurethane. These findings establish a foundation for the use of PNF-reinforced composite coatings as a lightweight, durable solution for protective applications in several industries such as aerospace, construction and defense.

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1 Introduction

Many advanced engineering structures are required to meet specific performance criteria for operation, in which vulnerability to external factors is important criteria. One of the solutions to reduce vulnerability is the use of protective coatings, which offer high-performance properties and external protection without significant increase in cost. Protective coatings are a layer of metal, organic polymer or inorganic compound on a surface which protects against external factors such as humidity or extreme temperature differences. For instance, the effect of coating against corrosion is demonstrated in Figure 1. The enhancing properties of protective coatings are widely utilized in several applications such as preventing barnacle formation on the ship bottoms, or in the food industry to protect soda cans from external impact [1,2]. Moreover, the market size of protective coatings was \$17 billion in 2025, and anticipated to reach \$33 billion by 2035, with 6.9% CAGR, showing an increasing interest in the usage of coatings in different markets [3].

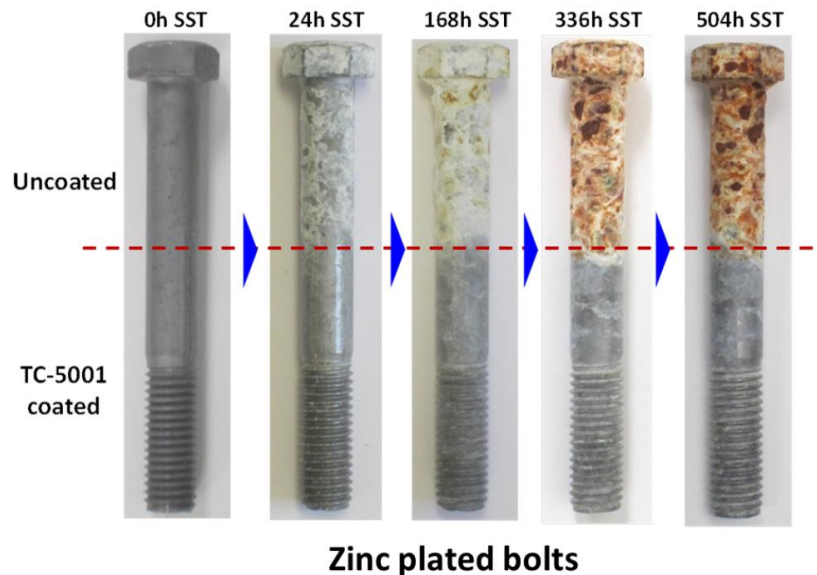


Figure 1. The difference between coated and uncoated metal surfaces against corrosion [4].

Coatings are chosen based on functionality and properties needed in the field, and most industries require several properties simultaneously. For instance, for the protection of cultural heritage objects it is important to use coatings with high transparency, non-toxicity and long lifespan [5]. On the other hand, textile industries require coatings with high flame retardancy, while also having antimicrobial properties and high protection against the UV light [6]. This demonstrates the demand for developing multifunctional coatings in several field applications.

The majority industries use metallic coatings, such as Zn- and Cr- based, or polymeric coatings and paints. However, there are several drawbacks of using metallic coatings, such as the high cost and weight of Zn- based coatings, or environmental issues associated with using Cr- based coatings. Hence, the development of organic polymer coatings attracts more attention, but they require modifications to become a useful alternative [7]. To address this need, various polymeric systems have been explored, and a wide range of polymeric coatings such as epoxy, polyurethane, acrylics or cellulose have been used in various coating applications [8]. Among these, polyurethane differs from other existing polymers with its versatility and ease of production, while offering excellent properties [9]. Therefore, modifying polyurethane has the potential of creating a coating with competitive properties on an industrial scale.

The most widely researched method of modifying a polymer is the introduction of a filler. For those purposes, nanofillers possess a significant advantage as potential filling materials because of their ability to provide large surface area. Nanofillers significantly improve mechanical and physical properties of the polymers [10]. For instance, engineered nanoparticles and nanofibers are used in organic coatings such as silica dioxide as a hardener or cellulose nanofibers (CNFs) as a toughener. Furthermore, the discovery of remarkable mechanical properties of carbon nanostructures has enabled their use as polymer nanofillers, offering mechanically strong and

durable composites [7,11]. Although nanoparticles are widely used for polymer reinforcement, there are potential environmental concerns that limit their use in places where sustainability and safety are crucial. For example, some studies have shown that carbon nanotubes (CNTs) have cytotoxic¹ effects, while metal and their oxides also have inflammatory² and toxic effects on living cells [12]. Therefore, there is growing interest in other types of nanofillers that can provide similar enhancing properties without such environmental concerns. In particular, nanofibers derived from high-performance fibers with a high aspect ratio fall into this category. High-performance fibers offer exceptional mechanical properties and are nowadays used as niche products for lightweight composites for aircraft or bullet-resistant body armor [13]. Thus, deriving nanofibers from high-performance fibers allows them to retain such properties with better interfacial connection with the polymer. Of these candidates, poly-p-phenylene benzobisoxazole (PBO) fibers demonstrate superior properties [14], which makes it an area of interest for obtaining nanofibers. This nanofiller has the potential of reinforcing polymer to create the next generation of coatings with high performance, which could be used in aerospace, defense or automotive industries as reinforcement and protection material.

Poly-p-phenylene benzobisoxazole (PBO) fibres were initially developed by the United States Air Force Materials Laboratory, later commercialized under the name of Zylon in 1988 [15]. It is one of the most promising materials in the 21st century, which exhibits exceptional strength, thermal stability and resistance to harsh chemical environments, gaining increased attention from the research community (see Figure 2).

¹ Toxic to living cells, capable of killing them

² Condition of redness, swelling, and pain caused by inflammation

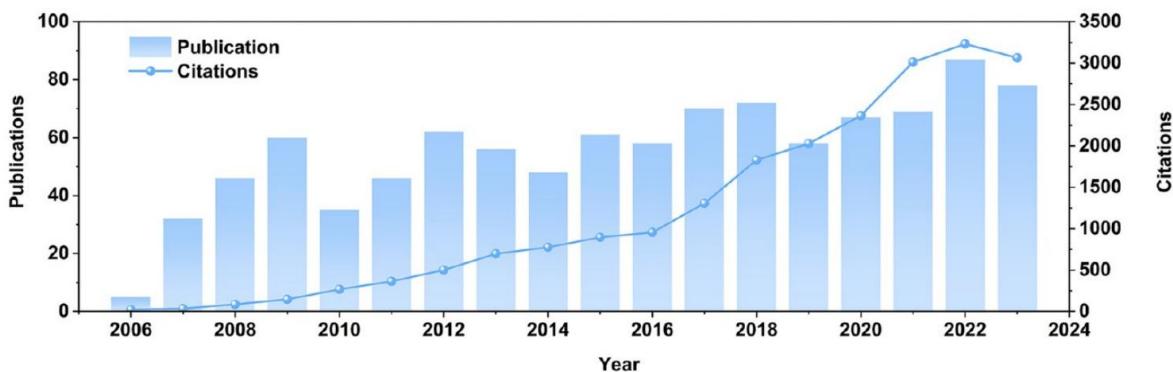


Figure 2. Increased trend on number of articles on PBO and its nanofiber from 2006 to 2023 [15].

However, addition of commercial PBO fibres into the matrix of the main material, such as polyurethane, hinders the formation of strong interfacial adhesion, which challenges the improvement of composite properties due to the low surface affinity and relatively inertness of fibres [16,17]. To effectively activate the reinforcement potential of this polymer fiber, previous studies have derived PBO nanofibers (PNFs) that retain original crystallinity after the synthesis. PNFs also have better adhesion, and it enhances the mechanical performance, thermal and chemical resistance of the matrix material [18]. Nevertheless, the reported methods of PNFs production are not efficient and not cost-effective due to the consumption of excessive amounts of raw materials, generation of large amounts of waste and toxic acid mist and being highly time-consuming. Therefore, alternative techniques for industrial applications must be developed to provide effective and fast fabrication of PNFs to achieve high performance of composites.

Furthermore, several studies indicate improvements in the strength, toughness and stiffness of polyurethane after introducing nanofibers into the polymer matrix, such as CNFs [11,19], CNTs [20], and aramid nanofibers [21]. However, there is no systematic literature reporting on the usage of PNFs for polyurethane reinforcement. Given the exceptional mechanical and thermal properties of PNFs, their potential as polyurethane reinforcement remains largely unexplored. Therefore, this

gap highlights the need to investigate whether PNFs can provide similar or superior enhancing properties compared to other well-established nanofibers.

Requirements

Current situation: conventional coatings often lack durability, thermal stability and barrier performance needed for harsh environments.

Novel approach: poly-p-phenylene benzobisoxazole (PBO) nanofibres offer superior properties, such as strength, thermal and chemical resistance.

Existing gap: there is no systematic work that investigates the production-efficient PBO nanofiber (PNFs) synthesis, and the development of PNFs based polyurethane (PU) composite coatings.

Engineering ethics & Standards

Safety: safe utilization of chemical consumables such as acids, use of personal protective equipment and compliance with Nazarbayev University laboratory safety regulations.

Environmental protection: chemical waste disposal control during fabrication and process optimized synthesis for the reduction in energy consumption.

Integrity: experiments are repeated for statistical reliability, testing performed according to ASTM³ standards (ASTM D412 Type C for tensile tests, ASTM D1002 for shear tests, ASTM B117 for corrosion resistance, ASTM D6110 for impact absorption).

³ American Society for Testing and Materials

Aim & Objectives

This study presents an efficient approach to producing PNF-based composite coating with improved reinforcement and protection properties. For these reasons, the following objectives were set:

- to synthesize high-quality nanofibers from commercial PBO fibers via controlled, short time processing methods.
- to examine its chemical consistency and diameter uniformity.
- to fabricate PNF/PU composite coatings, optimizing filler loading and functional properties.
- to conduct comprehensive characterization including tensile and shear strength, impact absorbance and corrosion resistance according to engineering standards.

2 Background

Two main components that build polyurethane are isocyanates and polyol, which can be altered to change the properties of polyurethane. These changes can significantly affect the properties, hence making the structural property relationship a crucial factor to consider making a polyurethane product [9]. Furthermore, polyurethane has various applications in automotive, appliance and wood industries due to its excellent physical and chemical properties, such as good bonding strength, or chemical and abrasion resistance, and ability to alter them according to the application needs [22]. However, for extreme engineering applications, like aerospace or marine applications, neat polyurethane lacks thermal stability and mechanical stiffness. To address these limitations, the incorporation of nanofillers, particularly nanofibers, has emerged as a crucial strategy. For instance, several studies investigated the effect of nanofibers on polyurethane performance. High optical transparency (>90%) and improved mechanical strength was achieved by using CNFs [11,19]. In the study of both cellulose and chitin nanofibers, chitin nanofibers demonstrated a better strengthening and toughening effect than cellulose due to acetyl amino groups, which creates additional hydrogen bonding with polyurethane. For example, enhanced properties of chitin nanofibers composite compared to neat polyurethane are shown in Figure 3. In another study, adding CNTs into polyurethane matrices introduced electric conductivity along with increased mechanical strength and durability [23]. Polyurethane reinforced with aramid nanofibers demonstrated 742% improvement in compressive strength and offered high durability with a strain recovery of 95% [21].

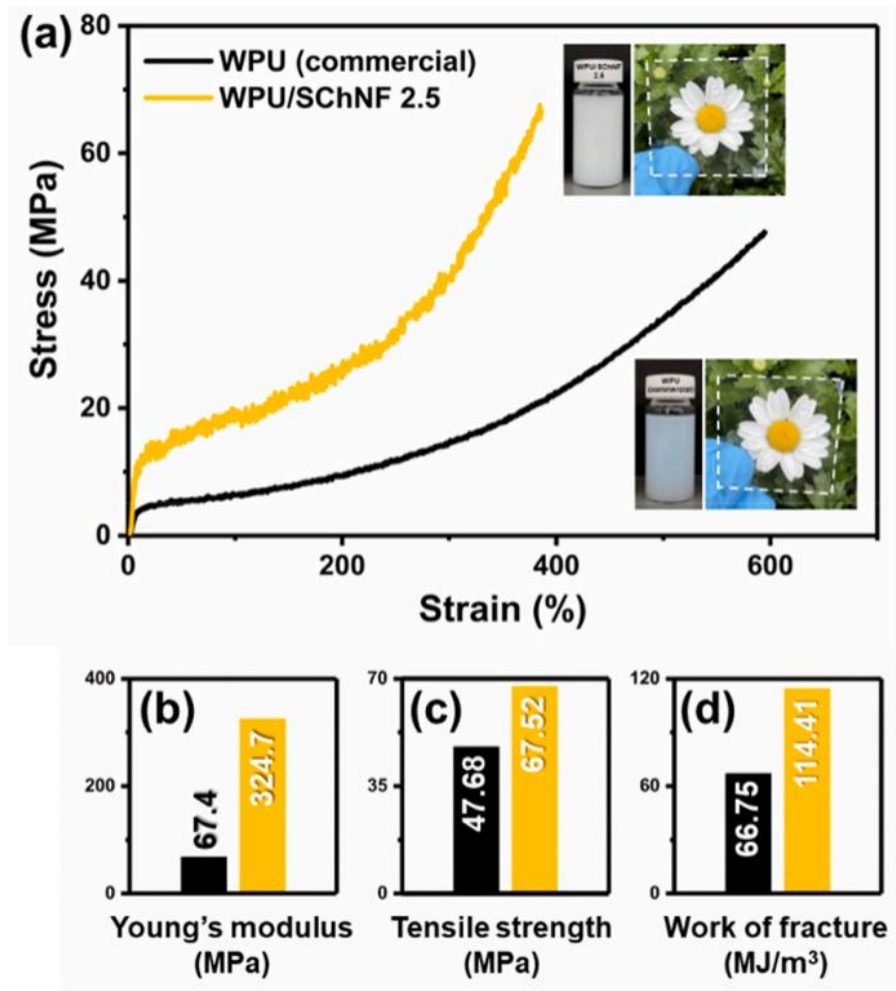


Figure 3. Mechanical properties of neat waterborne polyurethane (WPU) and chitin nanofibers enhanced WPU composite [11].

However, in studies on CNFs effect on polyurethane, additional chemical processes were applied such as succinylation and carboxylation to enhance interfacial bonding and compatibility of CNFs with polyurethane matrix [11,19]. Other studies on introducing CNTs in polyurethane reported that agglomeration was the main problem, which acted as an initiator of cracks due to enhanced stress concentration. Hence, dispersion techniques to avoid agglomeration were needed while increasing the content of carbon nanotubes [23,24]. Literature on polyurethane reinforced with aramid nanofibers demonstrated similar limitations as the tendency of nanofibers to self-aggregate,

which creates relatively weak interfacial bondings that affect stiffness of the composite [25]. Furthermore, the study on aramid nanofibers reported protection against fire due to the formation of char layers on combustion surface, which prevents further combustion [21]. However, this indicates that the composite needs to degrade first to create char. Moreover, Ciecierska et al. (2015) reported an increase of decomposition temperature of CNTs reinforced polyurethane up to 570°C but with a maximum limiting oxygen index of 33.4, which was reported as insignificant increase in thermal stability [24]. In contrast, PBO has a high limiting oxygen index and thermal stability, allowing it to resist heat at temperatures where aramid begins to char, or surpass decomposition limit of CNT/PU composite. Hence, despite the improvements provided by other types of nanofibers, there is still a need for a reinforcing material that offers intrinsic mechanical strength and thermal resistance, while avoiding chemical modifications and the severe agglomeration challenges associated with synthetic nanofibers. For these reasons, obtaining nanofibers from PBO fibers may offer a superior pathway for developing advanced polyurethane composites that combine exceptional thermal stability with robust mechanical reinforcement, effectively filling the performance gap left by conventional nanofillers.

The poly-p-phenylene benzobisoxazole (PBO) fibres are defined as the class of rigid-rod ordered polymers, which demonstrates high crystalline behavior, persistent molecular alignment and strong hydrogen bonding [26]. These polymer features supply the PBO with high mechanical performance such as tensile strength of 5.8 GPa and Young's modulus of 270 GPa [27]. PBO also holds exceptional thermal stability, surpassing other organic fibers, by not exhibiting softening behaviour up to the decomposition temperature, which reaches up to 600°C in air and 700°C in inert atmosphere [26,28]. Its limiting oxygen index (LOI) of 68 further shows the fibres ability not to shrink or burn in flames and be durable during fire events. In harsh chemical environments,

including organic solvents, acids and bases, PBO maintains strong retention indicating its outstanding chemical resistance. Table 1 and Figure 4. provide a summary of the properties of different fibres, where PBO reports one of the best performances.

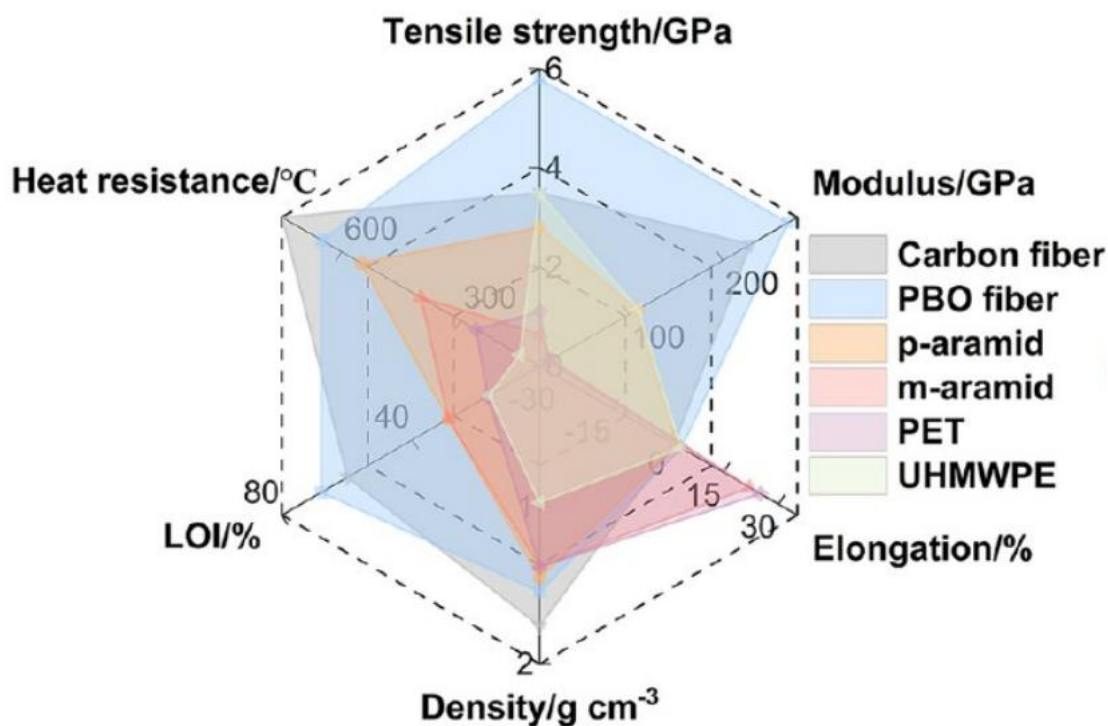


Figure 4. Comparison of various fibers properties [15].

Table 1.

Properties of various fibres [26]

	PBO	Kevlar (aramid)	Polyester	Spectra 1000 (UHMWPE)
Tensile strength (GPa)	<u>5.8</u>	3.4	1	3.1
Tensile modulus (GPa)	<u>270</u>	185	15	105
Elongation at break (%)	2.5	<u>2</u>	20	2.5

	PBO	Kevlar (aramid)	Polyester	Spectra 1000 (UHMWPE)
Moisture (%)	0.6	3	<u>0.4</u>	-
Decomposition temperature	<u>650</u>	550	260	150
LOI	<u>68</u>	30	17	16

However, PBO fibres have chemically inactive surfaces and are mostly inertness due to the lack of functional groups. These properties prevent sufficient chemical bonding with the main material, therefore exhibiting poor adhesion and negatively affecting the performance of composite [16]. However, many studies have previously identified that PBO nanofibers (PNFs), extracted from macroscopic PBO fibers, not only retain original crystalline structure and material performance, but exhibit larger specific surface area and rough surface with additionally active functional groups [29,30]. These properties have received significant attention as promising reinforcement material for advanced composites applications in extreme conditions (see Figure 5), such as battery separators [31], fire protection [32] and electrical insulation [33]. For example, Hao et al. used PNFs fibres with the size range of 5-10 nm to fabricate strong nanofiber-based membranes, achieving a tensile strength of 525 MPa and high thermal stability [31]. Moreover, Qian et al. investigated the aerogel with PNFs of 12-20 nm diameters sizes. It demonstrated enhanced flame retardancy, extremely low density between 3.6 and 15.7 mg/cm³, extremely high porosity of 98.9-99.7 % and improved thermal stability with the decomposition temperature up to 650°C [34]. Therefore, reducing the size of PBO fibers to the nanoscale is crucial for high-performance composites, but limitations still exist in its fabrication process.

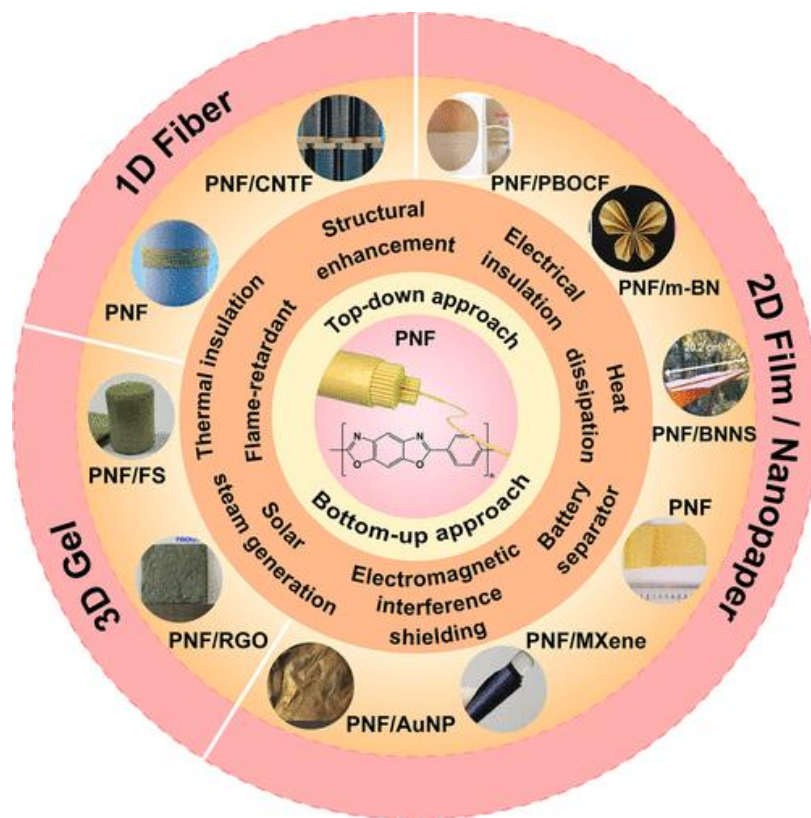


Figure 5. PNFs as a multidimensional advanced material and its application [15].

Even though many fabrication methods were developed by researchers, this project focuses only on the bottom down approach consisting of acid protonation and mechanical disintegration. In the study of Chen et al., PBO fibers were added to the acidic mixture of MSA (methanesulfonic acid) and TFA (trifluoroacetic acid) at a ratio of 9.2:0.8 and stirred mechanically for 10 minutes according to the principle of dissolution [35]. In this process, MSA and TFA acids work as a proton donor, accepting the atoms of nitrogen and oxygen on the PBO oxazole ring. Simultaneously, the created chemical process expands the spatial distance between molecular chains and adjusts the fiber surface, therefore increasing the specific surface area with the interfacial bonding. The mechanical stirring further accelerates this process of PBO size reduction. However, despite the achievement of PNFs with a diameter of 20 nm, this method is not efficient as large amounts of

raw materials are used therefore resulting in high waste production and release of the toxic mist. In the study by Ifuku et. [36], PBO fibers were treated by 10wt% NaOH also to break the oxazole rings. After it, the fibers were mechanically grinded in the ball-collision chamber for 1000h and significantly differed in size from 50 nm to 1000 nm. Therefore, while numerous processes exist, there are still no effective and reliable techniques to fabricate PNFs. Our study will focus on the implementation of both acidic protonation and mechanical disintegration via high-speed planetary ball mill to provide fast, safe and cost-effective solutions.

Introducing PNFs to the polyurethane matrix presents a dual challenge: achieving homogeneous dispersion and strong interfacial bonding between PNFs and polyurethane without chemical modification. As previously mentioned in studies on CNTs and aramid nanofibers, high surface energy of nanofibers lead to re-agglomeration during the mixing stage, which creates stress concentration points leading to early cracks [23, 25]. Therefore, this study utilizes planetary ball milling which has a distinctive advantage over traditional stirring methods. The high-energy shear forces generated during planetary ball milling not only exfoliate the PBO fibers but also allow their dispersion within the solvent medium. Furthermore, this mechanical exfoliation process increases the surface roughness of the fibers and can also induce creation of active sites that may bond with the hard segments of the polymer chains [37]. By integrating ball milling for reduction of agglomeration of nanofibers, this methodology aims to solve re-agglomeration problems typical of other synthetic nanofibers, thereby translating the superior properties of PNFs directly to the polyurethane composite and coating performance.

3 Materials and Methods

3.1 Design of experiments

The project was initially structured into three stages, which consisted of the initial project definition, PNF/PU composite fabrication and testing as well as preparation and testing of coatings.

Figure 6. demonstrates the graphical representation of this project's workflow.

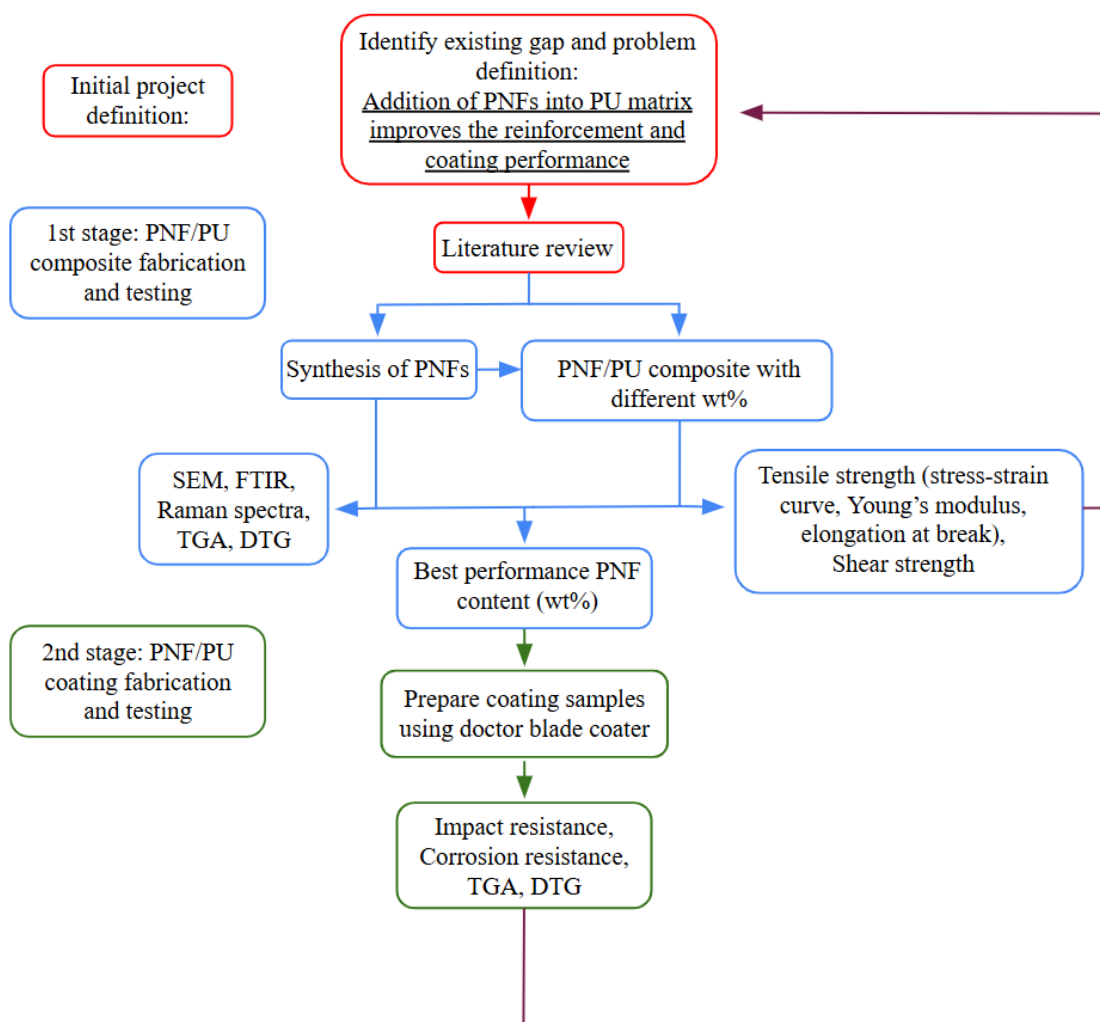


Figure 6. Project flow chart.

The initial stage is the starting point of the project, which consists of the identification of the current existing gap and the main objectives. This process was supported based on the literature

review with the results of previously conducted studies in a similar field. Since the conventional coatings were found to lack strength, thermal stability and barrier performance, the nanofillers were identified to improve needed performance and add multifunctional properties. With PNFs being considered one of the most promising nano additives to address the goal of this project, the next two project stages focus on integrating such nanofiber into the polyurethane matrix and confirming its superior properties through various characterizations and tests. Moreover, for this project a quantitative method of data collection was utilized, where material properties were evaluated via empirical measurements.

The first stage consists of the synthesis of PNFs from commercial short PBO fibers with subsequent morphological and chemical characterization to validate their size and structure. After acquiring the nanofibers, the PNF/PU composites with various nanofiller content (wt%) are fabricated to investigate improvement in the reinforcement through mechanical test, including tensile and shear strength followed by ASTM standard. By examining the shear strength of PNFs with different weight content in polyurethane matrix, the best performing wt% of the nanofiber is further employed into the coating as the second project stage.

The second stage focuses on the preparation of PNF/PU coating on the aluminum metal sheets employing doctor blade applicator. Samples are then also investigated morphologically and structurally in addition to evaluation of impact and corrosion resistance.

The tentative dates for each project task are provided on the Gantt Chart in Figure 7.



Figure 7. Gantt Chart.

Since the large number of test samples is fabricated in this project, to provide a clear demonstration of the achieved results, the names and descriptions of each are encoded as shown in Table 2.

Table 2.

Sample composition and processing parameters

Code	Description
0wt%	A reference sample without the addition of nanofibers
0.05wt%	Sample with 0.05wt% of nanofibers, ball milling of 60 minutes, 450 rpm
0.1wt%	Sample with 0.1wt% of nanofibers, ball milling time of 60 minutes, 450 rpm
0.25wt%	Sample with 0.2wt% of nanofibers, ball milling time of 60 minutes, 450 rpm
0.5wt%	Sample with 0.5wt% of nanofibers, ball milling time of 60 minutes, 450 rpm

3.2 Materials

PBO short fibers as seen in Figure 8a were obtained from DuPont through Chengdu Xincheng New Material Technology Co., Ltd. The synthesis of PNFs was performed using methanesulfonic acid (ACS reagent, $\geq 99\%$) and trifluoroacetic acid (ACS reagent, $\geq 99\%$), both obtained from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Duralumin sheet D16A with thickness of 2 and 3 mm, sourced locally, will be used as the base application material. Two-component polyurethane (PU) consisting of polyester polyol resin and diisocyanate hardener (see Figure 8b), produced locally, was utilized to prepare composite coatings. Per manufacturer recommendation, the resin-to-hardener ratio was 2.5:1 by weight. Toluene, obtained from the local manufacturer, was used for the dispersion of PNFs in polyurethane.

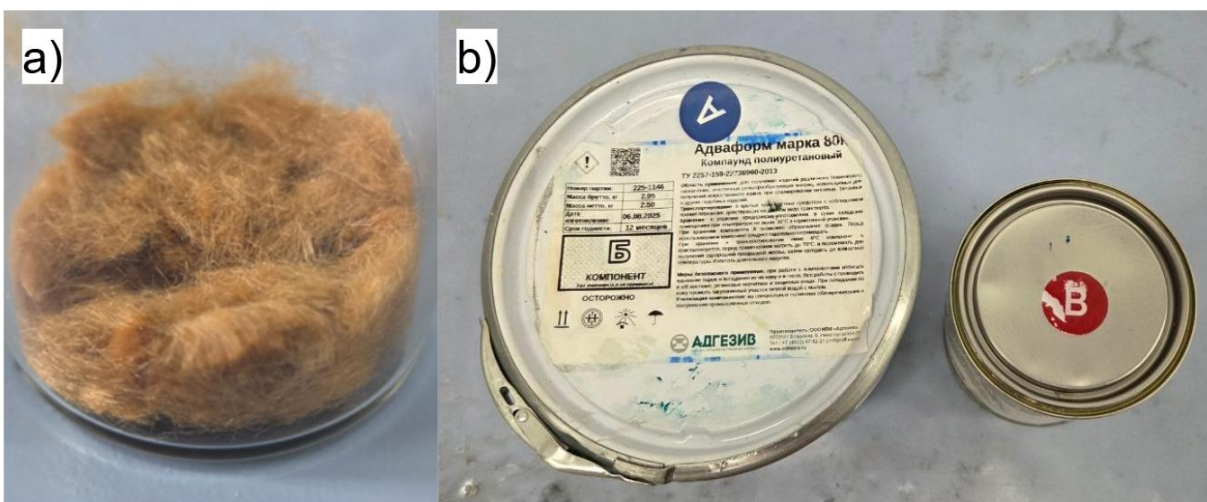


Figure 8. a) PBO commercial fibers, b) Two-component polyurethane.

3.3 Equipment

The YXQM series planetary ball mill, obtained from MITR Instrument Equipment Co., Ltd (Changsha, China), was used in the synthesis of PNFs and their dispersion in PU matrix. The Rawmid Professional RPB-02 high speed mixer, sourced locally, was used to assist the formation of nanofibers network. The PTFE filter membrane with a pore size of $0.22\ \mu\text{m}$, purchased from

LVDlab (Xinxiang, China), was utilized in the vacuum filtration. The Stegler 10D ultrasonicator (Moscow, Russia), the Cole-Parmer Stuart UC152 hot stirrer plate (Illinois, USA), Shimadzu AT-R analytical and TX4202L laboratory precision weighing scales (Kyoto, Japan), supplied locally, were used to break agglomerates, continuously mix the PU mixture and accurately measure the weight of the materials, respectively. The vacuum oven was supplied by Faithful Instrument CO., Ltd (Hebei, China) to dry the synthesized fibres. The vacuum filtration unit, beakers, petri dish, magnet and magnetic stirrer extractor, metallic spatula and weighing boats, sourced locally, were used throughout the experiments. Figure 9 illustrates the equipment used in the experimental part of the project.

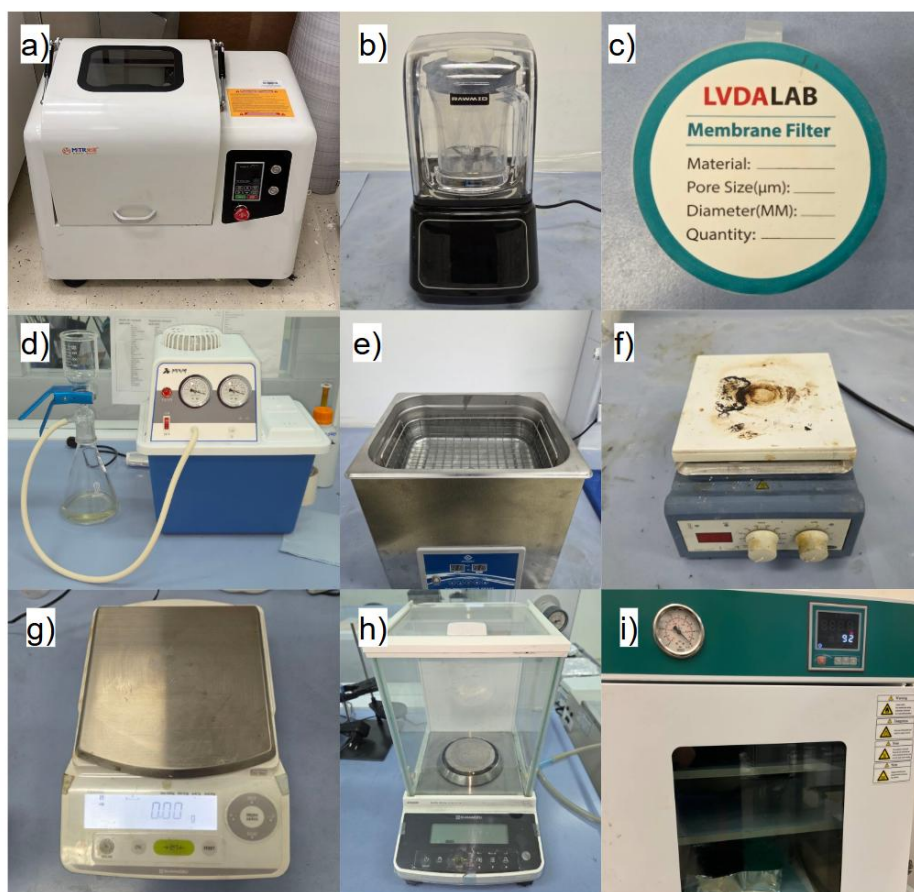


Figure 9. a) The YXQM series planetary ball mill, b) Rawmid Professional RPB-02 high speed mixer, c) PTFE filter membrane, d) Vacuum filtration unit, e) Stegler 10D ultrasonicator, f) Cole-

Parmer Stuart UC152 hot stirrer plate, g) TX4202L weighing scales, h) Shimadzu AT-R analytical scales, i) Vacuum oven.

3.4 PNFs synthesis

The synthesis of PNFs was performed using an acidic mechanically disintegration method, which was divided into two stages: acidic protonation and mechanical disintegration stage consisting of planetary ball milling and high-speed wall breaker. During the ball mill, the proton layer of PBO macrofibres were decomposed via chemical protonation, intense shear stress and high-speed collision of zirconia balls. This enhances the effective penetration of acids, therefore significantly increasing the specific surface area for the mechanical collision. During the mechanical disintegration stage, the surface of PNF becomes roughened and rich in hydroxyl groups, therefore improving the chemical and physical cross-linking with the matrix material, in our case polyurethane.

The process of the PNFs synthesis performed in this study is shown in Figure 10.

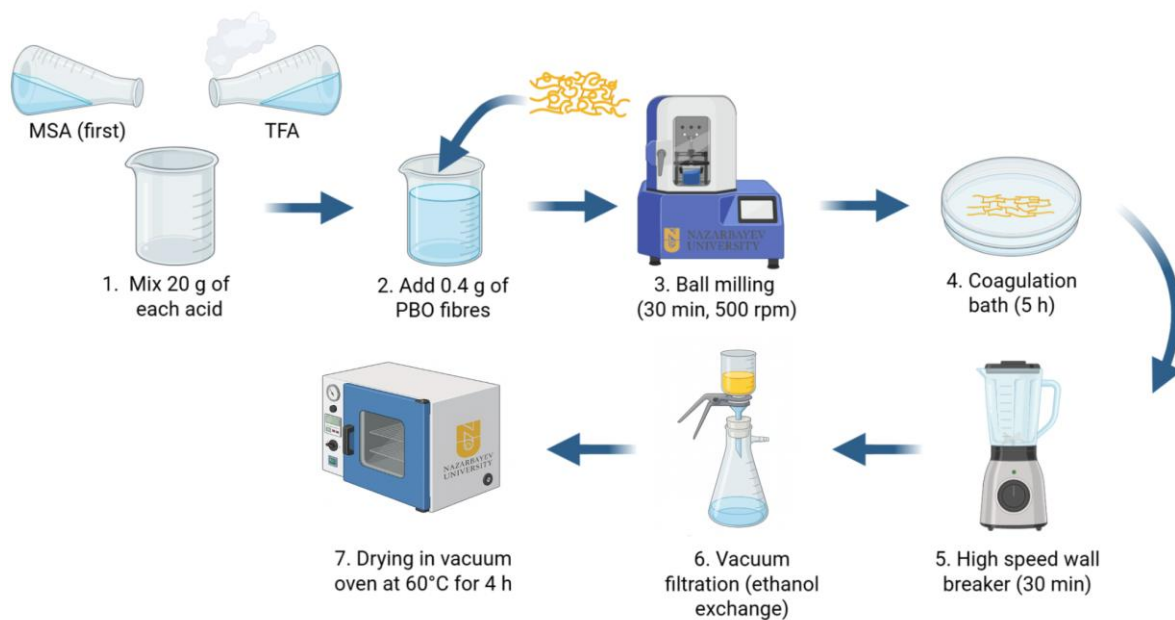


Figure 10. Schematic illustration of the PNFs synthesis.

Firstly, the PBO fibres are added to acetone solution for ultrasonic cleaning. However, since purchased commercial fibers are already clean, this step is only theoretical and in our case is skipped. Then, 20 grams of MSA were added to 20 grams of TFA in a glass beaker. This step was done in the fume hood wearing protective clothing, such as glasses, a mask, gloves and a coat, followed by safety rules since TFA evaporates toxic gases. The 0.4 grams of PBO is added into the acid mixture and is poured into a ball jar. Then, 120 grams of 10 mm zirconia balls are added to the acid mixture with PBO fibers and the jar is weighed. In order to balance the planetary ball system, the second jar is taken with a similar weight and placed opposite the jar with PBO. After, the planetary ball mill machine is turned on, with the configured parameters of 500 rpm for 30 minutes unidirectionally without any stop in between. During this process, the proton layer of PBO fibres starts to open, followed by the weakening of intermolecular connections. During this process they group together and form connections of reduced nanosized fibres. After the ball mill, PNF solution in acid is distributed to the bottom of a glass container and placed in a fume hood to dissipate the residual acid. Ethanol is subsequently sprayed for the coagulation bath treatment for 5 hours to remove excess acids. In this form, PNF gel is added to a high-speed wall breaker with ethanol as the solvent for a continuous 30-minute blending. This helps to open the network of re-cross linked nanofibres. After it, the PNF/ethanol solution is filtered through a vacuum filtration unit via PTFE filter membrane with a pore size of 0.22 μm . After filtration, a clean but wet fibrous PNF cake is obtained. To obtain dry PNFs for further integration into polyurethane (PU) matrix, they are dried in the vacuum oven for 4 hours at 60 °C. Figure 11. demonstrates the experimental setup with the procedures of PNF synthesis.

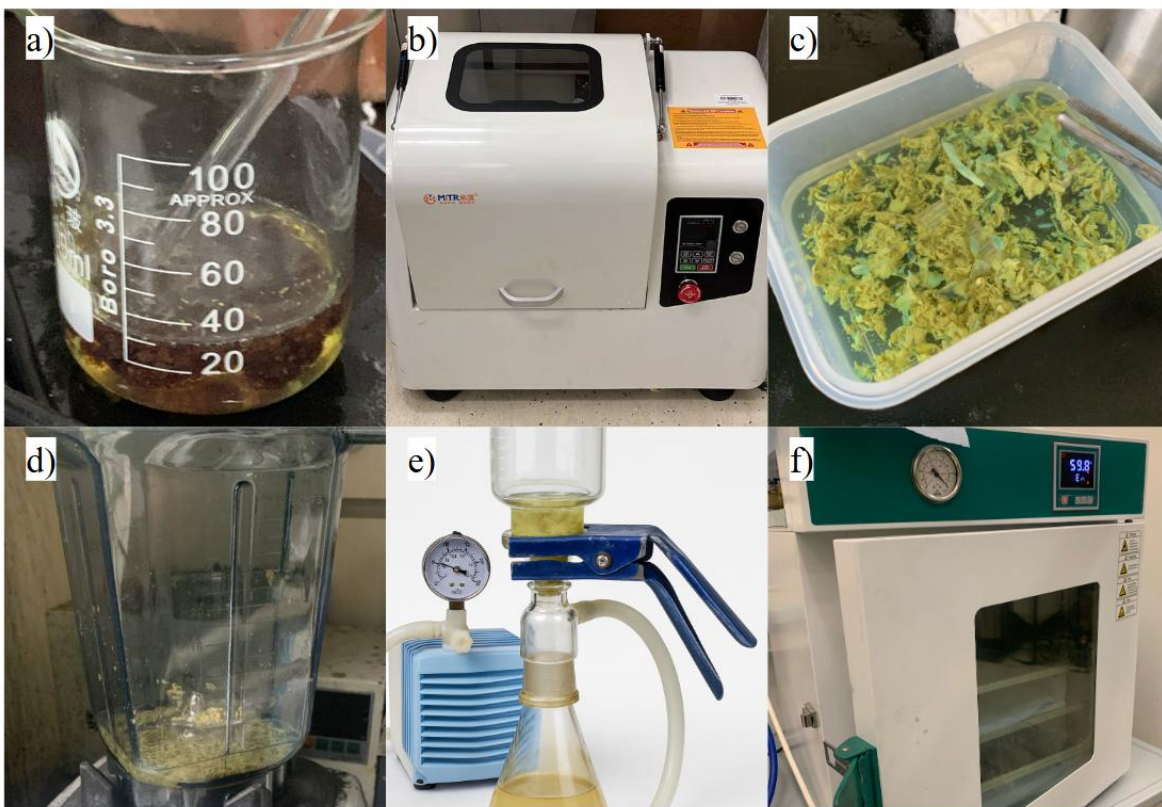


Figure 11. Experimental setup and procedure for the synthesis of PNFs: a) Mix of acid with PBO; b) Ball mill; c) Coagulation bath with PNF/acid solution; d) High speed mixer with PNF/ethanol solution; e) Vacuum filtration; f) Drying the filtrated wet PNF fibers in vacuum oven.

3.5 Preparation of PU composite, lap shear joints and coating

The process of preparing the PNF-based composite is illustrated in Figure 12, and the experimental process is shown in Figure 13. A planetary ball mill was used to disperse 0.1575 g of dry PNF into 10 g of toluene, obtaining a 0.25 wt% PNF-toluene solution. This mixture was poured into a ball mill jar containing 10-mm zirconia balls for milling with a 1:10 mass ratio. The ball milling was conducted at 450 rpm for 60 minutes. Then, a brownish-yellow, low-viscosity solution was obtained.

45 g of polyol resin was mixed with 10 g of toluene, and the solution was sonicated for 10 min. The PNF-toluene solution was then added to the polyol solution. The mixture was stirred on a hot plate with a magnetic stirrer set to 60 °C and placed in a fume hood to evaporate the toluene. After stirring, 18 g of isocyanate-based hardener was added to the polyol-PNF mixture, which was stirred continuously for 4 minutes to produce the PNF polyurethane (PU/PNF) composite. For creating single lap joints (SLJs), the composite was applied to aluminum sheets with dimensions based on ASTM D1002 standard. Coating was applied on aluminum by using a doctor blade. The composite, SLJs and coatings were then degassed in a desiccator for 8 minutes and cured at room temperature for 3 days. Different compositions of PU/PNF composite, SLJs and coatings were prepared by varying the amount of PNF added.

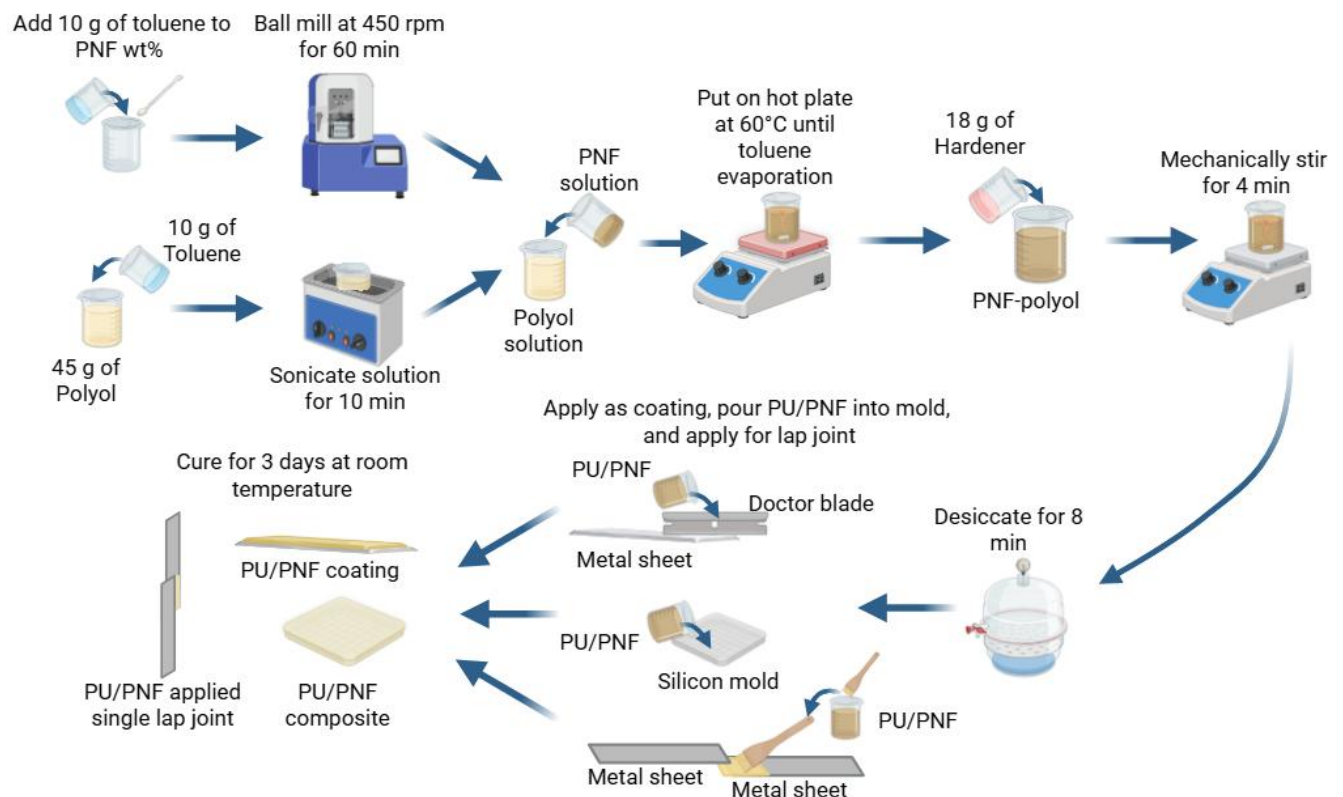


Figure 12. Schematic diagram of the composite preparation procedure.

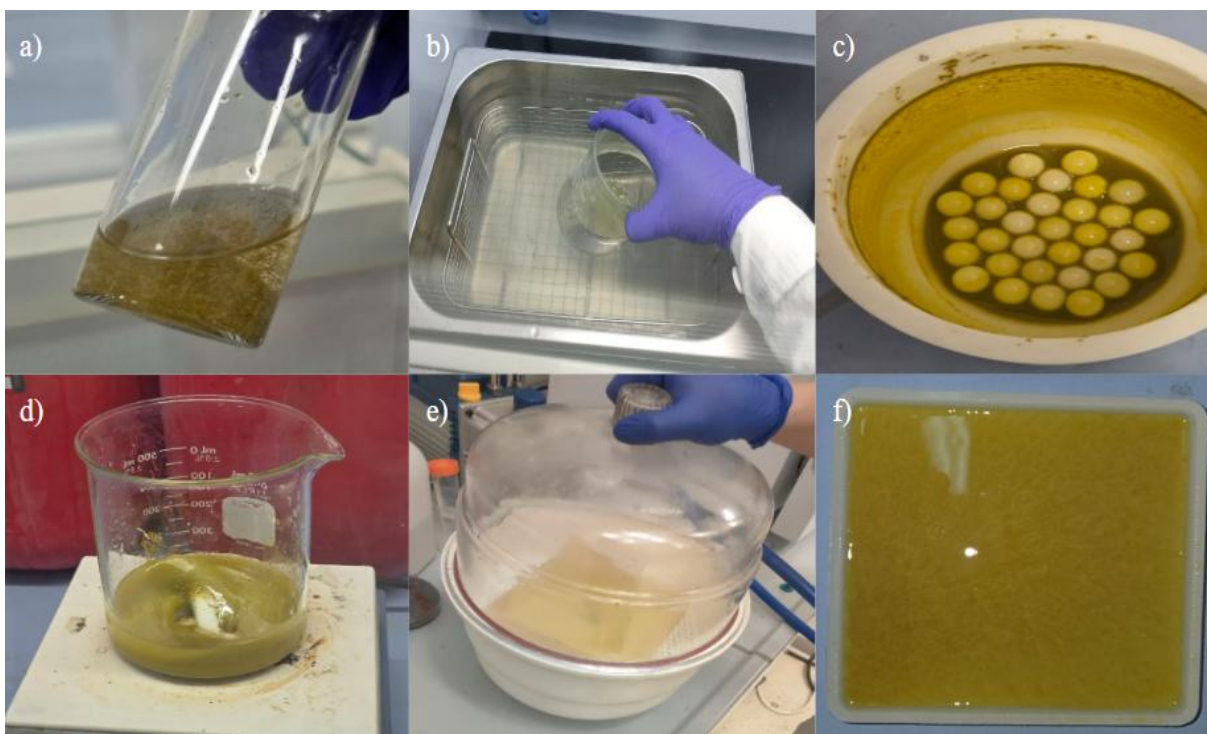


Figure 13. Experimental setup and procedure for the fabrication of PNF/PU composites: a) PNF-toluene solution; b) Ultrasonication of polyol-toluene solution; c) PNF-toluene solution after ball milling d) Evaporation process of excess toluene in PNF-polyol-toluene solution e) Desiccation process for reducing bubbles formation f) PNF/PU composite film during curing.

4 Characterization and mechanical measurements

4.1 Morphology

The microstructural characteristics, surface morphology and fractured surface of PBO fibres, PNFs, prepared composites and coatings are characterized using Scanning Electron Microscopy (SEM, Helios-5CX DualBeam by Thermo Fisher Scientific) as seen in Figure 14. Prior to imaging, the samples are dried in the vacuum oven and spray coated with a 5-7 nm layer of Au (gold). The analysis is performed in the secondary electron (SE) mode using an accelerating voltage of 5 kV and beam current of 86 pA (picoampere). To obtain the high resolution of PNF synthesized nanofibers, the through-lens detector (TLD) is implemented, while to achieve the resolution of macrosized commercial PBO fibers, the standard Everhart-Thornley detector (ETD) is utilized. The SEM is conducted primarily to investigate the surface of a specimen, which is scanned sequentially by the electron beam. At each location, the signals emit from the material and are further collected by the detectors. Such signals are then collected in series and combined in an image, whose pixel distribution is determined by chosen scan patterns [38].

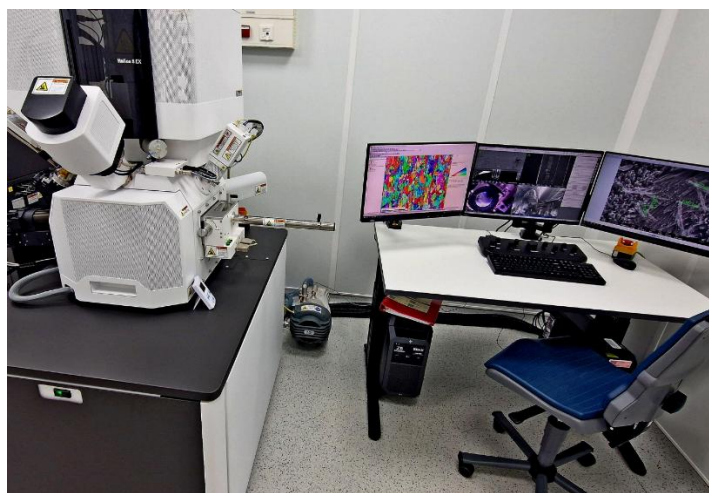


Figure 14. SEM, Helios-5CX DualBeam by Thermo Fisher Scientific.

The chemical structure of PNF and PBO fibers are evaluated using a Fourier Transform Infrared spectroscopy (FTIR, Nicolet iS12 by Thermo Fisher Scientific) and a Raman spectrometer (LabRAM HR Evolution&Omega scope by HORIBA&Aist-NT) as seen in Figure 15 (a) and (b). Prior to characterizing, the material samples are dried in the vacuum oven, since the wet condition of fibers substantially affects the analysis and may generate invalid results. In FTIR, the small piece of specimen is placed directly under the beam. The beam sends the infrared light through the material to analyze the absorption of specific light wavelengths. This causes the vibration of the chemical bonds, which interferogram data is then converted into a readable spectrum by a Fourier transform mathematical model [39,40].

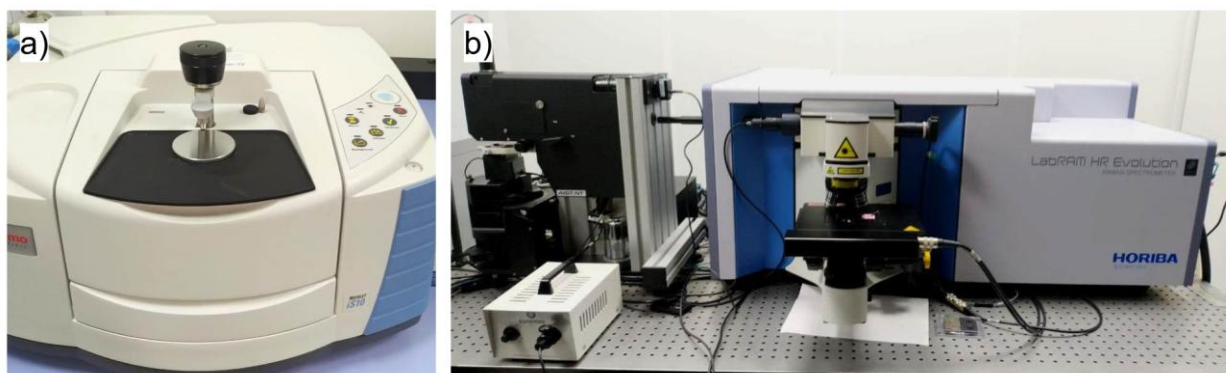


Figure 15. a) FTIR, Nicolet iS12 by Thermo Fisher Scientific, b) Raman spectrometer, LabRAM HR Evolution&Omega scope by HORIBA&Aist-NT.

In Raman spectroscopy, the chemical composition of material is defined as the wavelength shift of scattered light. When the high-intensity laser interacts with the specimen molecules, the light is scattered at different wavelengths due to inelastic interaction with the chemical bonds. The spectrum then is generated by plotting the intensity of the light against the wavelength shift, which shows the peaks corresponding to vibration of different chemical bonds [41].

4.2 Thermal stability

Thermogravimetric analysis (TGA) is employed using a simultaneous thermal analyzer (STA 6000 by Perkin Elmer, see Figure 16) to study the thermal stability of fibres and PNF/PU composites. The analysis is performed in the range from the room temperature up to 800°C with a constant heating rate under a nitrogen atmosphere for fibres and air atmosphere for composites. Under the heating, the thermogravimetric analyzer then monitors and records the weight of the sample over time. Those recordings provide data regarding the material properties such as thermal stability and decomposition temperature. DTG (derivative thermogravity), the first derivative of TGA, identifies the inflection points and provides information about the rate of mass change and the temperatures where mass loss occurs more rapidly [42].



Figure 16. TGA, STA 6000 by Perkin Elmer.

4.3 Mechanical Properties

The tensile test is an important test to understand the effect of PNFs on polyurethane composite under uniaxial stress, which was completed on a Microcomputer-controlled Electronic Universal Testing Machine (Model CMT5105, China) as seen in Figure 17. Polyurethane is a flexible material with a simple pure structure, and when nanofibers are mixed in, the internal structure becomes more complex, creating new load-transfer pathways. The tensile test allows us to capture

whether these pathways are effective and does the nanofiber-reinforced PU resist deformation better than pure PU. To get qualitative results, PU composites were prepared with different weight mass percentages of PNFs and then tested on a tensile test machine to determine the stress-strain curve, Young's modulus, tensile strength, and elongation at break. The cured composites were cut according to the ASTM D412 type C standard. ASTM D412 Type C is used because it is the established standard for testing vulcanized thermoset rubber and thermoplastic elastomers, materials whose mechanical behavior resembles polyurethane. The Type C specimen has a dumbbell-shaped geometry that localizes deformation in a reduced central region and prevents premature failure at the grips. Specimens are cut using an ASTM D412 Type C Rubber Tensile Sample Die Cutter from Dongguan Amade Instruments Technology Co., Ltd., in a dumbbell shape according to the dimensions from Table 3 and Figure 18.

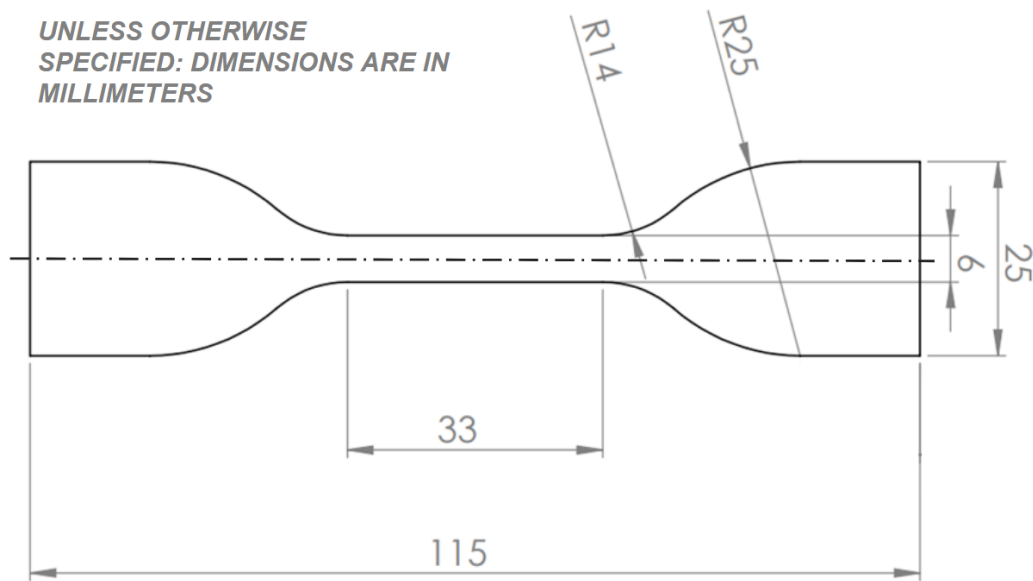


Figure 17. Model CMT5105 microcomputer-controlled Electronic Universal Testing Machine.

Table 3.

Dimensions of Specimen by ASTM D412 Type C

Parameter	Value
Total length	115 mm
Length of the narrow parallel section	33 mm
Gauge length	25±0.25 mm
Width in shoulder area	25±1 mm
Width in gauge length area	6±0.05 mm
Thickness	1.3 - 3.3 mm

**Figure 18.** Dimensions of a dumbbell-shaped specimen.

In addition, a crosshead speed of 50 mm/min was used, a rate chosen because of the polyurethane's viscoelastic nature, and this speed is recommended by the ASTM D412 type C standard. If the strain rate is too slow, the material begins to relax, creep, and deform time-dependently, producing curves dominated by viscous effects rather than true elastic behavior. If the rate is too fast, inertial

effects distort the measured stress. Therefore, the tensile test is the first test to confirm the improvement of the mechanical performance of PU with the introduced PNFs.

The test that follows is a single lap shear strength test, which is a common test to determine the bond strength of adhesives under shear stress. Polyurethane, as a surface protection, experiences shear from thermal expansion gradients, vibration, and impact spreading, so introducing nanofibers into the polymer may strengthen internal cohesion. The single lap-joint shear test was also performed on a Microcomputer-controlled Electronic Universal Testing Machine (Model CMT5105, China) to evaluate the behaviour of polyurethane. The ASTM D1002 is standard for the single lap shear strength test, which is followed for this project. According to the standard, the specimens were made from aluminum alloy 2024 and by dimension from Table 4 and Figure 19.

Table 4.

Dimensions of Specimen by ASTM D1002

Parameter	Value
Length of a metal sheet	125 mm
Width of a metal sheet	25 mm
Length of the adhesive	12.5 mm
Width of the adhesive	25 mm
Thickness of the adhesive	0.1 - 0.2 mm
Area of the adhesive	312.5 mm ²

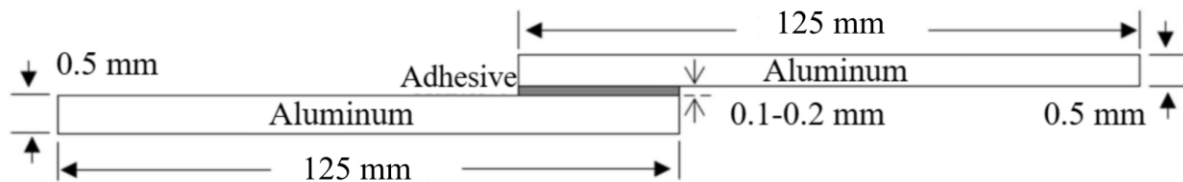


Figure 19. Single-lap shear test dimension.

Likewise, the crosshead speed for this test, as a standard proposes a range of 1.3-3 mm/min, was chosen at a minimum of 1.3 mm/min, as it is preferred for polymeric materials to avoid dynamic fracture. The slow loading rate also helps identify whether failure is cohesive (within the polymer), adhesive (at the interface), or mixed, which is critical evidence of how PNFs influences bonding and internal toughness. The thickness of aluminum alloy coupons is 1 mm to reduce bending during testing, where bending moments can reduce failure load by inducing mixed stresses. Therefore, the single lap shear strength test is important in determining the adhesive strength of enhanced PU, which is an important parameter as coating.

4.4 Impact resistance

The important test required is the Impact Test, which evaluates the dynamic loading resistance of metal coatings. Therefore, the Izod impact test provides a standardized method for assessing improved PNF/PU coatings under high-velocity loading. The Izod Impact resistance test was done on a TecQuipment TE15 Energy Absorbed at Fracture machine (see Figure 20).



Figure 20. TecQuipment TE15 Energy Absorbed at Fracture machine [47].

The suitable Izod impact test standard for polymeric materials and their composites is ASTM D256 [48]. It should be noted that the available TecQuipment TE15 Energy Absorbed at Fracture machine is primarily intended for demonstration purposes in the learning process and has certain limitations. In particular, the clamping configuration allows specimen thicknesses of only up to 3 mm, while standard Izod testing requires larger specimens with a minimum width of about 12.7 mm and specific standardized geometry. Therefore, full compliance with standard Izod testing procedures was not achievable. Despite these limitations, the machine provides a measurement of the energy absorbed at fracture, which can be used for comparative analysis between specimens. The standard specimen geometry is a 64x12.7x3.2 mm beam-type specimen with a V-notch of 45° in the middle, and a 0.25 mm tip radius and 2.54 mm depth. In this study, rectangular specimens with dimensions of 60×10×2 mm were prepared, with an additional 0.5 mm coating layer applied on one face. Due to machining limitations, a U-shaped notch was introduced using a metal saw rather than a standard V-notch (Figure 21). The notch depth was 1 mm, resulting in a remaining ligament thickness of 1 mm in the notched region. The notch was positioned at the center of the specimen to promote fracture initiation under impact loading, following the general principles of Izod testing. Producing accurate and precise results, preparation, notch placement, and testing conditions across all samples was consistent. The notch creates a controlled stress concentrator, so that every sample fractures at the same location and in the same failure mode. In this test specimen is placed vertically with the notch facing the hammer. The pendulum strikes the coated notched face. This geometry is sensitive to changes and helps detect crack initiation in PNF/PU, crack propagation speed, and energy absorption. During testing, the hammer's kinetic energy transfers instantly into the specimen, and the software records the energy absorbed (J) during fracture. The

Izod impact test provides a reliable and sensitive measure on how PNFs enhance the impact toughness of polyurethane coatings.

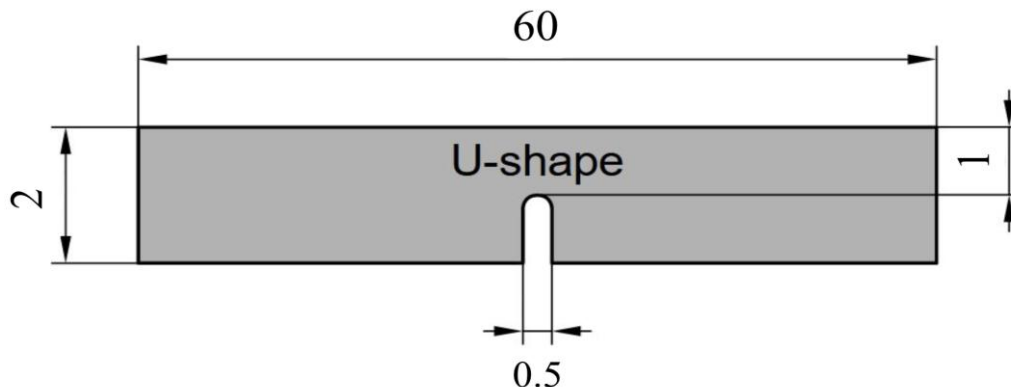


Figure 21. Impact resistance test dimension, in mm.

4.5 Corrosion resistance

Corrosion testing is essential for evaluating the protective performance of nanofiber-reinforced polyurethane coatings on aluminum. Nanofibers may strengthen the microstructure and reduce porosity, thereby slowing the penetration of chloride ions. The salt spray test accelerates these degradation processes, so the test was performed on XI'AN LIB Salt Spray Test Chamber S-750 (Figure 22a). This chamber allows doing the ASTM B117 standard, which will be used for testing PNF/PU coatings. This standard defines the parameters of the environment for the test that are in Table 5.

Table 5.

Parameters of Environment by ASTM B117

Parameter	Value
Orientation of Panels	15-30° from vertical
Salt Solution Concentration	5 ± 1 wt% NaCl solution
Temperature of Chamber	35 ± 2°C

Parameter	Value
Spray Collection Rate	1.0-2.0 mL/hr for each 80 cm ² collection area
Atomization Pressure	70-170 kPa

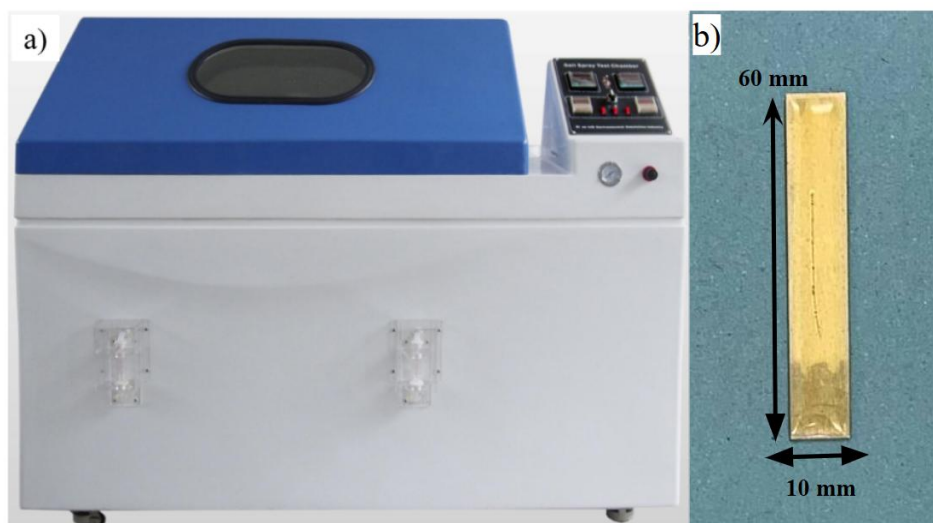


Figure 22. a) Salt-spray chamber S-750; b) PNF-reinforced PU coating on aluminum coupons.

The panels that are placed inside the chamber are aluminum alloy 2024 coupons with a protective layer of PNF-reinforced PU coating (Figure 22b). These aluminum coupons have dimensions of 60x10 mm with thickness of 2 mm. The surface of aluminum is cleaned with acetone, lightly abraded with 600-grit paper, rinsed, and dried before coating. PNF/PU is applied by brush in three coats to reach a dry film thickness of $100 \pm 20 \mu\text{m}$. After application, the panels are cured for 7 days at room temperature. This ensures full solvent loss and stable crosslinking, so incomplete cure does not affect the corrosion performance of the coating. The duration of exposure will be several: 24 hours, 48 hours, 7 days. This is needed to reveal early failures such as blistering, underfilm corrosion, loss of adhesion, or microcracking in the coating. Longer exposures may be

applied later, depending on the results. After exposure, panels are rinsed in deionized water, dried at room temperature, and investigated visually and microscopically for blister size and density, coating cracking, delamination, and color change. The performance of pure PU and PNF/PU coatings is compared to evaluating the hypothesis that nanofibers improve barrier behavior and slow chloride penetration at the coating-metal interface.

5 Results and Discussion

5.1 Morphology of PNFs and PBO analysis

SEM images reveal that original PBO fibers have a linear and uniform structure, as well as exhibiting average diameter of approximately 15 μm as is shown in Figure 23a. Ball milling with the high shear stress and interaction force from intensive collision of zirconia balls with PBO, breaks the proton layer of the fiber. This process increases the reaction area of MSA and TFA with the PBO surface, resulting in the weakening of intermolecular connections by accepting the PBO's nitrogen and oxygen atoms from the oxazole ring. Furthermore, in such a strong acidic environment, the partial hydrolysis of benzobisoxazole rings takes place which generates an increased specific surface, a rougher surface of PNFs and reduction in the fiber sizes. The SEM images in Figure 23 (b) and (c) demonstrate the noticeable changes in the fibers, where the diametral size in the range of 10-20 nm is achieved, confirming successful PNFs synthesis. The acid protonation and mechanical disintegration method not only results in forming nanofibers from the micro-sized PBO fibers but also promotes the formation of functional groups on the surface of PNFs. This would lead to a better reinforcement of PNFs in the polyurethane matrix, therefore improving the mechanical performance of the material. These observations are consistent with the previous studies, where similar acidic ball milling resulted in reduction of PBO diameter size and improving surface affinity of fibres. Such results further contribute to the enhanced reinforcement in polymers and coatings.

The synthesis of PNFs can be controlled by adjusting the chemical treatment and disintegration conditions, such as acid concentration, ratio of MSA to TFA, ratio of acid mixture to the polymer and ball milling parameters. Therefore, the selected variables discussed in section 3 resulted in satisfactory results.

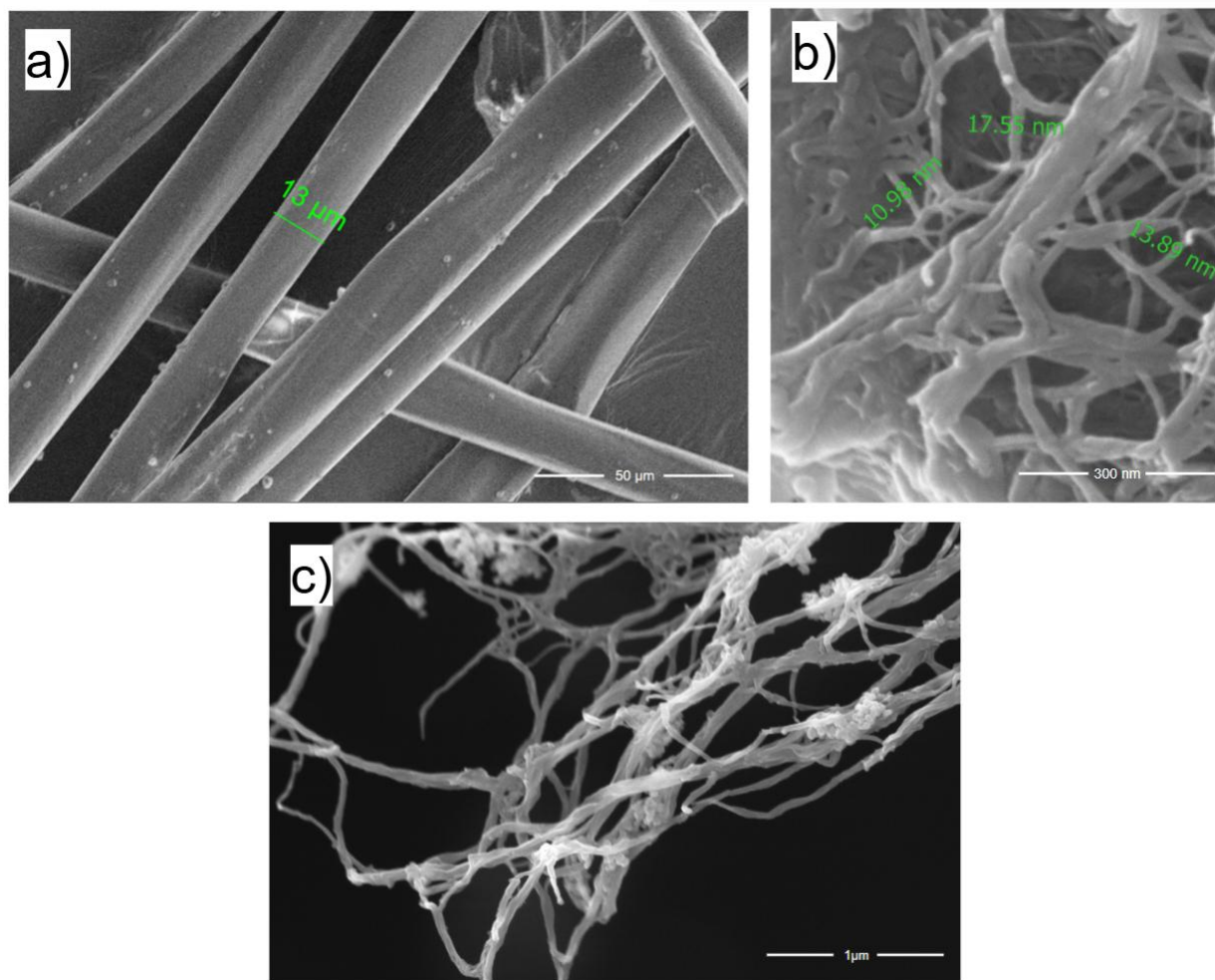


Figure. 23. SEM image of (a) original PBO fibres, (b) synthesized PNFs, (c) interconnected PNFs network.

The chemical composition was examined using FTIR and Raman spectrometries for both commercial PBO and synthesized PNFs fibers. The FTIR with the characterized peaks of PBO and PNFs is shown in Figure 24. It is seen that PNFs exhibit a chemical structure similar to the original poly-p-phenylene benzobisoxazole (PBO) fiber. Nevertheless, during the partial hydrolysis, some functional hydroxyl groups may occur on the benzobisoxazole rings, therefore slightly affecting results of PNFs spectroscopy [27,43]. However, the chemical structure overall remains primarily the same. Within the range from 3060 to 3100 cm^{-1} , the aromatic C-H stretch vibration occurs in

both fibres, which is attributed to the benzene ring. A similar aromatic hydrogen bond vibration is seen as the peak in the range of 700-900 cm^{-1} , and it is visible in both PBO and PNFs. The benzene ring associated with C-C stretching vibration corresponds to the wavenumber of 1500 cm^{-1} [27]. The C=N and C-O-C stretching vibrations correspond to the chemical structure of the oxazole rings, which appears in both fibers at 1620 cm^{-1} and 1050 cm^{-1} , respectively. The Raman spectroscopy is shown in Figure 25. It also indicates that PNFs have a similar chemical structure to PBO fibers. The vibrations of phenyl and benzene rings as well as C-C bonds of fibers correspond to the peaks of 1614 cm^{-1} along with other prominent peaks at 1541, 1271, 1168 and 919 cm^{-1} [35].

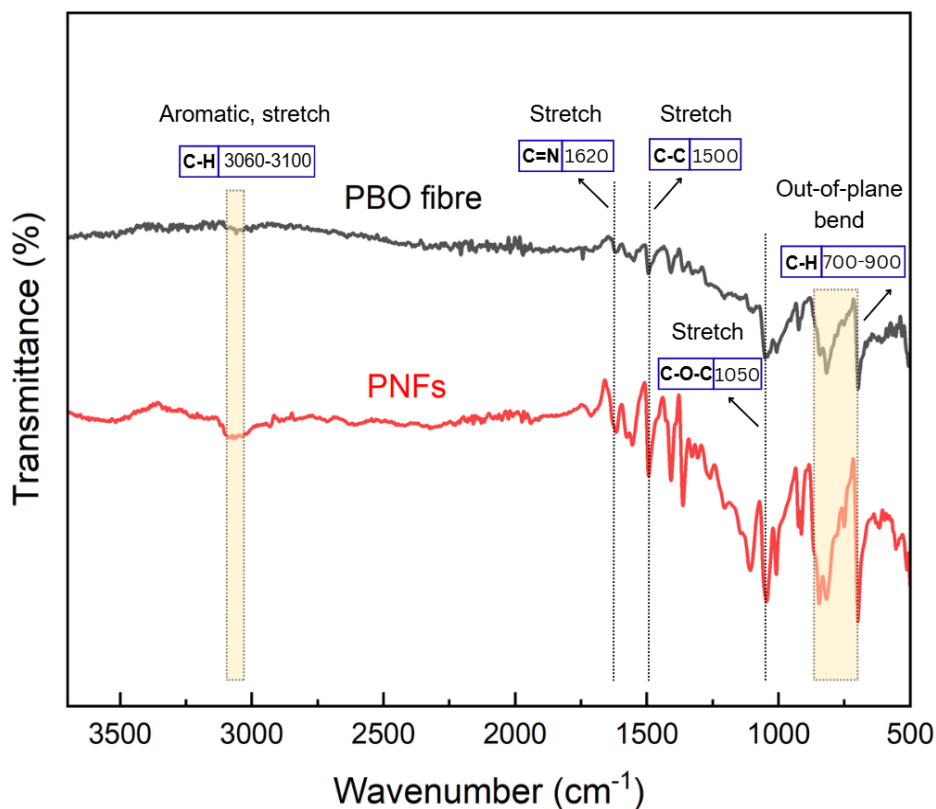


Figure 24. FTIR of PBO and PNFs.

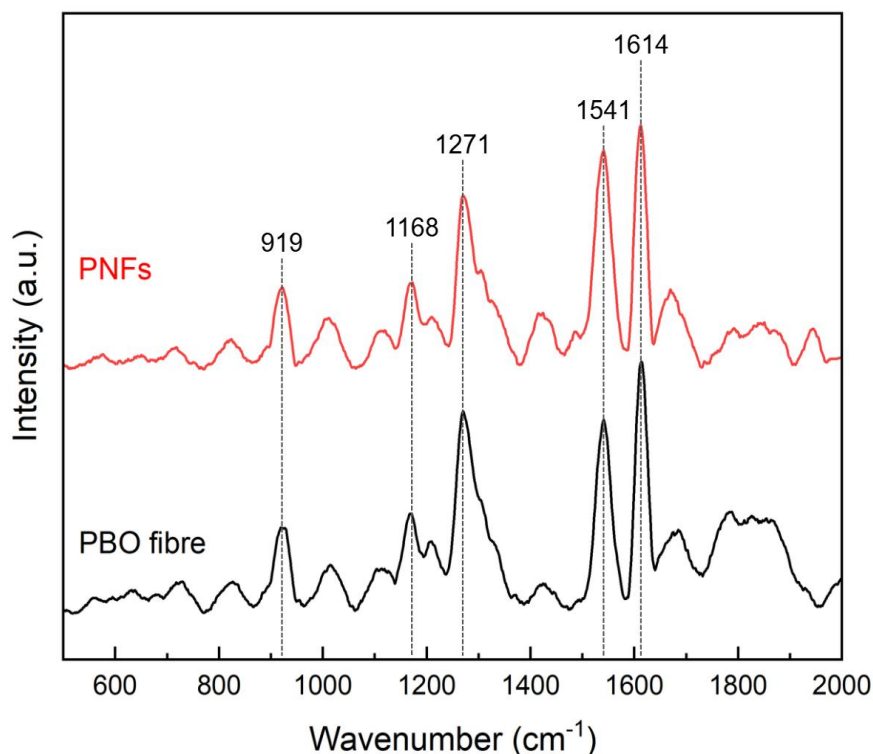


Figure 25. Raman spectra of PBO and PNFs.

5.2 Thermal stability analysis

The thermogravimetric analysis (TGA) under nitrogen atmosphere was performed to analyze the heat resistance of untreated PBO and synthesized PNF fibres. Commercial PBO fibres demonstrate excellent thermal performance with the smooth transition to degradation temperature at 640°C. This can be explained by the structure of commercial fibres, which exhibits high crystallinity and extremely crosslinked molecular arrangement. In comparison, processed PNFs decompose in noticeable 2 stages at 271°C (15wt% loss) and at 480°C (18wt% loss) as seen in Figure 26a. This behavior can be attributed to the presence of additional functional hydroxyl groups on the surface after the synthesis, which can be easily volatilized at high temperatures [27, 44]. Furthermore, the combination of MSA and TFA acids during fabrication breaks the main and side chains, therefore

disrupting the crosslinking of fibres and reducing the molecular weight. The overall decrease in degradation temperature by 160°C may result from the increase in specific surface area and partial reduction in structural integrity, making achieved nanofibres configuration more thermally sensitive. Regarding the DTG peaks in Figure 26b, PBO fibres demonstrate single-step decomposition due to the highly ordered structure, while PNFs exhibit an additional decomposition peak at 248.8°C. This can be once again explained by the significant change in the structure of nanofibres, where additional groups and broken chains are observed.

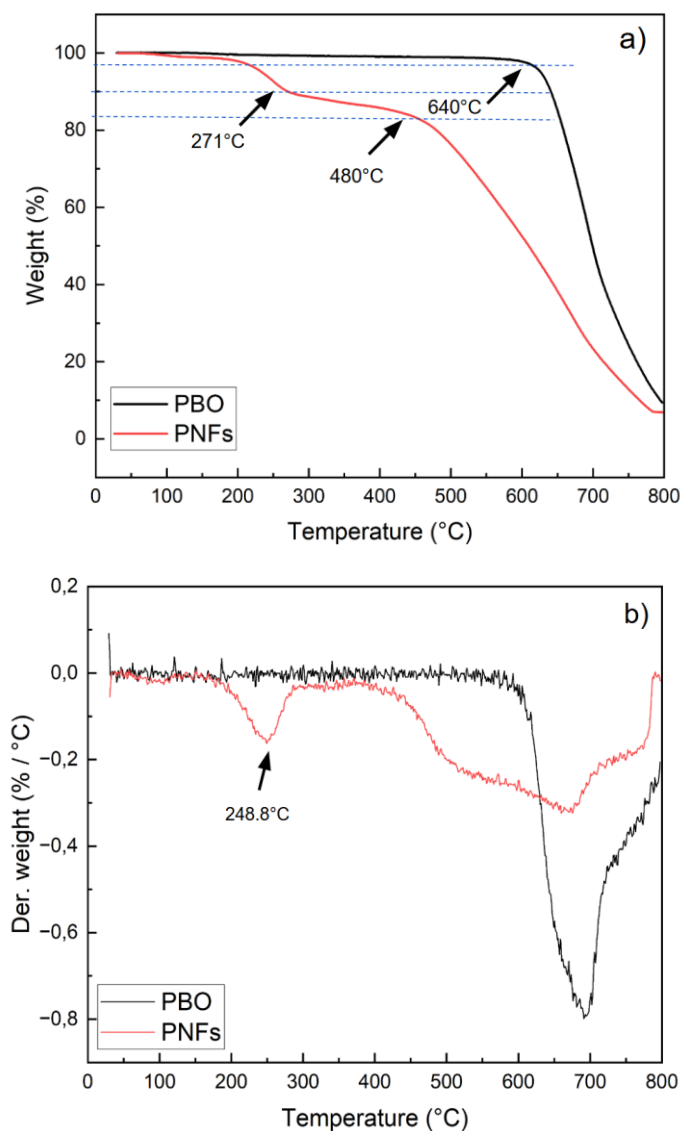
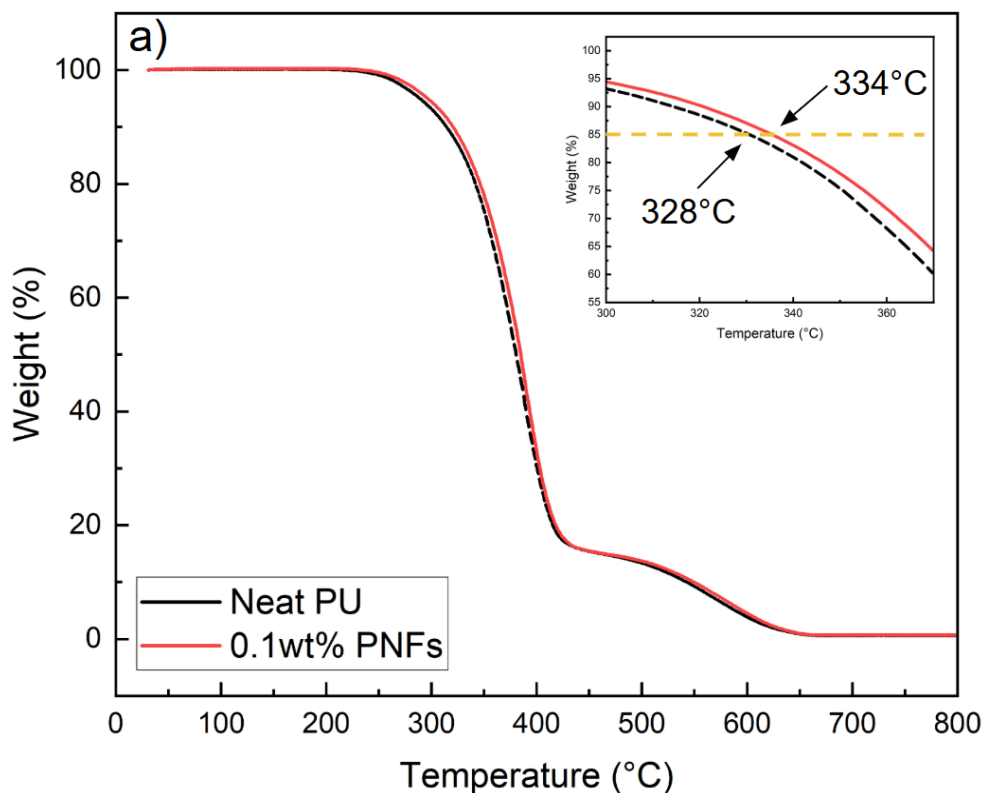


Figure 26. PBO and PNFs fibres: a) TGA, b) DTG curve under nitrogen atmosphere.

The thermal stability of polyurethane composites play an important role in various engineering applications, therefore the TGA analysis was also conducted for neat PU and the best performed PNF/PU at 0.1wt% during mechanical characterization (see Chapter 5.3). The results are presented in Figure 27a, where the decomposition temperature was recorded at 290°C. This temperature value arises from the material properties of polyurethane components, which are mainly soft. The addition of 0.1wt% of PNFs into PU nanocomposite demonstrates positive behavior by increasing the temperature of degradation by 6°C. A similar decomposition mechanism is seen in both PU samples as given in Figure 27b.



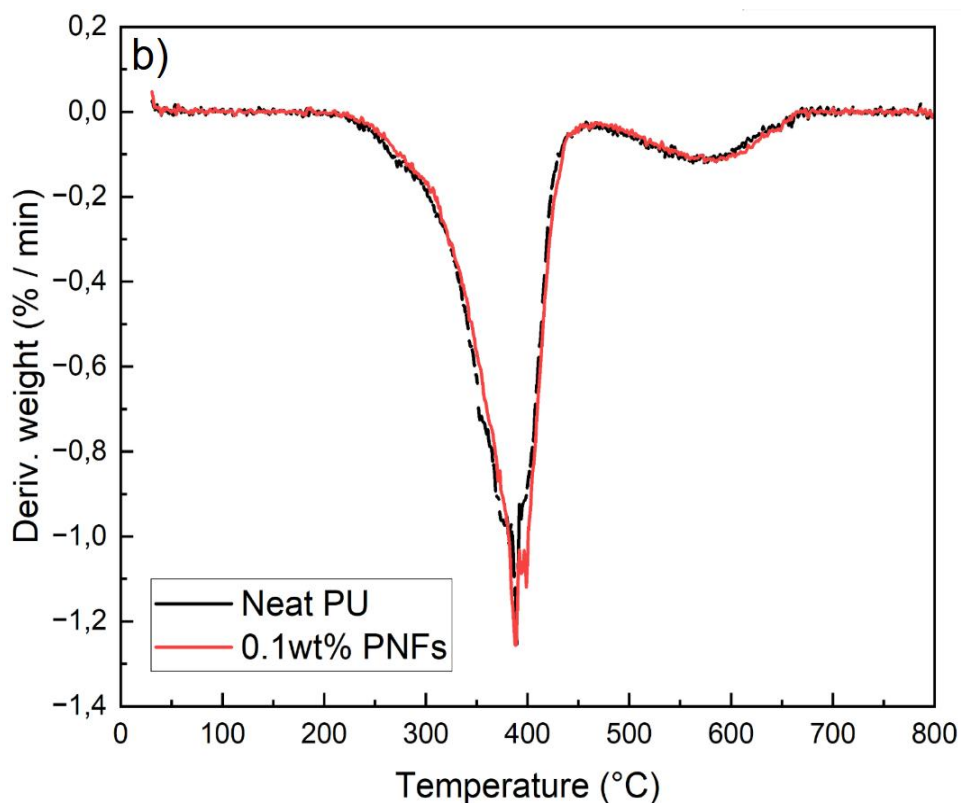


Figure 27. Neat PU and PU/PNFs composites with 0.1wt%: a) TGA, b) DTG under air atmosphere.

5.3 Mechanical properties

5.3.1 PU/PNF nanocomposites

The introduction of PNFs into polyurethane significantly changes the mechanical behavior of the resulting composites, as shown in Figures 28-30. Previous findings on 1D nanofiber reinforcements describe that low filler concentrations give noticeable strengthening when the fibers are well dispersed in the polymer matrix [27]. Therefore, samples were prepared in different concentrations (0wt%, 0.05wt%, 0.1wt%, 0.25wt% and 0.5wt%) of PNFs in the PU matrix. The mechanical behavior from the uniaxial tensile test of PU/PNF composites at different PNFs weight percentages is demonstrated in Figures 28-30, where REF stands for the neat PU.

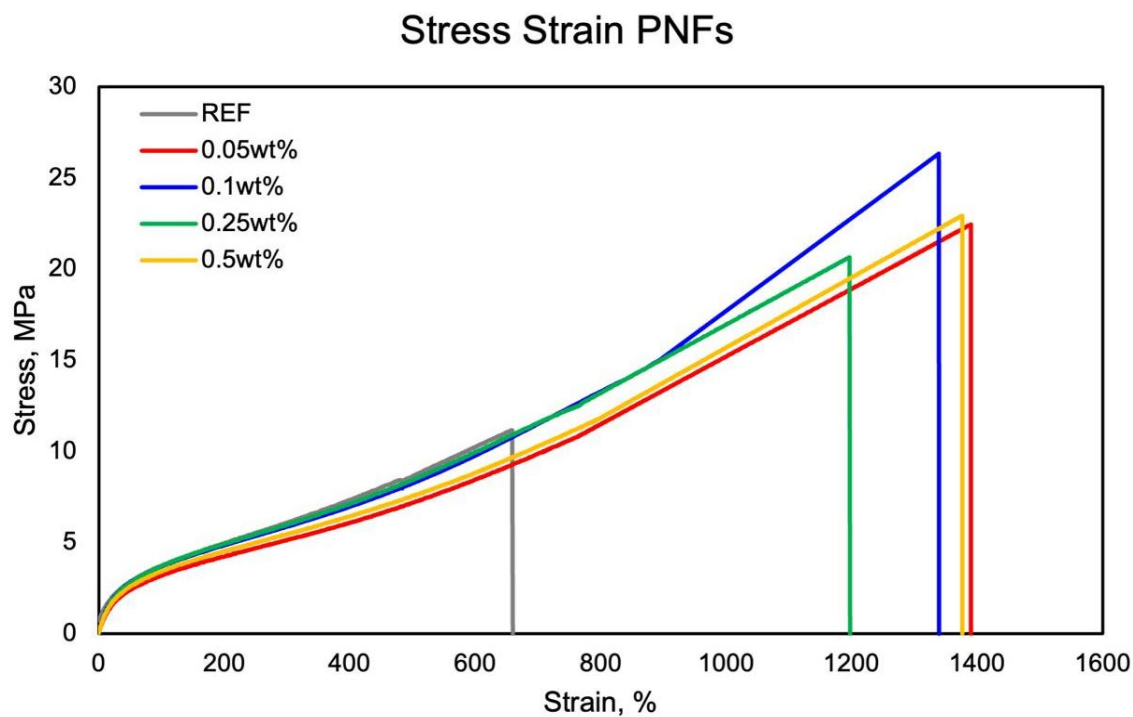


Figure 28. Stress-strain curve for different compositions of PNFs.

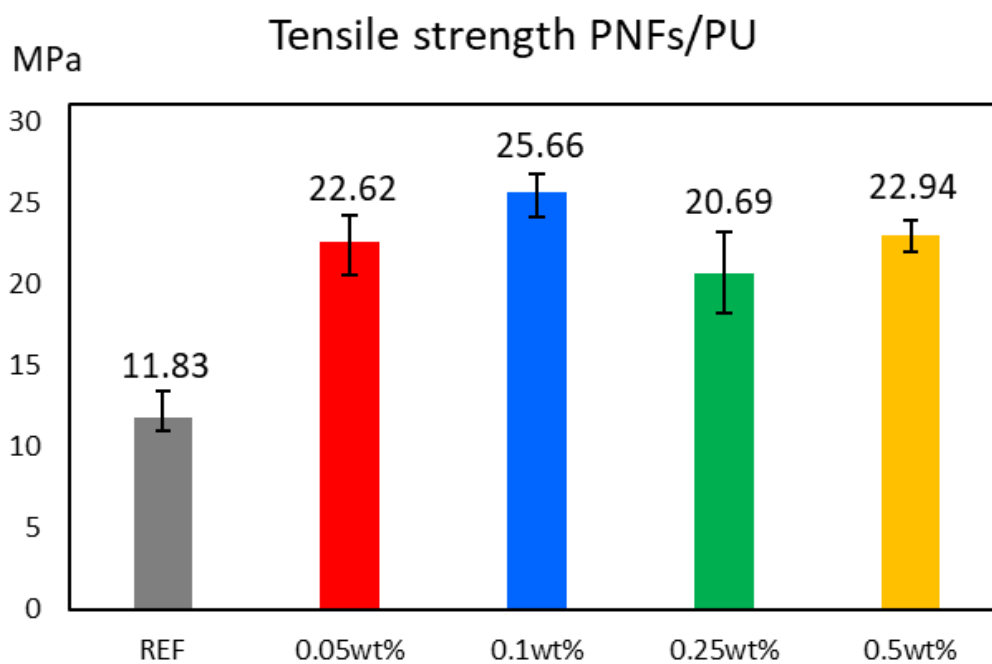


Figure 29. Tensile strength for different compositions of PNFs.

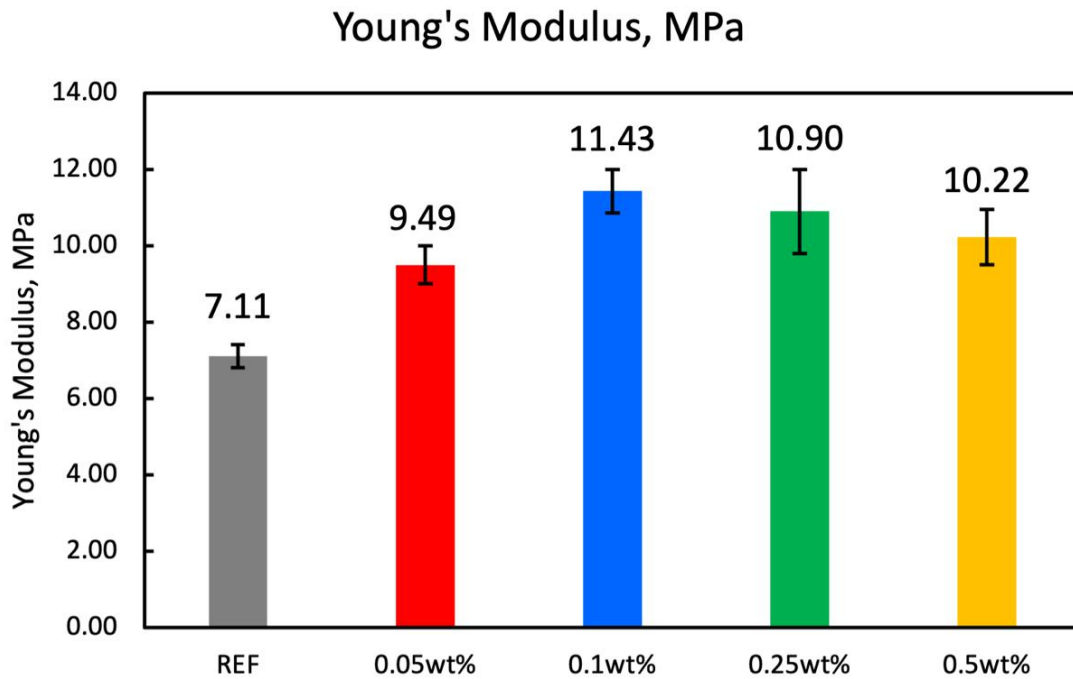


Figure 30. Young modulus for different compositions of PNFs.

Pure PU showed the behavior of a flexible elastomer with a tensile strength of 11.83 MPa (Figure 29), a Young's modulus of 7.11 MPa (Figure 30), and a moderate failure strain 660% (Figure 28). Introducing PNFs led to better performance, with the best improvement observed at 0.1wt% PU/PNF, achieving tensile strength of 25.66 MPa and Young's Modulus of 11.43 MPa. Other filler concentrations also yield significant improvements, with 0.05wt%, 0.25wt% and 0.5wt% samples reaching tensile strengths of 22.62 MPa, 20.69 MPa, and 22.94 MPa, respectively (Figure 28 and Figure 29).

The data also shows that further addition of PNFs after 0.1wt% decreased the performance of the composite. Such response indicates that adding an excess number of nanofibers leads to agglomeration, reduced interfacial adhesion and increase in stress concentration sites, which weakens the composite. Adding 0.05wt% of PNFs also demonstrated less performance, likely due to insufficient content of PNFs to fill up the PU matrix for optimal stress distribution.

Importantly, adding PNFs further enhanced flexibility instead of negatively affecting it. Elongation at break of the composites on average exceeded the baseline more than 2 times, with the best performing 0.1wt% PU/PNFs showing 1339% compared to 660% of neat PU. Stress is more effectively dissipated across the composite due to the dense reinforcement network formed by well-dispersed nanofibers. In such a structure, every nanofiber functions as a bridge for load transfer, supported by robust interfacial adhesion which creates an environment for optimal stress transfer, which explains why introduction of PNFs improved tensile strength of the composite [27]. Furthermore, Figure 31 also shows the durability test results in the salt spray chamber, where composites were subjected to saline mist for 7 days. Durability tests in saline mist revealed that continuous time in a harsh environment reduces tensile strength of the composites. The data on Figure 31 demonstrates that all PNF reinforced composites successfully retain a significant amount of their tensile strength, remaining between 20.55 MPa and 22.15 MPa, which is higher than both initial and exposed neat PU samples. However, structural retention varies depending on the filler concentration. The best performing sample (0.1wt%) experiences the greatest reduction in strength, decreasing to 20.55 MPa. In contrast, the sample with 0.05wt% demonstrates excellent environmental stability, showing only marginal decrease to 22.15 MPa. Furthermore, reference samples and samples with 0.25wt% have a small increase in strength after exposure which might be explained by the post curing process of the PU.

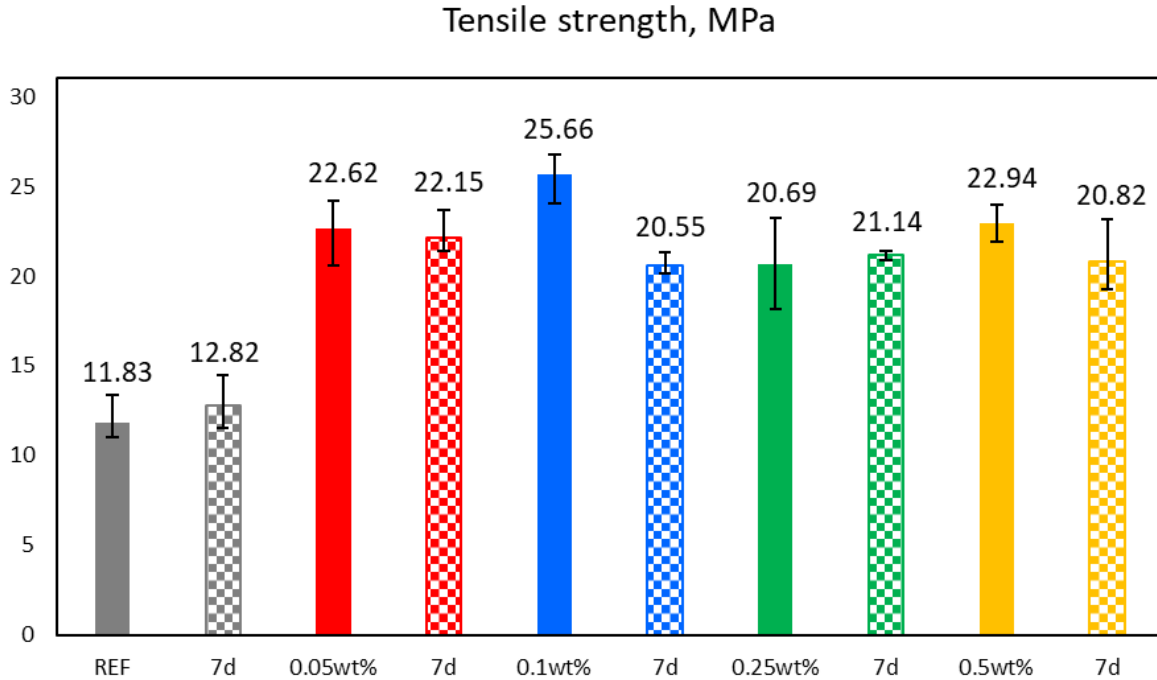


Figure 31. Tensile strength of composites before and after 7-day corrosion exposure.

5.3.2 Lap shear strength (Adhesive application)

The lap shear joint test results, measured as shear strength, are presented in Figure 32. The reference sample, which is 0wt% polyurethane, showed a shear strength of 1.29 MPa. Significant improvement in shear performance was observed by coated samples. For each weight percentage, 10-12 samples were tested. The addition of 0.05 wt% PNF reinforcement to PU increased the shear strength to 2.39 MPa, corresponding to an enhancement of approximately 85% compared to the reference sample. For 0.1 wt% PNF/PU a lower value of 2.24 MPa was observed, which still gives an improvement of 74%, indicating strong interfacial bonding. At higher concentrations, a noticeable decrease in performance was observed. The 0.25 wt% sample showed a shear strength of 1.20 MPa, which is lower than the reference sample. Likewise, the 0.5 wt% sample exhibited a value of 1.32 MPa, showing only a slight improvement compared to the reference. This low shear has resulted due to high presence of PNF in the PU, which creates stress concentration and early

fracture. Therefore, the analysis for each weight percentage is needed to avoid such cases of over supplying the nanofibers into elastomers. The overall trend shows that PNF improves its shear strength, with the highest performance observed at 0.05 wt%. At higher concentrations, possible agglomeration or reduced dispersion of PNF may negatively affect interfacial adhesion.

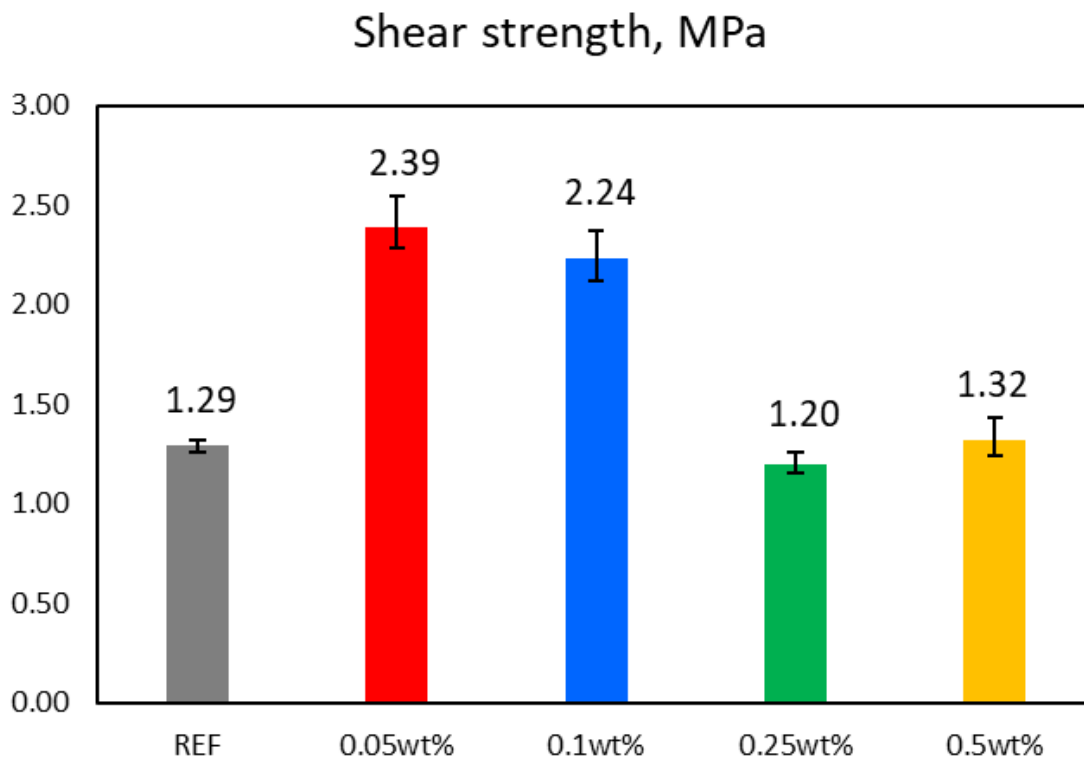


Figure 32. Shear strength of lap-joints for different compositions of PNFs.

5.3.3 Impact Resistance

The Izod impact test performed on the TecQuipment TE15 is based on the pendulum principle, in which the energy absorbed by the specimen during fracture is determined from the loss of potential energy of the swinging hammer. Before testing, the pendulum is raised to a fixed initial angle α relative to the vertical and released; in the absence of a specimen, it swings through and rises to an angle β on the opposite side. When a notched specimen is placed in the clamp, part of the

pendulum's kinetic energy at the lowest point of the swing is consumed in initiating and propagating the crack and in fracturing the remaining ligament. As a result, the pendulum follows through to a smaller angle β . The energy absorbed at fracture, E , is then obtained from the difference in the potential energy of the hammer before and after impact, in accordance with ASTM D256 [45] and the operating principle of the TecQuipment TE15 apparatus [46]:

$$E = m \cdot g \cdot (h_1 - h_2) = m \cdot g \cdot L \cdot (\cos \beta - \cos \alpha)$$

where: E is energy absorbed at fracture, m - mass of the pendulum hammer, g - gravitational acceleration, L - length of the pendulum arm, α - initial release angle of the pendulum from the vertical position, β - angle of the pendulum reached after fracturing the specimen, from the vertical, h_1 - initial height of the pendulum's center of mass above the lowest point, h_2 - maximum height of the pendulum's center of mass after impact.

The TecQuipment TE15 measures the follow-through angle β after each impact and converts it directly to absorbed energy in Joules. Prior to each set of tests, a no-load swing was performed to verify the friction-and-windage offset of the pendulum, and this baseline value was subtracted from each reading so that the reported energy corresponds to the net work done on the specimen, as recommended by ASTM D256 [45] and consistent with standard practice for pendulum-type impact testing [47, 48]. Because all specimens had the same nominal cross-section in the notched region, the absorbed energies are reported in Joules and used directly for comparative analysis between coatings, rather than being normalized per unit cross-sectional area.

The impact test results, expressed as energy absorbed at fracture in Joules, are presented in Figure 33. For each weight percentage, 7-8 specimens were tested, and the reported values correspond to the mean and error bars of maximum and minimum values taken into data set. The uncoated

aluminum specimen showed the lowest energy absorption, with an average value of 0.99 J, indicating low resistance to dynamic loading. A significant improvement in impact performance was observed for all coated samples. For the 0.05 wt% PNF/PU coating, the absorbed energy increased to 1.68 J, corresponding to an enhancement of 70% relative to the uncoated reference. A further increase was obtained for the 0.1 wt% PNF/PU coating, which yielded the highest value of 1.83 J, an improvement of 85% over the uncoated specimen and indicating optimal energy dissipation at this PNF loading in the PU matrix. Beyond this concentration, the absorbed energy decreased: the 0.25 wt% sample absorbed 1.69 J (+71%) and the 0.5 wt% sample 1.51 J (+53%), values that remain considerably higher than the uncoated case but are below the peak observed at 0.1 wt%. The overall trend confirms that the introduction of PBO nanofibers into the PU matrix enhances the impact resistance of the coated aluminum, with an optimum at 0.1 wt% PNF/PU. Likewise at higher loadings the enhancement is reduced, most likely due to nanofiber agglomeration within the coating and the associated formation of stress-concentrating defects, which decreases the effectiveness of energy dissipation.

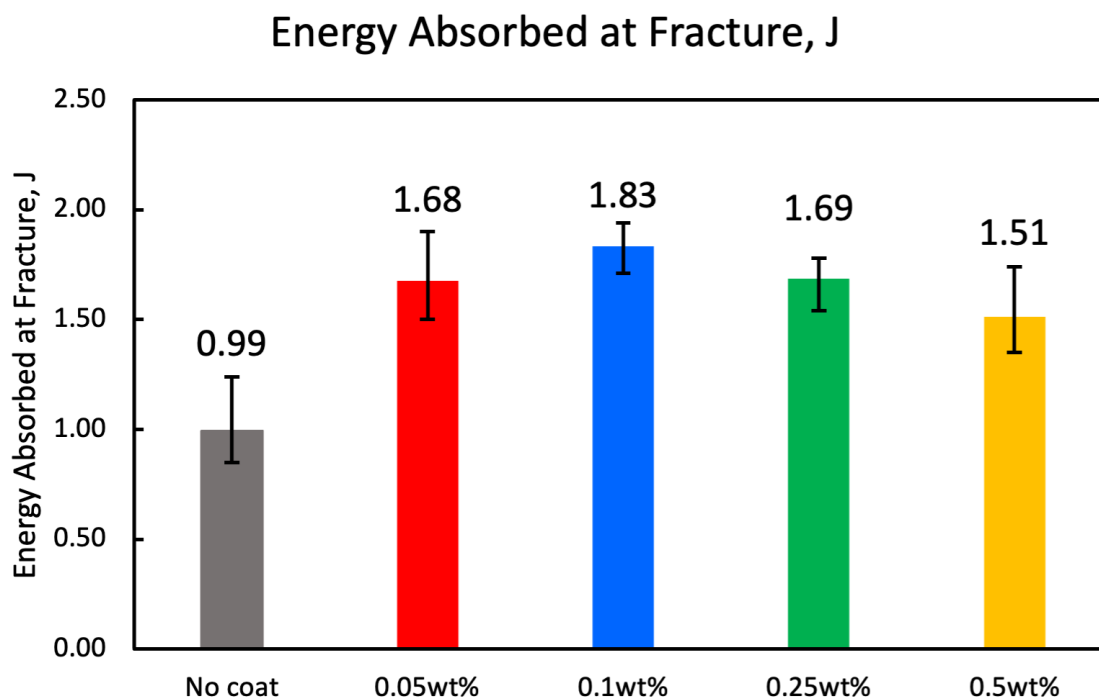


Figure 33. Energy absorbed at fracture for different compositions of PNFs.

5.3.4 Scratch test

To investigate the protective performance of PNF/PU composites, the prepared samples were placed in a corrosive environment for 7 consecutive days (168 h). Prior to loading into the salt spray chamber, the scratches at the middle of each sample were introduced. Such artificial defects imitate the appearing mechanical damage in different engineering applications and assist in evaluating the surface degradation before and after environmental exposure. As seen on Figure 34, the coatings exhibit completely different morphology upon visual inspection. Even though swelling of coatings should have occurred theoretically, no changes in the thickness or in terms of tactile characteristics were observed.

After the testing, aged coatings exhibit the formation of localized spots associated with corrosion and appear to be brighter than unaged samples.

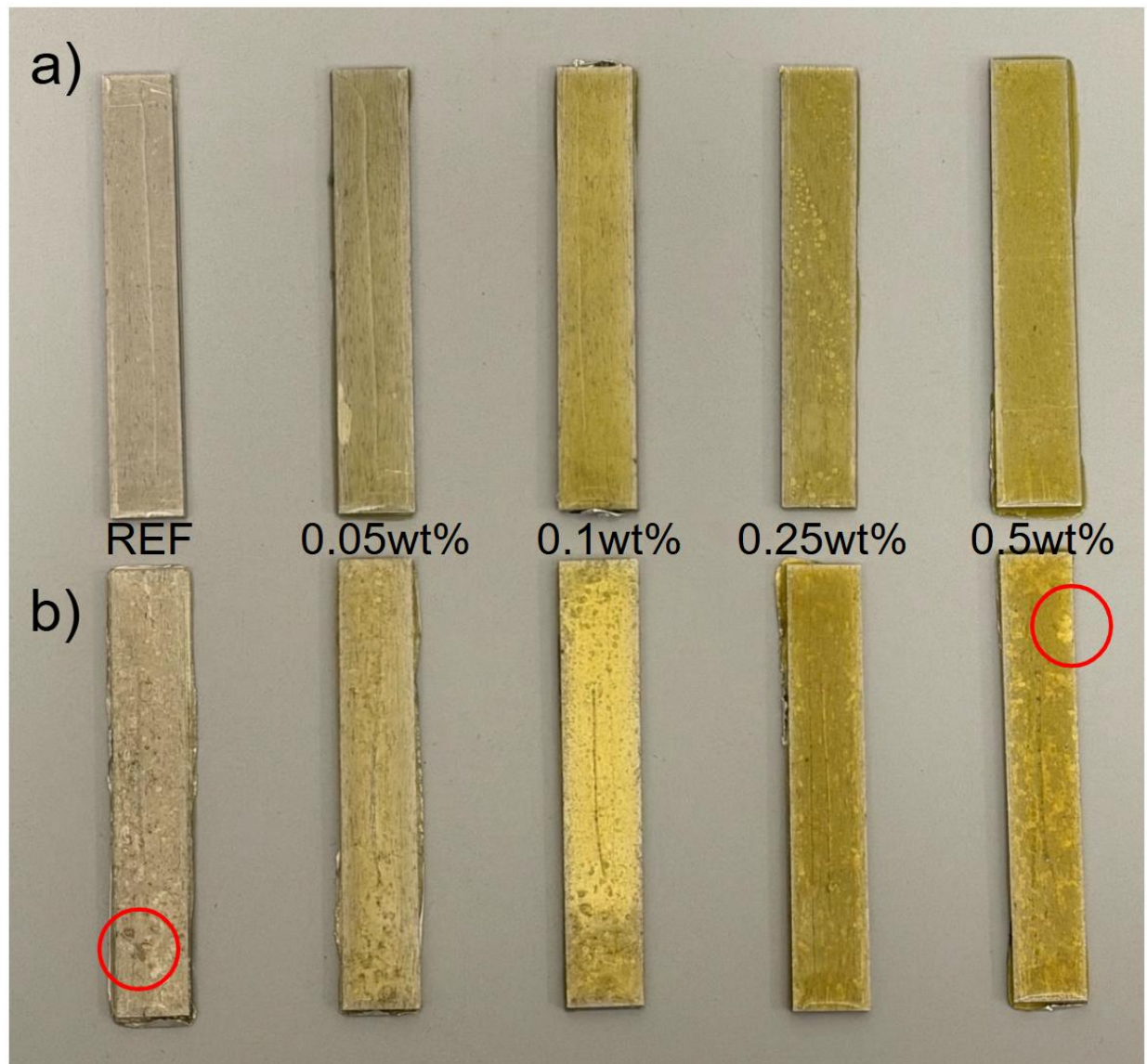


Figure 34. Visual comparison of PNF/PU coating before and after experience to corrosive environment.

6 Numerical modeling of composites

Polyurethane is considered as an incompressible material, meaning that under deformations material does not change its volume. In such materials, Poisson's ratio is taken as 0.5 which causes singularities in conventional computational mechanics of stress-strain calculations. Therefore, these materials are usually described by strain energy density functions, which have relation between invariants of strain tensor I_1, I_2, I_3 or principal stretch ratios $\lambda_1, \lambda_2, \lambda_3$, and such relations are called hyperelastic models. There are several hyperelastic models (Ogden, Yeoh, Marlow, etc.), each one having optimal use based on the experimental data available [49]. For our case, it was decided to choose the Marlow hyperelastic model because this model fits the best for only 1 type of data available (uniaxial tensile data in our case).

The Marlow hyperelastic model does not include any constant values because strain energy density is assumed to be only a function of the first invariant of the strain tensor [49]:

$$W = W(I_1) \quad (1)$$

From that, assuming $I_3 = 0$ for incompressible materials, I_1 can be represented as:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \frac{I}{\lambda_1^2 \lambda_2^2} \quad (2)$$

For uniaxial mode, Eq. (2) becomes (assuming $\lambda_2 = \frac{I}{\sqrt{\lambda_1}}$):

$$I_1 = \lambda^2 + \frac{2}{\lambda} \quad (3)$$

The variation of I_1 in both Eq. (2) and Eq. (3) are from 3 to $+\infty$ which validates that data from uniaxial tensile tests can be utilized by this model to identify strain energy density. To achieve it for 3D problems, I_1 is needed to be calculated first and then corresponding value of λ is found

using Eq. (3). After that, stress from experimental data is found and the strain energy density is determined through the equation below:

$$W(I) = \int_0^{\lambda(I)-1} \sigma(\varepsilon) d\varepsilon \quad (4)$$

Where σ and ε are nominal stress and strain which are taken from the uniaxial experimental data and directly feed into the Eq. (4).

Marlow model was applied to validate the experimental results for composites with different PNF loadings. The model was implemented using Abaqus/Standard using the geometry specified by the ASTM D412-C standard. The Marlow model was used to simulate the hyperelastic response of the PU matrix. Meshing of the specimen was done using 8-node linear brick, hybrid elements with constant pressure (C3D8H), which is suitable for incompressible elastomers. Boundary conditions were established in accordance with the experimental tensile test setup: one end of the specimen was fully fixed, while the other end was applied to displacement boundary condition. Finally, the simulated force-displacement data was obtained, and stress-strain curves were plotted using gauge length and its cross-section area.

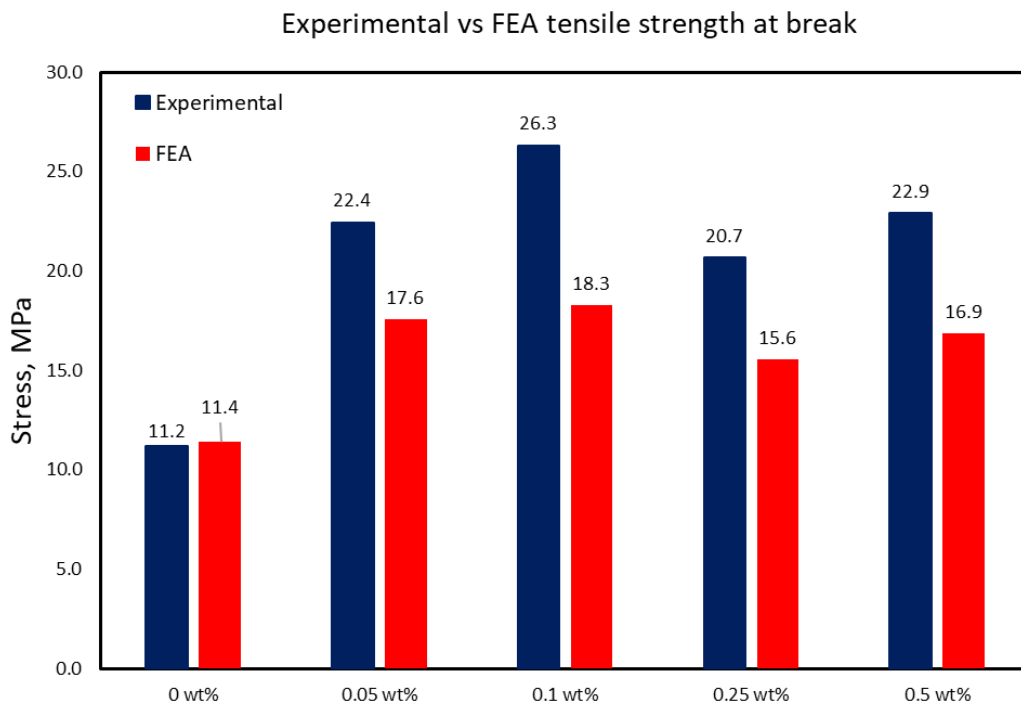


Figure 35. Experimental and FEA tensile strength at break.

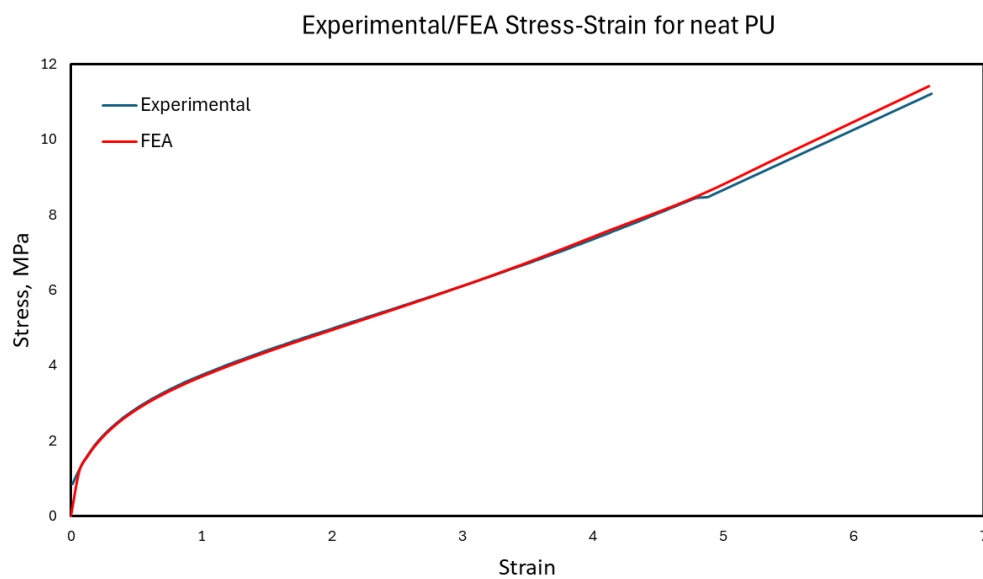


Figure 36. Experimental and FEA stress-strain curves of neat PU.

The results obtained for pure PU demonstrated excellent agreement with the Marlow model with little deviations due to fluctuations in the experimental data. Tensile strength at breaking strain

also demonstrates the close agreement between experimental and numerical data (11.2 MPa for experimental and 11.4 MPa for FEA, Figures 35-36).

The same approach was applied to model composites, where initial assumptions relied on the randomly oriented fibers in the composite structure. Because of that, it was assumed that composites can be taken as a whole material, and homogeneous approach towards material properties can be applied. However, Figures 37-40 show that this can be applied only initially until the moment PNFs start aligning with the load direction which causes the composite to suddenly stiffen (Figure 37).

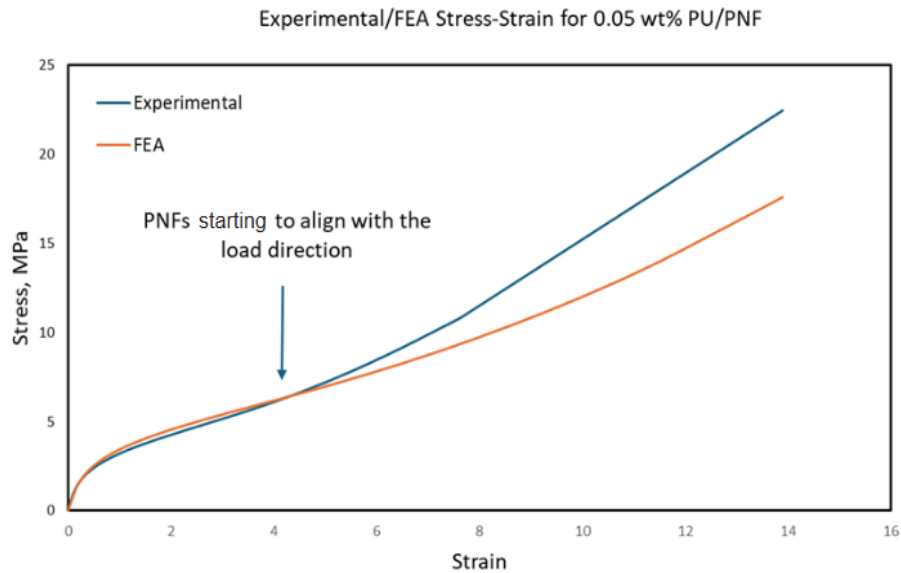


Figure 37. Experimental and FEA stress-strain of 0.05wt% PU/PNF.

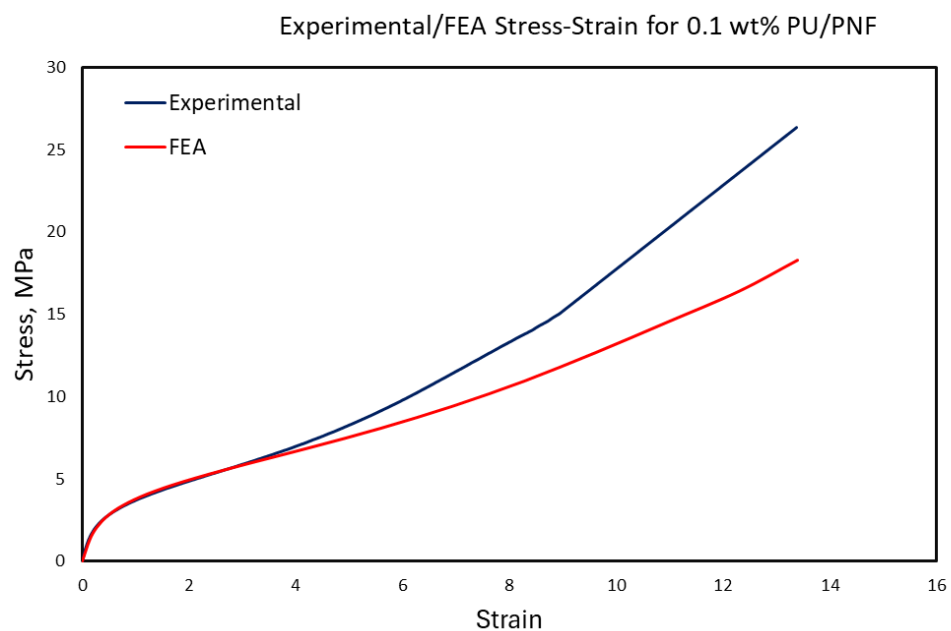


Figure 38. Experimental and FEA stress-strain of 0.1wt% PU/PNF.

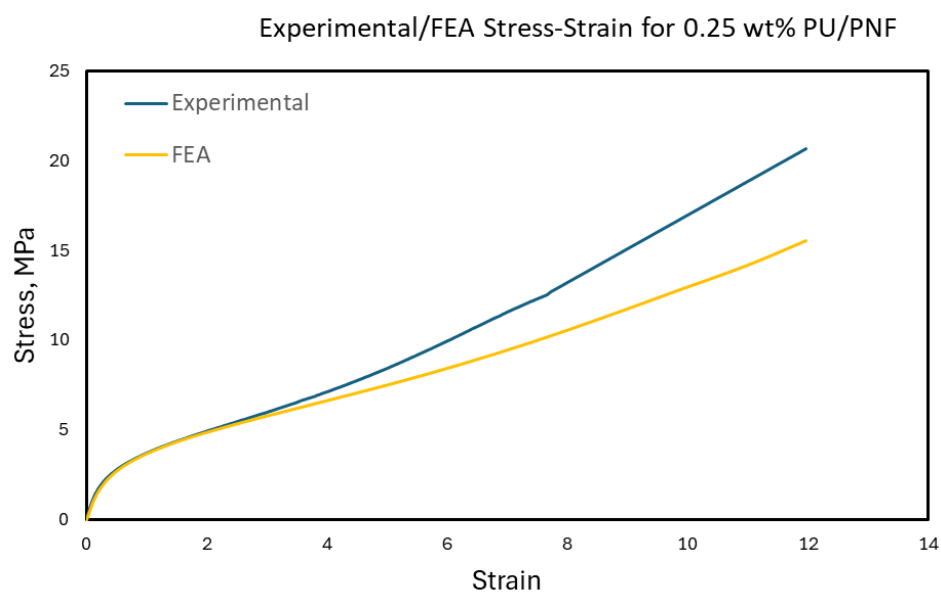


Figure 39. Experimental and FEA stress-strain of 0.25wt% PU/PNF.

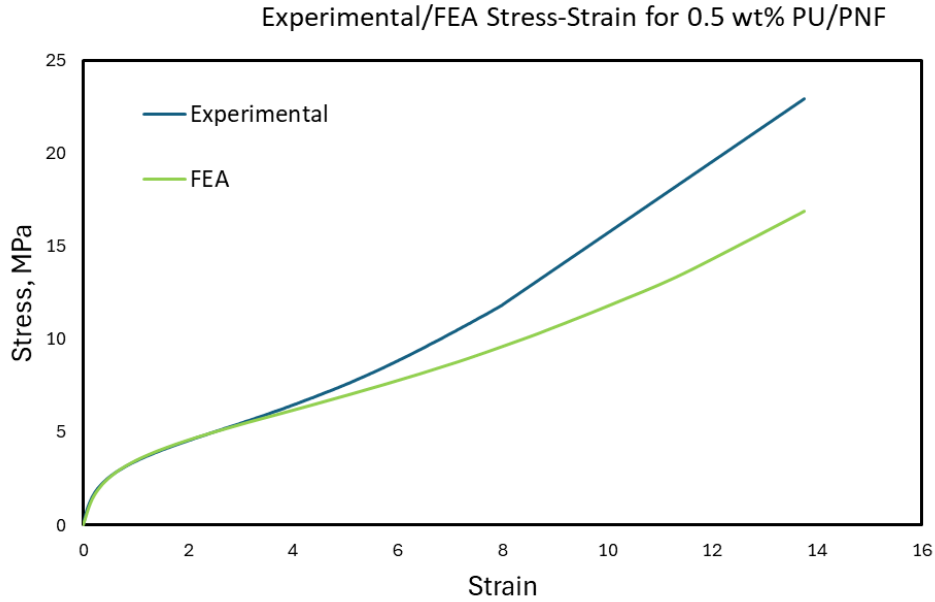


Figure 40. Experimental and FEA stress-strain of 0.5wt% PU/PNF.

The primary limitation of the present modelling approach lies in the use of pure hyperelastic constitutive models to represent heterogeneous material like PU/PNF nanocomposite. While Marlow hyperelastic model demonstrates close agreement with the neat PU, it fails to capture behavior of nanocomposites.

Hyperelastic models assume that the material is homogeneous and continuum-based, which in case of PU reinforced with PNFs becomes invalid. As was mentioned before, in Figures 37-40, the experimental results show sudden increase in stiffness, which can be associated with nanofiber alignment along the load direction. These dynamics cannot be predicted by Marlow model because it does not account for filler-matrix interactions, fiber orientation and reorientation under load, and local stress transfer mechanisms between phases. Therefore, the model underestimates the material behavior under high strains, showing that using only hyperelastic models is insufficient for accurately predicting the response of heterogeneous composites.

To overcome the limitations mentioned above, it is recommended to adopt Representative Volume Element (RVE) to get more accurate results. This method allows modeling heterogeneous setups like nanocomposites (Figure 41), where interaction between nanofillers and polymer matrix can be defined in detail [50]. Such approach would enhance model prediction, especially at higher strain levels, where microstructural effects dominate.

However, it should be noted that this approach requires more computational power, complex modelling and detailed material characterization. Because of these constraints, it was difficult to implement RVE model in the scope of this study.

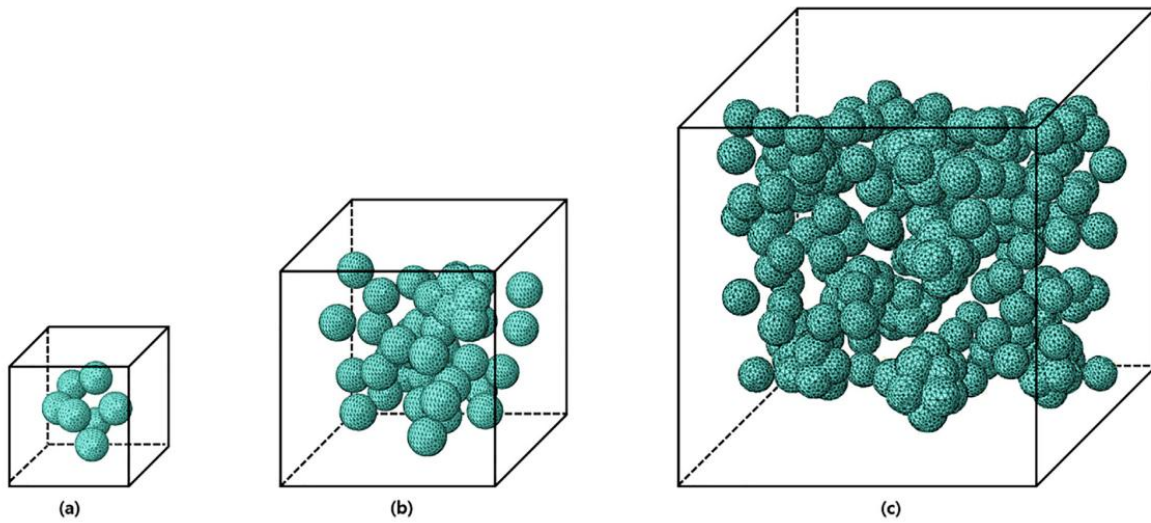


Figure 41. Example of RVE samples with specified volume fraction for further simulation [50].

7 Conclusion

This project demonstrates an efficient and reliable route for producing poly (*p*-phenylene benzobisoxazole) nanofibres (PNFs) by the acidic mechanically disintegration method and introducing them into polyurethane (PU) matrices to fabricate next-generation high-performance composite coatings. PBO microfibrres with an initial diameter of approximately 15 μm were successfully converted into nanoscale PNFs with diameters 10-50 nm, achieving an average 800-fold reduction in fibre thickness. The mechanical testing of PNF/PU composites revealed that the addition of a low nanofibre content brings notable reinforcement. The best-dispersed 0.1 wt% PNFs composite achieved a 217% improvement in tensile strength and 160% in Young's Modulus relative to pure PU, with 25.66 MPa tensile strength, 11.43 MPa Young's modulus, and 1390% strain. The highest shear strength was observed for 0.05 wt% of PNFs, with an increase of 185% correlated to 2.39 MPa. Moreover, numerical analysis showed close agreement with the neat PU, while deviating for composites, indicating necessary steps to develop RVE separate modelling with PNFs and PU to get more accurate data. Overall, this study establishes a foundation for integrating PNFs into elastomeric matrices and provides strong evidence that PNFs are promising future reinforcing nanofiller, which can serve highly efficiently at protective coatings. Moreover, this project shows that PNFs have potential in aerospace, marine, and construction industries, where lightweight structural reinforcements and protective layers are essential.

8 Limitations and recommendations

Although this study successfully demonstrated the reinforcement potential of PNFs in polyurethane, several limitations should be acknowledged. The synthesis of PNFs relied on methanesulfonic and trifluoroacetic acids, which are highly corrosive and generate toxic mist, restricting the scalability of the process. The fabrication route is also batch-based and not yet adapted for continuous industrial production. Within the composite, performance peaked at very low filler contents (0.1 wt% for tensile and impact, 0.05 wt% for shear), while higher loadings led to agglomeration and reduced properties, indicating that dispersion remains a limiting factor.

The testing program also has constraints. Impact testing was carried out on a TecQuipment TE15 apparatus with a U-notched specimen rather than the standard ASTM D256 V-notch geometry, so absolute impact energies should be interpreted as comparative values. Corrosion exposure was limited to seven days of salt spray and assessed visually, without electrochemical quantification or long-term weathering. The Marlow hyperelastic model also captured the response of neat PU well but failed to describe the stiffening of composites at high strains, where nanofibre alignment dominates.

Future work should therefore focus on greener and more scalable synthesis routes, including reduced acid consumption, solvent recovery, or alternative method, and on surface functionalization of PNFs to extend the useful loading window beyond 0.1 wt%. The mechanical assessment should be repeated on fully ASTM-compliant impact equipment and complemented with other standards like drop-weight and fatigue testing. Corrosion performance should be evaluated over longer exposure periods and supported by electrochemical impedance spectroscopy. Numerically, a Representative Volume Element approach is recommended to capture filler-matrix interaction and fibre reorientation. Finally, future iterations should include

life cycle and techno-economic analyses, together with industry collaboration, to translate the present proof-of-concept into a scalable and competitive multifunctional coating system for aerospace, marine, construction, and defense applications.

CRedit authorship contribution statement

Nurmerey Aidos: Writing - original draft & final version (Chapter 4 - Measurement and Characterization, sections 4.3-4.5; Chapter 5 - Results and Discussion, section 5.3.2 and 5.3.3; Chapter 7 - Conclusion, Chapter 8 - Limitations and Recommendations); Investigation; Visualization. **Madina Nurgaziyeva:** Writing - original draft & final version (Chapter 1 - Introduction; Chapter 2 - Literature review; Chapter 3 - Experimental details, sections 3.1-3.4; Chapter 4 - Measurement and Characterization, sections 4.1 and 4.2; Results and Discussion, section 5.1, 5.2 and 5.3.4, Chapter 7 - Conclusion); Investigation; Visualization. **Beibars Zhenis:** Writing - original draft & final version (Chapter 1 - Introduction; Chapter 2 - Literature review; Chapter 3 - Experimental details, section 3.5; Chapter 5 - Results and Discussion, section 5.3.1, Chapter 6 - Numerical modelling of composites, Chapter 7 - Conclusion); Investigation; Visualization. **Sherif Gouda:** Conceptualization; Supervision; Funding acquisition; Validation.

Declaration of competing interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work presented in this capstone project final report.

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