



A review of advancements in synthesis, manufacturing and properties of environment friendly biobased Polyfurfuryl Alcohol Resin and its Composites

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ABSTRACT

The quest for environmentally friendly and sustainable materials in the production of fibre reinforced composite materials has led to the use of biobased materials, which are easily accessible and renewable. Biomass-derived chemicals, their derivatives, and their applications have become increasingly prevalent in various industries and processes, greatly contributing to the goal of ecological sustainability. The biobased Polyfurfuryl Alcohol (PFA) resin is one of such polymeric materials that is gaining attention for composite applications due to its endearing Fire Smoke and Toxicity properties. Derived from agricultural by products such as sugar cane bagasse, it has been known for applications within the foundry, coating, and wood industries. However, there has been a growing interest in its use for fibre reinforced composite applications. For this reason, this work intends to provide a comprehensive review of the PFA resin in relationship to fibre reinforced composites applications. The work provides an in-depth discussion on the synthesis, curing process, manufacturing, and properties of the PFA resin as well as its composites.

1. Introduction

The development of advanced fibre-reinforced polymer FRPs has been marked by a series of advancements in fibre and matrix materials, manufacturing processes, design techniques and exciting applications. In fact, the year 2022 marks 50 years of first commercial application of carbon fibre in an everyday product, the fishing pole by Toray industries [1]. Over the years, the impressive properties of fibre-reinforced polymer have led to an ever-increasing number of industries adopting these for various applications. In general, petroleum based synthetic thermosets such as epoxies, phenolics, and polyesters are reinforced with carbon or glass fibre reinforcements for most composite material applications. According to a report by Witten and Mathes [2], the global production volume for composites in 2021 was reported to be 12.1 million tonnes, with 52 kt of Carbon Fibre Reinforced plastic (CFRP) produced in Europe alone. Estimated forecasts place global demand for Carbon Fibre Reinforced Plastic (CFRP) at 200 kt to 285 kt between 2025 and the end of this decade [1,3]. This inadvertently implies that

large amounts of non-degradable petroleum-based polymers and composites are continually manufactured globally, most of which are discarded as industrial waste products after being used [4]. In fact, It is estimated that waste obtained from end-of-life components will reach up to 50 kt per year in 2030 [3]. In addition to the environmental challenges posed by end-of-life waste, the petroleum-based polymers and polymeric composites also pose other environmental concerns such as a high embodied energy and greater greenhouse gases (GHG) emissions. These are a consequence of the highly energy intensive manufacturing process for the fibres as well as composites. Owing to these environmental concerns and sustainability problems, this century has seen remarkable developments in green materials in the field of polymer science through the development of bio-composites [5], as an alternative to petroleum based composites, to mitigate this challenge. Additionally, the associated benefit of a reduction in Green House Gas (GHG) emissions from the production of fully bio-based composites potentially provides cost incentives from the perspective of carbon capture [6].

Over the last decade, the growth in the production and application of

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bio-composites in different industries has experienced a tremendous increase. Bio-based composites are finding increasing use for various applications within industries such as automotive, rail, sports goods, and aviation, amongst others. This renewed interest stems from the need to find environmentally friendly and sustainable alternatives to the prevailing petroleum-based composite products. According to a report by the Nova Institute [7], an estimated 4.5 million tonnes of bio-based polymers were produced worldwide in 2022. The report further projects an increase in the development of biobased polymer production capacities to 9.3 million tonnes by 2027, indicating an average compound annual growth rate (CAGR) of about 14%. Sustainability, industrial ecology, eco-efficiency, and green chemistry are the fundamental and ongoing drivers of this sector, spearheading the production of the next generation of materials, goods, and processes. Recently, research, technological advancement and modifications of naturally existing polymers, as well as the synthesis of novel new polymers from renewable monomers have rapidly expanded [8]. One such area that has experienced rapid growth is the bio-resin sector. For example, the global demand for furfuryl, which is a feedstock for many of these types of resins, was about 340,000 tonnes annually with an estimated value of USD 551 million in 2019 and is projected to reach USD 700 million in 2024, growing at a CAGR (Compound Annual Growth Rate) of 4.9% between 2019 and 2024 [9]. The continuous development and commercialization of bio-based resins are becoming increasingly important and have enabled the expansion of bio composite applications in various industries.

The PFA resin, also known as furan resin is one such biobased resin [10–13]. It is considered as one of the fully bio-based resins, a dark brown organic polymer obtained by the acid-catalyzed polymerization of furfuryl alcohol derived from renewable agricultural waste [8, 14–19]. The resulting highly crosslinked network forms a solid that possesses comparable mechanical properties to many petroleum based thermosets as well as remarkable thermal and chemical resistance to acids, alkalis, and solvents [20]. From an environmental point of view, the PFA resin has a remarkably lower GHG emissions as measured in terms of CO₂ equivalent emission i.e. kg-CO₂-eq, compared to petroleum-based resins [11,21,22]. Its eco-formulations can reduce up to 50% of CO combustion [23]. This is due to its derivation from furfuryl alcohol, which has a global warming potential (in terms of kg-CO₂-eq) of 1.3, compared to the unsaturated polyester resin at 7.5 and epoxy at 6.5 [24]. A conceptual illustration of the environmental merit of the PFA resin can be seen in the evaluation of the dependence of CO₂ footprint on the embodied energy of thermoset polymers and composite subsets

within the material database of the ANSYS CES Granta EduPack 2022. The results show the Furan (PFA) flax composites with a CO₂ footprint primary production value range of 2.93–3.32 kg/kg to be among the lowest candidate materials with low primary production embodied energy, as shown in Fig. 1.

In fact, a recent life cycle assessment examining end-of-life technologies for bio composite waste in aviation industry by Špela et al. [25] found that pyrolyzing 1 kg of basalt fibre/furan resin composites produced 0.394 kg of CO₂ equivalent emissions, while solvolyzing the same amount of material resulted in 0.467 kg of CO₂ equivalent emissions. In addition to the benefit of low GHG emissions and low embodied energy, the bio-based polymers like PFA are also more sustainable as the feedstock is a by-product of the food waste.

Traditionally, PFA resin has been used in a variety of applications, including but not limited to binders for moulding sand in foundries [26–30], chemical resistance and mechanical property enhancer in polymer concrete [16,31–33], adhesives for wood composite panels [34–36], coatings [37–39], a precursor to different carbonaceous products [18,40–46], and corrosion-resistant materials [42,47,48]. More recently, its commendable mechanical and thermal properties have resulted in its use in fibre-reinforced polymer composite applications. The advantages of its outstanding thermal stability and fire smoke toxicity (FST) characteristic as well as its environmental friendliness, have enabled it to be used in some specialized applications in industries such as railways and aerospace as a viable alternative to traditional resin [49–51]. These developments in the potential of the PFA resin system in fibre-reinforced applications have prompted UK companies such as SHD Composite Materials Ltd., Bitrez, and Net Composite to show interest in further advancing and commercializing the development of its prepreg for applications in industries. In recent years, research efforts aimed at a fundamental understanding of the PFA have been made.

A review of the literature on the PFA resin reveals that tremendous work has been done on its preparation, chemistry, kinetics, and characterization, particularly for non-composite applications. Several authors [42,48,52–55] have reported on its precursor (furfural alcohol) and highlighted the furan derived processes and its capabilities for a wide range of applications. However, a comprehensive review aimed at cataloguing their mechanical, thermal, degradation behaviour and recent advancements in fibre-reinforced applications is still lacking. Therefore, this paper aims to provide an in-depth analysis of the PFA resin, with a focus on its applications in fibre-reinforced composites. It is intended to serve as a useful reference for researchers and industry developers seeking to further advance widespread utilization of

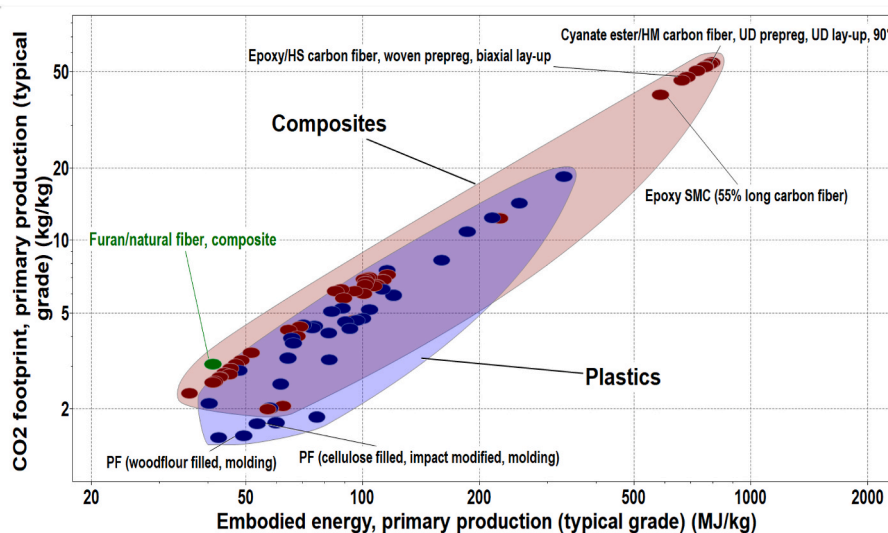


Fig. 1. Comparison of the CO₂ footprint of material production [kg/kg] and embodied energy [MJ/kg] for Furan/natural fibre composites and petroleum-based composites using data from ANSYS Materials (CES Granta Edu Pack 2022).

eco-friendly PFA resin in high-performance composites for industrial application. In this article, an overview of the polyfurfuryl alcohol resin is provided in Section 1, and this is aimed at providing background on the resin and its applications. A brief historical background of the PFA resin, its synthesis, structure and chemistry, cure kinetics, processing, and manufacture are discussed extensively in Section 2. Section 3 presents a detailed review of the documented properties of the PFA resin and its reinforced composites with a focus on mechanical, thermal, water absorption, and FST properties. Lastly, applications employing the use of PFA composite are highlighted and discussed in Section 4, with concluding remarks presenting suggestions for further development.

2. Polyfurfuryl alcohol resin

Similar to conventional thermoset resins (Epoxy, Phenolic), PFA resin is a thermally cross-linked polymer [56]. However, it is bio-based because its main monomer, Furfuryl alcohol (FA), comes from renewable resources such as agricultural waste, e.g., rice hull, sugarcane bagasse, and corn cob. The early history of the development of PFA resin can be traced back to 1923, after the start of the industrial production of furfural a year earlier [48]. Before that, however, Scottish chemist John Stenhouse had discovered resin's ability to be produced from furfural in 1840 [48]. Iroegbu et al. [57] reported the discovery of furfural by Johann Wolfgang Dberiner in 1832, while furfuryl alcohol, the main precursor, was confirmed by studies by Limpricht et al. [58] identified according to the same report. Despite these historical events, initial commercialization began in the early 1920s, with work to commercialize furfural from corncobs initiated by LaForge and Mains of the Bureau of Chemistry [59,60]. Between 1920 and 1953, Peter and Dunlop at the Hull Research Facility of the Quaker Oats Company significantly advanced the commercialization of furfuryl derivatives, which include the PFA [55,57]. In 1970, it successively found its use in the aerospace industry [61]. Subsequently, it was further researched and developed for various other applications and recently introduced into fibre-reinforced applications.

2.1. Synthesis of polyfurfuryl alcohol resin

Various methods for synthesizing PFA resins have been published in numerous studies. The pathway to the PFA resin manufacturing process begins with the extraction of furfural by acid-catalyzed hydrolysis from pentosan-rich hemicellulose obtained from viable agricultural waste [60,62–66]. Conventionally, the extracted furfural is converted to furfuryl alcohol via a catalytic hydrogenation reduction process [39,42, 67–69]. Then, the furfural alcohol (FA) is converted by acid catalysis to

obtain PFA resin. The entire process is illustrated in Fig. 2.

The furfural alcohol (FA) can be catalyzed by different types of acids. Studies show that either a strong or weak acid type can be used as a catalyst for the process. Some commonly used acid catalysts used for polymerization include mineral acids such as sulfuric acid [70], nitric acid [71], organic acids (maleic anhydride, oxalic acid, *p*-toluene-sulfonic acid monohydrate (PTSA)) [72–74], and acid zeolites (zeolite Y) [75]. Greener and more sustainable catalysts such as Algerian modified clay (maghnite- H^+ or mag- H^+) have also been found effective for polymerization as well as a potential replacement for hazardous acidic catalysts [76]. Fundamentally, the synthesis process involves mixing the furfural alcohol (FA) with the acid catalyst in a properly weighted ratio at a controlled temperature and time. This is done systematically to prevent explosions during the polymerization reaction while maintaining sufficient viscosity and a low moisture content in the final product. Researchers have employed various techniques to achieve this. An early understanding of the process by Purnal in his patent [77] described the synthesis process to involve several steps.

The first step is the addition of acid to buffer-free hot furfuryl alcohol in an amount sufficient to initiate and continue the reaction to establish the boiling point of the reacting mixture. This was followed by continuing the reaction while boiling the furfuryl alcohol-water mixture until the condensation reaction had progressed to the desired point. Next is the removal of the acid from the system and lastly the distillation of the product to obtain a substantially anhydrous initial resin. The process of this invention offered a solution to alleviate the explosive exothermic difficulties encountered during the polymerization reaction process during synthesis. This technique was an inspiration for numerous subsequent works. As suggested in recent literature, in most cases, the acid is dissolved in a given volume of deionized water and gradually mixed with an aqueous solution of furfuryl alcohol (FA) in a given weight ratio with vigorous stirring. The mixture is heated to the FA-water azeotrope temperature for some time. Thereafter, the reaction mixture is cooled, and the pH is neutralized by the addition of an alkali such as sodium hydroxide (NaOH). The resulting emulsion mixture is broken by a saturated salt solution such as sodium chloride (NaCl) and then separated to remove the aqueous phase and water. It is worth noting that the choice of processing time and temperature depends on the type of acid used. Beyond the synthesis of the PFA resin for reinforced composites, studies have shown its advancement for other advanced applications such as, resin modification [13,51,78–80], a precursor for various materials including polymeric carbon beads used as adsorbent for volatile organic compounds [81], carbon membranes for separation and purification applications [45], and as a nanocomposites for sodium-ion battery cathode material [82]. In addition to the viscous liquid form,

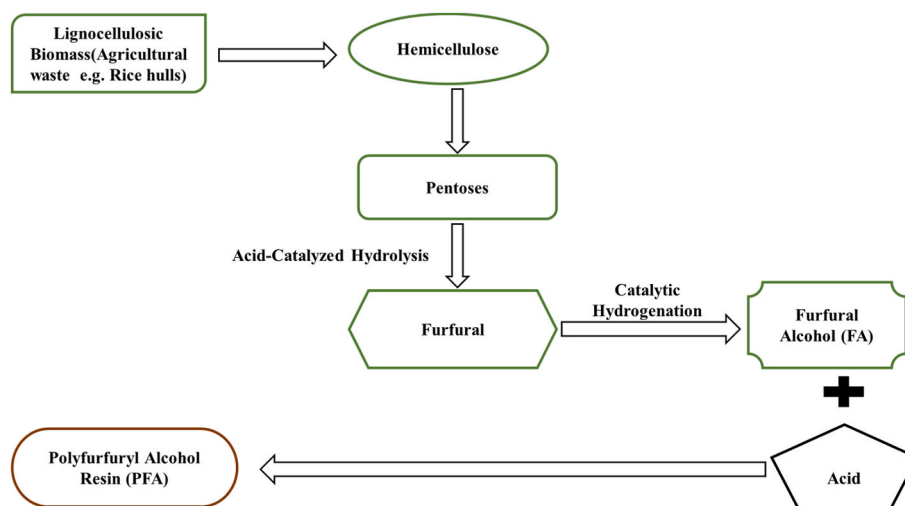


Fig. 2. Schematic of PFA manufacturing process.

Polyfurfuryl Alcohol PFA resin has also been synthesized as powder, flakes, film, and nanospheres [81].

2.2. Structure and chemistry of polyfurfuryl alcohol resin

A good amount of research has been done using various analytical techniques to understand the polymerization chemistry involved in the synthesis and curing of PFA resin. The molecular structural arrangement of the PFA resin contributes significantly to physical properties such as viscosity, bonding (interaction), and thus to its processing (resinification, prepreg, and curing) and thermomechanical properties, especially in fibre-reinforced applications. In fact, the mechanism of deepening and red-shifting colour formation of the resin was suggested by Choura et al. [83] to involve a series of events of enhanced conjugation caused by linear condensations that produce oligomers that can undergo hydride-ion exchanges with the protonated chain ends of growing species, yielding methyl-terminated oligomers and carbenium ions in which the positive charge is shared by a methyne carbon atom and two adjacent furan rings. Despite initial assumptions that the exact molecular structure is difficult to determine due to the rapid three-dimensional crosslinking during polymerization [84], many studies have been conducted in an attempt to elucidate the molecular chemistry of the crosslinking mechanism. Tondi et al. in Ref. [85] detailed a review of various scientific studies suggesting that the molecular structure arrangement be linear, ring-opening, α , β -unsaturated γ -lactons, Methylene bridge, conjugated or Diels-Alder. They further suggested a mechanism that encompasses the ring opening of some furanic rings, producing a double bond that promptly combines with the linear PFA to produce structure through Diels-Alder crosslinking, as shown in Fig. 3.

Kherroub et al. [86] posited that the crosslinking mechanisms involve a series of acid-catalyzed condensation steps, which produce linear oligomers that can contain both types of molecular bridged structural arrangements, namely methylene and dimethylene moieties.

Overall, the consensus remains that the cure chemistry of its thermoset nature indicates that the crosslinking mechanism, which occurs as a function of time and temperature, is a product of polymerization and primarily consists of two steps. The first consists of linear oligomer formation through polycondensation and the other composition of a structural network of ring-opening and Diels arrangements leading to high branching density [48,87–89]. This was corroborated by Joshua et al., in Ref. [90] who found that Diels-Alder crosslinking and branching were prevalent in the polymerization of PFA resin. He attributed a significant influence on the viscosity of the resin to the chain-branching mechanism. These reactions explain the high crosslink density of PFA resin [19]. Recent studies by Delliere and Guigo [91,92] offer insight into functionalities provided by the side ring opening reaction that occurs during polymerization, which results in the formation of carbonyl moieties, and used to generate tough and ductile materials via the creation of Schiff-based macromolecular architectures, introducing the concept of degree of open structure (DOS). As a proof of

concept, they reacted a flexible biobased amine (Priamine 1071) with the carbonyls of PFA resins to form Schiff bases and observed it is possible to change the macroscopic mechanical behaviour of the PFA, passing from a brittle material to a progressively more ductile material by increasing the stoichiometric ratio of amine. In a related study [93], they observed that the furan ring-opening process occurs predominantly on the terminal furans of PFA macromolecular chains. They also proposed two pathways for the opening of the furan ring, as shown in Fig. 4.

The first being a hydrolytic ring opening that produces levulinic-like species, while the second is an oxidative furan ring opening that produces conjugated aldehydes. With the latter being responsible for the formation of the rigid shell that forms on the external surfaces of PFA resins on a macroscopic level. With the aid of FTIR and Resonant Raman spectroscopy, Francesco et al. [94] found that the viscous form of PFA resin is mainly composed of short polymeric chains formed by small furan oligomers with a low degree of polymerization. This is characterized by the presence of isolated furfuryl alcohol and furfural residues similar to 5-hydroxymethylfurfural. In contrast, the cured PFA resin is formed by more pronounced cross-linked structures, characterized by several ketones and alkene double bonds, as well as a significant presence of Diels-Alder structures. They further observed that both forms of PFA resin contained an unspecified number of carbonyls and C=C bonds derived suggestively by ring-opening processes. During the polymerization of furfuryl alcohol (FA), these side reaction can influence the final polymer structure [95]. The polymerization reaction of the PFA resin can be complex, so variables such as acid catalyst type, concentration, temperature, and solvent type have a significant impact on the overall process [53]. At room temperature, the rate of polymerization can vary from hours to weeks, depending on the acid catalyst [71]. Origo et al. [71] and Wang et al. [96] postulated that a strong mineral acid generally results in a very rapid cure, while a complete cure is difficult when using weak acids. Therefore, the polymerization kinetics can be varied considerably for specific applications [97].

2.3. Cure kinetics polyfurfuryl alcohol resins in fibre-reinforced application

Efficient processing of the bio-based PFA resin for various applications requires knowledge of its processing conditions (curing temperatures, time and pressure). Therefore, the essence of understanding its cure behaviour cannot be overstated. Researchers have employed various techniques to understand the cure behaviour and evaluate the kinetics of PFA resin from different perspectives. For example, Domínguez and Madsen [98] reported on the study of the PFA resin in which they employed the model free kinetics method to study the curing process of the resin under vary amount of catalyst. In their further research work, they [99] reported the determination of the gel point of the PFA resin by rheological isothermal tests at different curing temperatures where they observed a reduction in the rate of viscosity change when compared to the rate of viscosity change during the pre-gel stage. This observation was further researched upon as the resin's rheological and

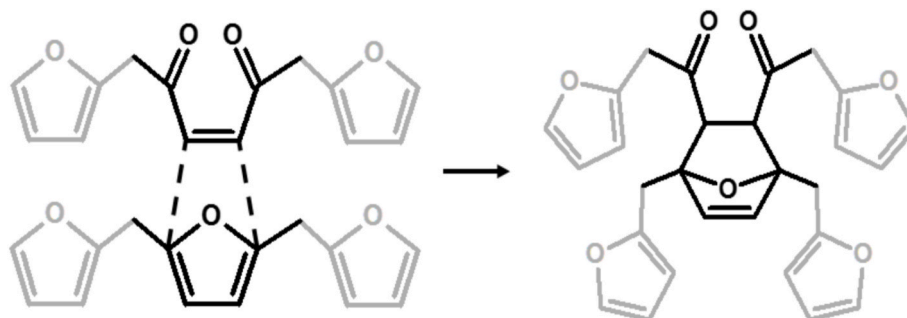


Fig. 3. Diels-Alder crosslinking reaction between linear and ring opened PFA structures [85].

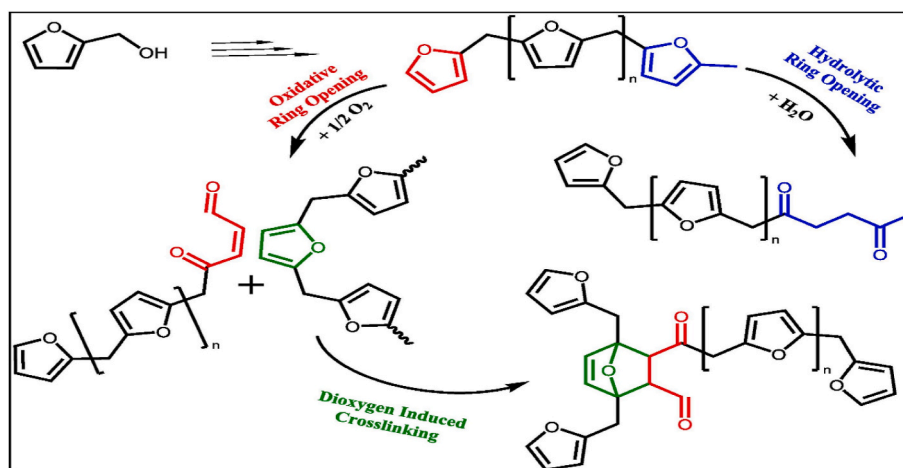


Fig. 4. Illustration of the two pathways proposed for end-chain ring opening in PFAs [93].

chemorheological behaviour was studied at pre-gel stage and reported in Ref. [14]. The study recorded the flow activation energy of the PFA resin to be $63.396 \text{ kJ mol}^{-1}$ as calculated by Arrhenius model and found the flow activation energy to increase with a corresponding increase in the amount of catalyst. However, despite documenting a curing activation energy of 96 kJ mol^{-1} , they found no catalytic dependence on the curing activation energy. A related research by Domínguez et al. [100] developed a new exponential model to study the chemorheological behaviour of bio-based polyfurfuryl alcohol (PFA) resin during the post-gel curing stage. The complete curing and polymerization complexity of the resin was also studied using chemorheological and isoconversional analysis by Guigo et al. [101]. Vargas Scheubner and Guthausen [102] studied the polymerization of the resin through the influence of nanoparticles on the curing reaction kinetics. Further studies on the kinetics of the resin were carried out by Lopez De Vergara et al. [103] using a chemical characterization method to understand the mechanism responsible for the main reactions of the resins during curing. They observed that the Friedman and Vyazovkin isoconversional method yielded a similar curve profile as shown in Fig. 5, the evolution of activation energy with the degree of conversion as the curing process progressed.

Sadler et al. [90] detailed the resin polymerization reactions and kinetics of the study from a molecular structure viewpoint. Regarding the manufacturing process, Imani and co-worker [104,105] investigated its reaction kinetics to determine the resin's pot and shelf life, respectively. Additional attempts have been made to characterize the PFA resin through kinetic studies by varying catalyst type, quantity and filler effect [19,106]. Recent studies by Kempainen et al. [107], employed the use of reactive molecular dynamics (MD) modelling techniques to model the

polymerization of the PFA resin as well as to predict its mechanical properties. They found the predicted mechanical properties of the polymerized resin to agree with the literature values. The outcome of such studies has provided industrial manufacturers with the fundamentals of a window for selecting parameters suitable for using the selected manufacturing process cycle in various applications, including fibre reinforced composites. Despite the successes, it is worth noting that all previous research studies were performed using synthesized neat resin alone, leaving the kinetic studies of fibre-reinforced Polyfurfuryl alcohol-based prepreg largely unexplored. In this regard, our recent research [108] addresses the gap in knowledge by providing an explanation of the curing mechanisms and demonstrating the use of model-free kinetics to study the cure mechanism of biobased glass/PFA prepreg. Our study determined the average activation energy for the cure reaction of the biobased glass/polyfurfuryl prepreg to be $88.9 \pm 4.9 \text{ kJ/mol}$. By utilizing validated models, we were able to optimize the cure cycle for rapid curing under fills the gap and provides explanation of curing mechanisms as well as demonstrates the use of model free kinetics to study the cure mechanism of the biobased glass/PFA prepreg.

2.4. Polyfurfuryl alcohol resin processing and fibre reinforced PFA composites manufacture

With the resin processing condition window determined via various kinetic methods, the processing and manufacturing of fibre reinforced PFA composites with different manufacturing processes is made possible. Conventional manufacturing techniques such as hand layup, autoclave processing, resin transfer moulding (RTM), microwave processing and compression moulding are some of the commonly used techniques in the manufacture of fibre reinforced PFA composites. Several types of fibre have reportedly been used as reinforcements in the manufacture of PFA based composites. For example, conventional fibre like glass fibre was used in the manufacture of PFA based composite for comparative property studies with fibre reinforced phenolic composites by authors [15,50,109]. Natural fibres such as abaca, flax, basalt, rayon and jute have also been reported as reinforcement for PFA based composites for various investigative and comparative research studies [110–113]. PFA based materials, like other thermosetting matrices for composites, requires a careful control of processing conditions to monitor the viscosity achieved in the final composite, which is highly dependent on temperature and polymer structure. Fibre wettability, bubble formation and growth, and composite consolidation are all affected by the continuous transition of resin from a low-viscosity liquid monomer at the start to a solid polymer at the end of the phase [114].

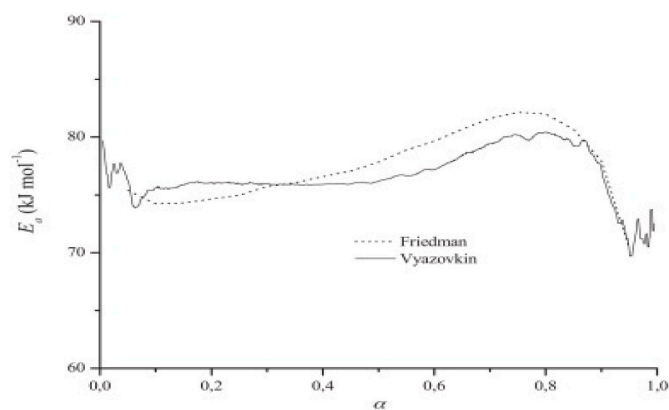


Fig. 5. Activation energy change with the degree of cure by the Vyazovkin and Friedman methods for the furan resin [103].

2.4.1. Polyfurfuryl alcohol resin and laminate curing

With appropriate curing parameters and processes, the PFA resin, like other matrices, can be cured in neat or fibre-reinforced form. However, unlike some other resins which are relatively easy to cure, same cannot be said about the PFA resin. This type of resin requires careful application of processing conditions because volatiles and water (moisture) evolve during the curing process. These emissions are by-products of (i) solvent water from the resin; (ii) solvent water from the catalyst; and (iii) condensation water from curing of the resin [115]. In fact, according to Foruzanmehr et al. [89] and Deka et al. [116] 1 mol of water in vapour evolves for every mole of crosslinked resin formed during curing due to the exothermic reaction. This phenomenon allows for the occurrence of potential problems such as warping, voids, and delamination which result in reduced mechanical properties of the final cures resin or composite when processed incorrectly. Examples of these are shown in Fig. 6, where (a) the bubble effect in form of voids are visible on a cured neat PFA resin due to poor rapid cure cycle and (b) the delamination effect is observed in a glass/PFA composite is due inadequate degassing during the compression moulding manufacturing process. To mitigate this challenge, a slow and multi-stage curing cycle is typically employed during processing. This is done to potentially limit the amount of water formed during the condensation reaction during curing [117].

A combination of multistep curing and modification of manufacturing methods have also been reported to help mitigate this challenge. For example, Dominguez et al. [115] effectively employed the combination of a two-steps curing cycle and the double-vacuum-bag technique effectively to study the volumetric composition and mechanical properties of the glass fibre/PFA composites with an emphasis on porosity content. They concluded that in order to further improve the properties of composites, higher water removal efficiency during manufacture, lower porosity, and addressing the less brittle stress-strain behaviour of the furan matrix need to be considered. Other water reduction techniques include intermittently opening and closing moulds in manufacture using compression moulding processes by Džalto et al. [118]. Employing this technique in their further works [10,119] enabled the use of porosity and morphology analysis of natural (Hemp and Rayon) and synthetic fibre (E-glass) reinforced PFA composites, as shown in Fig. 7, in the investigation of the effect of the water absorbance characteristics of the reinforcing fibres on the processability of PFA composites at short cycle times.

They discovered that the overall level of porosity is influenced by the water absorbance capacity of the reinforcing fibre and the effective transfer of water from the resin to the fibre, including the single fibre wetting and textile architecture. This revelation underscores how the hydrophilicity of natural fibres improves the processing and manufacturing of high-performance PFA composites. The study concludes that the porosity and morphology of PFA composites are more significantly influenced by material composition than by processing

time and process control. Overall, a review of major studies reveals the cure processing temperature could range from 20 °C to 180 °C, and cure duration between 1 h–96 h, regardless of the manufacturing method employed [110,117,120–122]. The lengthy manufacturing process cycle has been a significant drawback that has limited the industrial scaling up of its use for applications. Hence, the motivation for our previous research work [108] where we employed cure kinetic model to optimized the manufacturing cure cycle of a glass/prepreg leading to a 50% reduction in curing time.

3. Review of properties of polyfurfuryl alcohol reinforced composite

3.1. Mechanical properties

The mechanical properties of PFA resin and its reinforced composites depend on the configuration of several factors. Some of these factors include curing conditions and parameters, manufacturing method, fibre type, fibre orientation, form type (fabric or fibre), and matrix modification, amongst others. As a result, several studies have been conducted to evaluate the strength and other properties of this resin and composites as a function of some of these factors. The mechanical properties of the PFA resin and its reinforced composite are well reported. In comparison to other neat resins, Crossley et al. [123] found the cured neat PFA resin to have an average tensile strength of 29.2 ± 6.4 MPa and a tensile modulus of 2.8 ± 0.14 GPa. The study observed that the tensile properties of the cured neat PFA resin were comparable to those of cured neat phenolic resin, which exhibited an average tensile strength and modulus of 32.8 ± 3.3 MPa and 2.48 ± 0.04 GPa, respectively. A similar comparison between the PFA resin and conventional resins was highlighted by Elejoste et al. [124] as shown in Fig. 8.

In the study of renewable resource green blends from PFA and lignin, Deka et al. [116] reported the flexural strength and modulus of the pristine resin to be 23 MPa and 1.9 GPa, respectively, while recording 15 Jm^{-2} as the impact strength found using the Izod test. The study found the effect of blending improved the properties of flexural strength, storage modulus, and glass transition significantly. Similarly, Wang et al. [125] documented 38.05 MPa, 2.2 GPa, and 2.50 kJ/m^2 as the respective values for the flexural strengths, flexural modulus, and impact energy of the neat PFA resin. They found the impact strengths, flexural strengths and moduli of a cured blend of furfuryl alcohol/epoxy/methyl-tetrahydro-phthalic anhydride blends with different ratios were found superior to the neat cured PFA resin [125, 126]. A comparison of the PFA resin to conventional resins such as epoxies, polyester, and phenolics across literature as shown in Fig. 9 reveals, the PFA resin exhibits comparable flexural properties enabling it to withstand substantial amount of bending stresses while maintaining structural integrity.

The addition of fibre reinforcement has proven to improve the

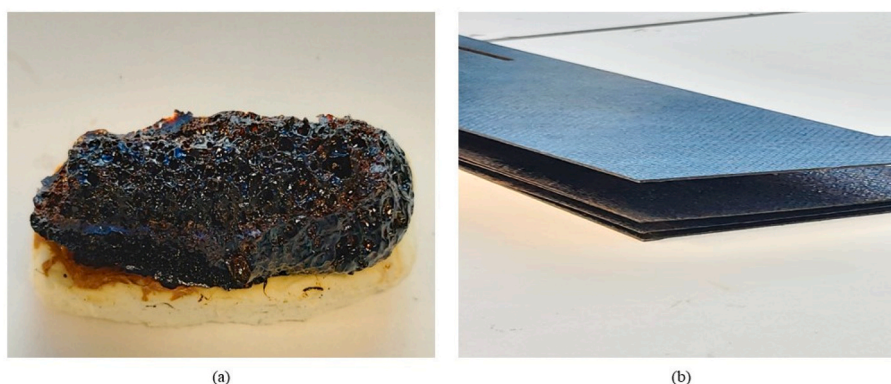


Fig. 6. PFA laminate curing. (a) Bubble defects of an improperly cured PFA resin, (b) delamination of an improperly cured PFA Prepreg.

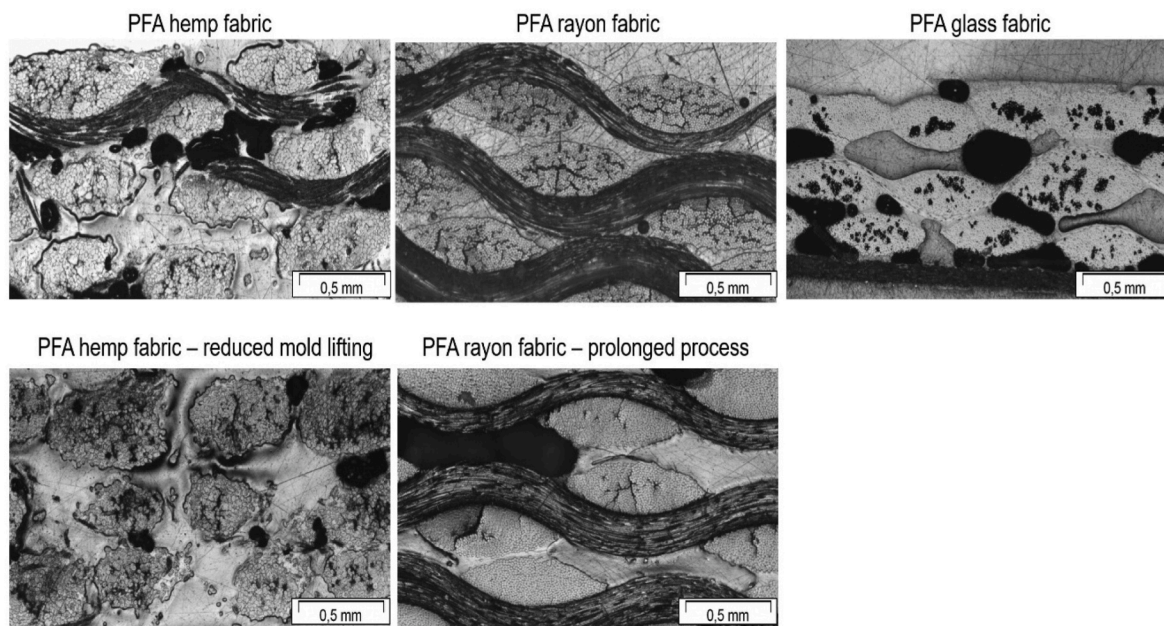


Fig. 7. Micrographs of PFA composites produced from fabric [119].

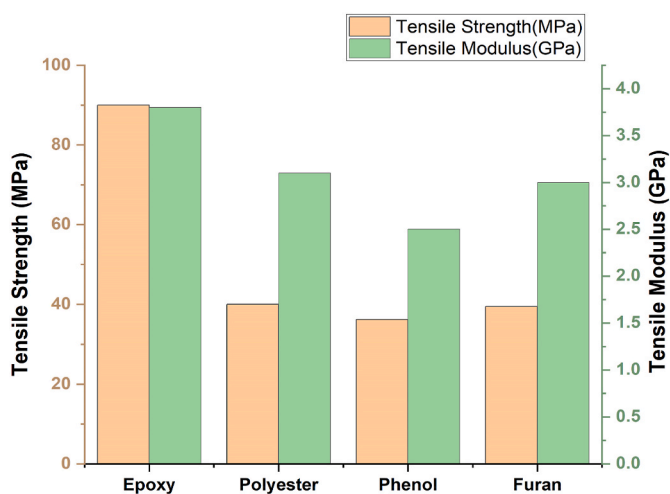


Fig. 8. Tensile properties comparison between PFA resin and conventional resins. Data adapted from [124].

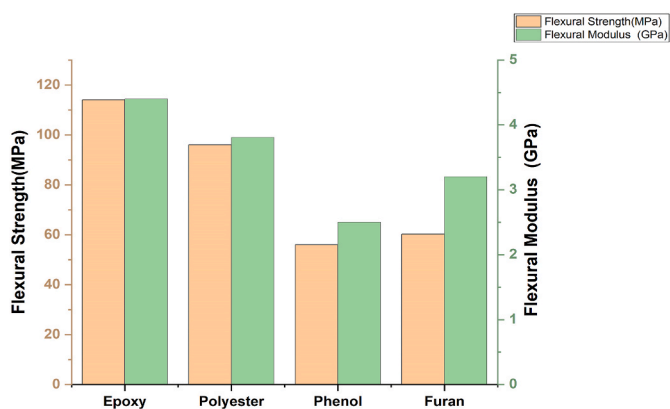


Fig. 9. Flexural properties comparison between PFA resin and conventional resins. Data adapted from [113,127,128].

mechanical properties of the PFA-based composite. For instance, Sharib et al. [122] found that incorporating 0.5% poly(lactic acid) (PLA) fabric into PFA resin resulted in increase in tensile strength from 11.2 ± 1.1 MPa to 33.2 ± 3.5 MPa. Conversely, this addition caused a reduction in flexural strength, although the flexural modulus increased from 1.96 GPa to 3.37 GPa for the same weight percentage of PLA fabric in the PFA resin. Another study investigating the impact of alkali treatment on poly(furfuryl alcohol)-flax fibre composites [129] reported a 10% enhancement in flexural strength and modulus for flax fibre treated with 1.5% and 2% NaOH in comparison to the cured pristine PFA resin. They attributed this to the bonding effect of the fibre reinforcement with the matrix. In related a work on agave and sisal fibre - reinforced poly(furfuryl alcohol) composites belonging to the family of natural fibres by Motaung et al. [130] sisal and agave fibres were found to also improve the mechanical and thermal properties of the neat PFA resin. They observed improvement in flexural strength of the natural fibre-reinforced composites which also was attributed to the effective impregnation of the PFA matrix into the fibre enhancing the interfacial bond strength. In addition, both fibre-reinforced composites were found to display quite comparable thermo-mechanical properties. Similarly, studies on cork reinforced PFA composites were investigated by comparing cork powder and cork granules, as observed by char et al. [131] where the observed improvements in the thermomechanical and mechanical properties were attributed to good adhesion between the PFA and the cork cells. Strong adhesion between fibres and the polymer matrix is known to enhance impact resistance and toughness through several mechanisms in a composite laminate. Although cured furan PFA resin itself is inherently brittle due to its highly crosslinked structure, it has been shown to exhibit impact strength comparable to conventional resins. For instance, Fig. 10 presents a comparison across the literature of the Izod impact strength values of neat PFA resin versus traditional epoxy, polyester, and phenolic systems. The PFA resin shows impact strengths lower than the epoxy and polyester resins but higher than the phenolic resin.

The impact behaviour of the hemp shives PFA based composites was also studied by Pernevan et al. [136], wherein they observed 3.47 and 4.42 kJ/m² as the Charpy impact strengths values for the hemp shives PFA based composites with 20% straw lignin and 20% flax lignin, respectively.

In addition to tensile, flexural, and impact characteristics, other

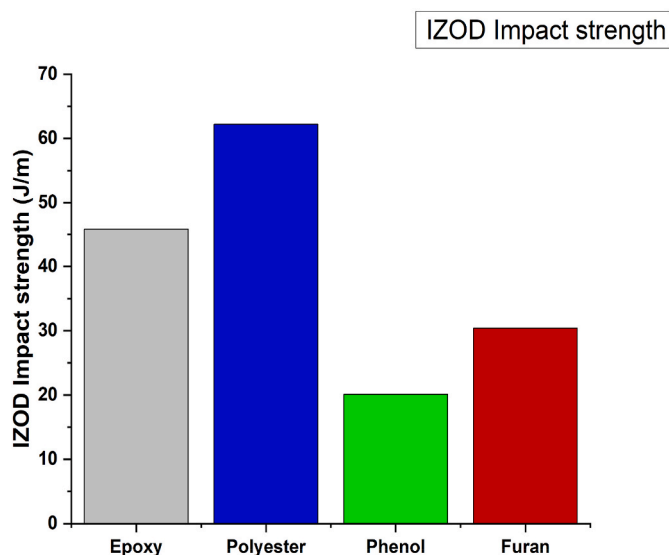


Fig. 10. Impact strength comparison between PFA resin and conventional resins. Data adapted from [132–135].

mechanical properties of PFA resin and its fiber-reinforced composites have also been investigated. For example, PFA composites with natural flax fiber reinforcements were found to display remarkably high interfacial shear strength of 23.7 MPa [137]. This value exceeded that of comparable flax fiber composites made using Elium, epoxy, and vitrimer matrices by 75.1%, 50.2%, and 20.25%, respectively. These results demonstrate the potential of PFA resin systems to achieve excellent mechanical performance, especially when reinforced with natural fibres. Furthermore, several studies have explored how different manufacturing methods and configurations influence the resulting mechanical behaviours of PFA-based composites. Table 1 summarizes the findings of some studies on the mechanical properties of some of the common fibre-reinforced PFA-based composites.

Looking at the data in Table 1, the observed variations in the mechanical properties, irrespective of the type of the reinforced fibre composite, strongly suggest that multiple factors have a significant impact on these properties. This concept was corroborated by Ref. [144] who found out that parameters such as type of resin, type and dosage of catalyst, and curing time have little effect on Young's modulus but significant effect on tensile strength. The data from Table 1, further reveals in broad terms that natural fibre reinforced PFA composite such as flax/PFA tends to possess lower mechanical properties than glass/PFA or carbon/PFA. Comparative research studies between fibre reinforced PFA composites and conventional fibre reinforced composites have also been documented in literature. For example, a comparative study of the mechanical properties of the PFA-based composites with conventional resin-based by Crossley et al. [138], reveals that the mechanical performance of the Glass/PFA was shown to be equal to that of the glass-reinforced epoxy, polyester, and phenolic composites with only a minor performance loss observed in the flexural strength in comparison to Glass/phenolic. Similarly, Ipakchi et al. [15] reported 45% and 33% higher flexural and tensile strength in glass/PFA composite than that of a glass/phenolic composite, respectively. Giannis et al. [109] also found the tensile strength of glass/PFA to outperform both Glass/Polyester and Flax/PFA composites.

So far, the mechanical properties of the PFA and its reinforced composite have only been discussed in terms of their tensile, flexural, and impact capabilities. This is because other mechanical properties like fracture toughness, off-axis, shear, and creep properties lack or have extremely little data in the scientific literature. In spite of these limitations, attempts have been made to study other related mechanical properties of fibre reinforced PFA composites, such as fatigue and load

bearing behaviour. Mak and Fam [145] published the results of a comparison study comparing the carbon/PFA resin and carbon epoxy composites in terms of their fatigue life and stiffness degradation. Under quasi-tension loading, they observed a 24% drop in strength and identical stiffness to that of carbon fibre reinforced epoxy composite. Applying the Whitworth phenomenological model, the stiffness retention at the end of life (2,000,000 cycles) was predicted to be 80% for epoxy-based CFRP and 65% for PFA-based CFRP. Giannis et al. [109] also conducted fastener pull-through and bearing strength tests between glass/polyester and glass/PFA, where they discovered no significant difference between the two materials in terms of pull through load.

3.2. Thermal properties

Numerous studies have established the thermal stability of PFA and its composites. Its excellent thermal and fire properties have been attributed to its extensive charring [146]. The aromatization that the resin achieves through thermal dehydration of the Diels – Alder adduct structures explains its thermal resistance, stability, and response to fire [146]. According to Rivero et al. [29], the degradation behaviour of the PFA resin is similar to that of a typical phenolic resin. Overall degradation occurs at temperatures ranging from 350 °C to 600 °C, which they attribute to the occurrence of molecular chain scission/fragmentation. At temperatures above 600 °C, they observed the development of carbonaceous residue or char. Monti et al. [146] observed through thermogravimetry that the mechanism of thermal decomposition of the resin chemical bonding structure causes disintegration of the crosslinked structure to produce volatile combustible chemical moieties, while at the same time a rearrangement to a stable structure that produces char occurs.

Guigo et al. [17] in a comparative study with a PFA Silica hybrid discovered that the degradation of the resin involved several steps beginning with the chain scission at over 200 °C. This allows for the weakening of the chemical bonds leading to second and third decomposition steps that occur at about 320 °C. The thermal decomposition temperature, which corresponds to the 10% weight loss was around 340 °C. In a related study of the thermo-oxidative degradation of the Polyfurfuryl Alcohol/plasticized lignin blend [147], it was found that the neat PFA exhibited better thermal stability compared to the blend. It was found that the thermal stability of the PFA decreased with increasing lignin content. Menager et al. [131] in agreement with other authors [74,88] confirmed a multi-step degradation process of the PFA resin with a corresponding degradation temperature of 10% weight loss is about 378 °C. Recently, a characterization study by Ma et al. [120] also found that the thermal stability of PFA resin is improved with increasing modified hollow glass microsphere (HGM) content (0%–20%). The mass residual rate was also reported to have increased from 53% to 64.4%. For fibre-reinforced PFA-based composites, their degradation behaviour has been compared to some conventional composites. The degradation behaviour of the glass/PFA composite was reported to be comparable with that of a glass/phenolic composite in a study by Ipakchi et al. [15]. Their study revealed char yields of up to 77–85% for PFA samples measured at 800 °C. For natural fibres such as kenaf bio fibre, the degradation pattern has been reported to show a four-stage degradation pattern. The green composite (kenaf/PFA) showed the same decomposition onset temperature as the neat PFA resin, however, the maximum decomposition rate decreased from 468 °C to 458 °C with increasing fibre content and a 45% retention of char residue. The decrease was attributed to an increase in the thermally unstable non-cellulosic structure of the fibre composite [140]. Similarly, in Ref. [110], Talent and Wang reported a 7% mass loss at 200 °C in a study that addressed the thermal degradation of a unidirectional Cordenka rayon/PFA composite. At a temperature of 275 °C, the composite showed rapid mass loss attributed to the degradation of the cellulosic structures of the unidirectional cordenka rayon (CR) fibres. The degradation effect worsened as the per cent fibre weight in the composite

Table 1

Mechanical properties of different fibre reinforced Polyfurfuryl Alcohol composites documented in the literature. VARTM = Vacuum-assisted resin transfer moulding, HL = Handlay-up, CM = Compression moulding, VB = Vacuum Bag, VM = Vacuum moulding, UD = Unidirectional.

PFA Composite	Manuf. method	Cure Cycle	Fibre Content	Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural Modulus (GPa)	Flexural strength (MPa)	Impact strength (kJ/m ²)	Ref. and year
Chopped Strand Mat Glass Fabric	HL/VB	Room temperature for 140 min s, 50 °C for 45 min s and 80 °C for 45 min s, 80 °C for ~18 h s (Post cure)	68 (%wt)	93 ± 8	7.2 ± 1.0	–	–	–	[109]
Flax Prepreg	VB	150 °C for 15 min s	60 (%wt)	64 ± 9.5	8.5 ± 0.8	–	–	–	[109]
2 × 2 Twill Flax Prepreg	VM	150 °C for 20 min s (5 °C/min ramp)	–	34.9 ± 1.84	6 ± 0.47	–	–	–	[138]
UD Flax	VM	150 °C for 20 min s (5 °C/min ramp)	–	59 ± 4.3	10 ± 0.8	–	–	–	[138]
UD Flax Prepreg	CM	140 °C for 20 min s (5 °C/min ramp)	–	211 ± 24	25.6 ± 1.9	–	–	–	[138]
2 × 2 Twill Flax Prepreg	CM	140 °C for 20 min s (5 °C/min ramp)	–	69 ± 3	10.4 ± 0.4	–	–	–	[138]
Chopped Strand Mat Glass Fabric	VM	20 °C for 150 min s 50 °C for 45 min s 80 °C for 45 min s	44 (%wt)	103	7.7	4.7	110	–	[111]
Non-woven Mat Hemp	VM	150 °C for 15 min s	23 (%wt)	–	–	~2.9	–	–	[111]
UD stitched Flax Fabric	–	–	41 (% vol)	–	–	9.6	99.4	–	[111]
Twill woven Carbon Fabric	–	–	39 (% vol)	–	–	26.2	364.7	–	[111]
Plain weave Glass Fabric	–	–	47 (% vol)	–	–	9	104.6	–	[111]
Glass non-crimp Fabric (0/90)	HL/CM	Room temperature for 12 h 50 °C for 8 h and 150 °C for 7.8 min s	73 (% vol)	324 ± 26	27.0 ± 0.6	–	–	39.7 ± 6.2	[139]
Glass non-crimp Fabric (±45)	HL/CM	Room temperature for 12 h 50 °C for 8 h and 150 °C for 7.8 min s	73 (% vol)	55.0 ± 5	11.5 ± 1.4	–	–	39.5 ± 2.2	[139]
Flax non-crimp Fabric (0/90)	HL/CM	Room temperature for 12 h 50 °C for 8 h and 150 °C for 7.8 min s	53 (% vol)	70 ± 3	13.0 ± 0.3	–	–	16.6 ± 1.4	[139]
Flax non-crimp Fabric (±45)	HL/CM	Room temperature for 12 h 50 °C for 8 h and 150 °C for 7.8 min s	53 (% vol)	46 ± 5	7.7 ± 0.5	–	–	9.8 ± 2.3	[139]
Flax non-woven Fabric	HL/CM	Room temperature for 12 h 50 °C for 8 h and 150 °C for 7.8 min s	52 (% vol)	48 ± 7	9.0 ± 0.6	–	–	7.1 ± 0.9	[139]
Kenaf Fibre	HL/CM	50–55 °C for 30 min s 60 °C for 4 h 80 °C for 4 h 100C for 1 h (Post cure)	20 (%wt)	~41	~1.36	~4.6	~75	60	[140]
Woven Flax Fabric	CM	170 °C for 2 h	40 (%wt)	15.53	–	2.4	23.2	24.9	[113]
Flax Fabric	VARTM	60 °C at 4 h (1 °C/min ramp) 95 °C for 4 h (Post Cure)	31.5 (% vol)	41	5.6	~7	~80	~80	[123]
Glass Fabric	VARTM	60 °C at 4 h (1 °C/min ramp) 95 °C for 4 h (Post Cure)	44.6 (% vol)	850	36.5	~30	~850	~350	[123]
Woven Flax & Polyester Prepreg	CM	150 °C for 7 min s	52–65 (%wt)	38–56	5–9	–	–	9–28	[118]
UD Glass Fibre	HL	1 week	39.1 (% vol)	520	26.6	–	–	–	[141]
Rayon (Cordenka)	CM	40 °C for 12 h 60 °C for 12 h 80 °C for 6 h. 110 °C for 1 h (Post Cure)	64 (%wt)	121	5.58	5.91	87.4	–	[110]
Rayon (Cordenka)	CM	40 °C for 12 h 60 °C for 12 h 80 °C for 6 h. 110 °C for 1 h (Post Cure)	51 (%wt)	77.2	4.32	6.96	95.4	–	[110]
Rayon (Cordenka)	CM	40 °C for 12 h 60 °C for 12 h 80 °C for 6 h. 110 °C for 1 h (Post Cure)	75 (%wt)	86.6	4.78	3.12	48.8	–	[110]
Plain weave Glass Fabric	CM	170 °C for 40 min s	20-25(% wt)	–	–	–	267	24	[50]
UD Glass Fabric	HL	7 days	66.4 (% wt)	–	–	–	39.2	–	[89]
UD Carbon Fabric	HL	2 Weeks 3 h Post cure	–	860 ± 110	93 ± 6	–	–	–	[142]

(continued on next page)

Table 1 (continued)

PFA Composite	Manuf. method	Cure Cycle	Fibre Content	Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural Modulus (GPa)	Flexural strength (MPa)	Impact strength (kJ/m ²)	Ref. and year
Basalt Fabric	HL/CM	80 °C for 8 h & incremental to 220 °C	71(% wt)	–	–	5.45 ± 0.90	94.15 ± 8.50	70.51 ± 6.31	[125]
Woven Glass Fabric	HL	80 °C for 24 h 100C for 24 h (Post cure)	58 (%wt)	150	1.6	12.75 ± 0.18	201.99 ± 1.52	–	[15]
Jute Mat	CM	150 °C for 90 min	50 (%wt)	11.0 ± 1.3	371 ± 15	–	–	–	[143]

increased.

3.3. Water absorption

It is known that water absorption affects the physical, mechanical, and thermal properties of fibre-reinforced composites [148,149]. For composite applications where exposure to the atmosphere or wet conditions is required, evaluation of this property is very important. The PFA resin is known to be inherently hydrophobic [41,102,130] and therefore, it can be expected to result in increased water resistance of its composite. Menager et al. [131] noted this in their work on green composites with cork residues, where they discovered that the hydrophobicity of PFA composites increases with a corresponding increase in PFA content. The resin was also found to improve the moisture resistance of the treated flax fibre in a study by Jia and Fiedler [53]. The study found that treated flax fibre absorbed only 1.389% of its original weight in water over 10 days. Similarly, Pohl et al. [139] found that the non-hygroscopic behaviour of glass/PFA composite explained its low water absorption rate of 2.4% after 72 h compared to the high absorption rates of 21% and 36% observed for non-crimp flax/PFA and non-woven flax/PFA, respectively. They proposed that the significant difference in water absorption between flax-based composites is attributed to the swelling effect of fiber configuration. In a related study on green composites [140], Deka et al. reported that the water uptake of the pure PFA resin at saturation is 1.12%. Furthermore, Motaung et al. [118] found that the agave-reinforced PFA composite absorbed more water than the sisal-reinforced PFA composite in their comparative investigation of natural fibre reinforced polyfurfuryl alcohol composites. They attributed this to the reinforcement's hemicellulose concentration level. Similarly, Foruzanmehr et al. [89] found the absorption rate of the Glass reinforced bio-sourced furan composites to be 3.35 times higher than the Petro-based Glass/epoxy composite. At saturation, moisture absorption was found to be higher in Glass reinforced bio-sourced furan composites. However, they attributed this to the high porosity level of the glass/PFA. The effect of which was evident in their interlaminar shear property, which showed a 13.1% increase in favour of petro-based Glass/epoxy composite after 90 days. Relatedly, Sangregorio et al. [143] reported no increase in mass of Jute/PFA over 8 h in their work, whereas a 25% increase in mass was observed for Jute/Humins composite after half an hour attributing this to the low porosity level in the PFA based composite in comparison to the humins-based composite.

Beyond investigating the water absorption behaviour of PFA-based composites, the evaluation of their absorption behaviour in other fluids has also been studied. Giannis et al. [109] investigated and compared the absorption behaviour of glass/PFA and flax/PFA composites to glass reinforced polyester composites in various fluids such as motor oil, hydraulic oil, diesel oil, antifreeze, windscreen wash, pesticide, and distilled water. The study observed that the glass reinforced polyester composites exhibited the lowest absorption rate with less than 1% in most cases while both cases of the PFA-based composite were reported to absorb a significant amount of fluids, with the Flax/PFA absorbing the most. Additionally, they discovered that fluid immersion affected the surface properties of the glass reinforced polyester composites and glass/PFA samples, resulting in a decrease in Barcol hardness. They also evaluated the tensile properties of several composites following immersion in various fluids and found that stiffness and

strength decreased in all of the composites, with the effect of fluid exposure being more detrimental on the Flax/PFA composites than on others. Relatedly, Eldridge and Fam [141] conducted a study on the environmental aging effect on tensile properties of glass reinforced PFA composite in comparison to glass reinforced epoxy composite. The study found that the glass-reinforced PFA composite was more susceptible to salt water because it retained 80, 44, and 39% of its original strength at 23 °C, 40 °C, and 55 °C on exposure to water with a 3% salt concentration for up to 300 days, whereas the glass-reinforced epoxy composite retained 86, 72, and 61% of its strength under the same temperatures and exposure conditions. Similarly, Mcswiggan and Fam [142] reported a comparative research of the tensile property retention of aged carbon fibre reinforced PFA composites, conventional carbon fibre reinforced epoxy, and carbon fibre reinforced epoxidized pine oil composite. They recorded a tensile strength retention of 83, 81, and 82% for carbon fibre reinforced PFA composites at 23 °C, 40 °C, and 50 °C, respectively, after 240 days of exposure to salt water, compared to 101, 90, and 95% for carbon fibre reinforced epoxy at the same temperature and exposure.

3.4. Fire, smoke and toxicity properties

Evaluating the flammability and flame retardancy properties of bio-composites is essential, and a key aspect of this evaluation is the fire, smoke, and toxicity (FST) properties test. In recent years, fire, smoke, and toxicity (FST) properties are increasingly important factors in the choice of fibre reinforced polymer composites for industrial applications. For example, within the rail industries, these properties are stringent fire, smoke and toxicity FST requirements such as the R1HL3 classification are used to evaluate fibre reinforced composite parts to be used in indoor applications in railway vehicles [124]. In the aerospace sector, meeting the flammability requirements outlined in FAR 25.853 and FAR 25.855 is imperative for all materials used in aircraft interior component [150]. The PFA and its fibre reinforced composite exhibit remarkable fire behaviour as they have little tendency to emit smoke due to the fact that they char intensely [124] This is due to the high aromatic content, which accounts for the transition to a carbonaceous barrier that serves as a thermal shield when the resin surface is exposed to fire. This is evident from the work of Crossley et al. [123], which compared the flammability of glass and flax-reinforced PFA composites with epoxy, phenolic, and polyester-reinforced glass and flax composites, respectively. Using the UL94HB and UL94VB flammability test methods, they observed that both glass and flax reinforced PFA composites passed the UL94HB test with minimum smoke and no flame, attaining a standard rating of C. However, with the vertical burn test (UL94VB), they noted that the flax-reinforced PFA composite failed the vertical burn test (UL94VB), while the glass-reinforced PFA composite, was found to pass the same test without drips or smoke, earning a V-0 rating. Similarly, other authors have documented the fire, smoke, and toxicity (FST) performance of the PFA resin and its reinforced composite in comparison to related composite materials. Table 2 below details some of the results documented in the literature.

4. Applications of fibre reinforced polyfurfuryl alcohol composites

The application of fibre reinforced PFA composites in various

Table 2
Table showing the fire and smoke properties of the PFA, and its fibre reinforced composites documented in the literature.

Material Form	Test Method	Time to Ignition (TTI)s	Total heat released (THR) (MJ/m ²)	Peak of heat release rate (PHRR) (kW/m ²)	Total smoke released (TSR)(m ² /m ²)	Maximum Average Rate of Heat Emission (MARHE)(KW/m ²)	Specific extinction area (m ² /kg)	Effective heat of combustion (EHC) (MJ/kg)	Reference
Neat PFA resin	Cone calorimetry	25	38.6	981	290		709	17.3	[121, 151]
Flax/PFA composite	Cone calorimetry	104 ± 2	45 ± 5	450 ± 50	315 ± 10			16	[113]
Neat PFA resin	Cone calorimetry	50	75.4	393				19.8	[117]
Neat PFA resin	Cone calorimetry	98	30.9	682	15.3	154	36.8		[146]
Glass/PFA	Cone calorimetry	125	19.6	44,09		16,96			[50]
Jute/PFA	Bench scale fire calorimetry	60	–	979					[143]
Neat PFA	Cone calorimetry	78	23.0	254.8		73.1			[124]
Basalt/PFA Prepreg	Cone calorimetry	77	22	269.5		80.5 ± 10.85			[124]

applications has gained much attention recently. Several joint European Union projects to develop the PFA resin and composites have yielded impressive results. For example, in the FIRE RESIST project [50], where the aim was to study the resin for fireproof composite applications, it was found that the developed glass fibre reinforced PFA composite achieves an HL3 classification of the fire safety standard for rail applications. The glass/PFA laminates were also used in a sandwich construction of an innovative partition that met stringent fire test criteria well below the 60-min limit. A related BIOCOMP project of the European Commission through the 6th Framework Program evaluated the applicability of the PFA resin for composite fabrication [109,111,152]. The outcome of the project led to comparable prototypes of automotive exterior panels, vehicle mounts and bathroom floor sandwich panels made of glass and natural composite (Flax/PFA) respectively. Fig. 11 highlights the different fibre reinforced PFA based composite developed for applications.

Similarly, the European Union BIOBUILD project aimed to create bio composite with lower embodied energy than existing construction materials developed and produced full scale building components out of flax and jute/PFA composites, which attained a Euroclass B fire rating. Within the rail industry, UK-based TRB Lightweight Structures Ltd. has developed and produced a railway carriage carbon reinforced polymer (CFRP) sandwich panel door appropriate for subterranean rail applications utilizing a carbon fibre/PFA prepreg and recycled foam [155]. Bercella S.R.L., Element Materials Technology, and Composite Evolution Ltd. collaborated on a project that saw the usage of biobased fibre reinforced PFA composite for manufacturing cantilever seat supports that are positioned on the wall of a train carriage rather than the floor [154].

5. Concluding remarks

This article has presented an extensive review of the PFA resin and its fibre-reinforced composites. A review of existing studies on resin structure, chemistry, and cure kinetics was highlighted and the fabrication of its reinforced composite was discussed, detailing the key challenges during the curing process as well as some mitigation techniques found in the literature. In addition, the mechanical and thermal properties of the resin and its common fibre-reinforced composites were reviewed, highlighting that its mechanical properties are comparable to those of conventional matrices and their composites, as posited by literature. Regardless of the fibre/PFA configuration, it is evident from the review that the mechanical properties of the various composites are highly dependent on factors such as curing conditions and parameters, manufacturing process, fibre type, fibre orientation, shape type (fabric or fibre), and matrix modification, among others. The review also noted the excellent thermal stability and fire response of PFA resin and its composites. Despite the thermal benefits and structural potentials of reinforced PFA composites, it is clear from the literature that the major drawback of a lengthy manufacturing process cycle has often prevented the industrial scaling up of their use for applications. Therefore, there is a need for researchers to develop applicable techniques to aid in the reduction of manufacturing process time without any detrimental effect on its mechanical or thermal properties. Diverse techniques have been successfully employed to achieve a similar goal with conventional resin and its composites. However, with the PFA resin and its composites, these same techniques are directly inapplicable due to their unique curing nature. As a result, it does require an adequate research study of its curing mechanism to enable process optimization for rapid manufacturing. Despite the positives of biobased PFA resins, there is still much to be desired in some key areas of research. These include the need to expand the research of its sustainability to include a documented, data driven complete life cycle analysis from production to end of life. Also, from the mechanical property standpoint, a lot more research is desired in evaluating its mechanical properties, such as compressive properties, fracture toughness, shear properties, creep behaviour, and

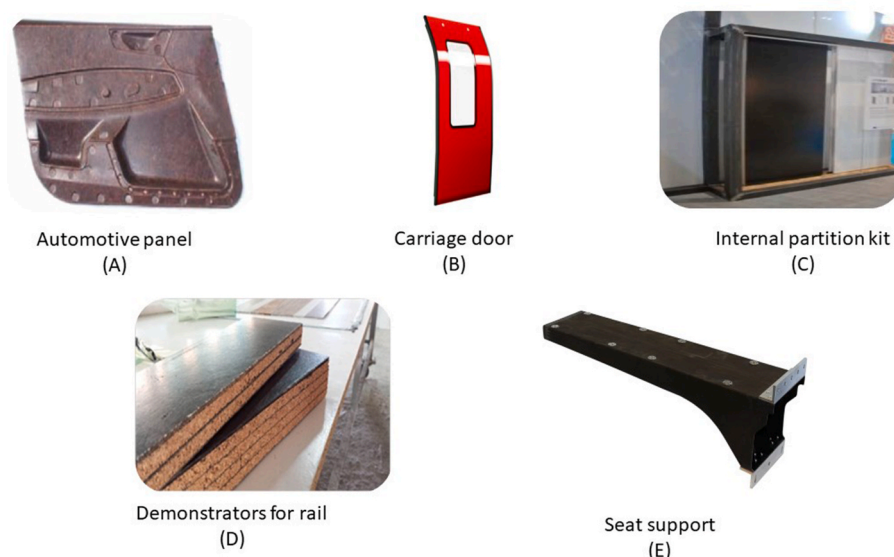


Fig. 11. Examples of different fiber-reinforced PFA-based composites developed for applications. (A) [152], (B) [155], (C, D) [153] and (E) [154].

impact damage analysis, as these properties of the PFA and its composites are still lacking. This review highlights that the bio-based sustainable PFA composites are set to be an adequate replacement of traditional petroleum based thermoset composites in many applications and this review provides the researchers and manufacturers with a consolidated reference resource for future developmental activities.

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CRediT authorship contribution statement

D.C. Odiyi: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing – original draft, Validation, Project administration, Software. **T. Sharif:** Supervision, Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Project administration, Writing – review & editing. **R.S. Choudhry:** Supervision, Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Project administration, Writing – review & editing. **S. Mallik:** Visualization, Investigation, Conceptualization, Funding acquisition. **S.Z.H. Shah:** Methodology, Formal analysis, Investigation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

- [1] Zhang J, Lin G, Vaidya U, Wang H. Past, present and future prospective of global carbon fibre composite developments and applications. *Composites Part B* 2023; 250:110463. <https://doi.org/10.1016/j.compositesb.2022.110463>.
- [2] Witten E, Mathes V. *The European market for fibre reinforced plastics/composites in 2021 - market developments, trends, challenges and outlook*. 2022.
- [3] Khurshid MF, Hasan MMB, Abdkader A, Cherif C. Processing of waste carbon and polyamide fibers for high performance thermoplastic composites: a novel manufacturing technology for unidirectional tapes structure. *J Ind Text* 2022;51: 7256S–76S. <https://doi.org/10.1177/15280837221077705>.
- [4] Larrañaga A, Lizundia E. A review on the thermomechanical properties and biodegradation behaviour of polyesters. *Eur Polym J* 2019;121:109296. <https://doi.org/10.1016/j.eurpolymj.2019.109296>.
- [5] Gurunathan T, Mohanty S, Nayak SK. A review of the recent developments in biocomposites based on natural fibres and their application perspectives. *Compos Part A Appl Sci Manuf* 2015;77:1–25. <https://doi.org/10.1016/j.compositesa.2015.06.007>.
- [6] Miller SA. Natural fiber textile reinforced bio-based composites: mechanical properties, creep, and environmental impacts. *J Clean Prod* 2018;198:612–23. <https://doi.org/10.1016/j.jclepro.2018.07.038>.
- [7] Skoczinski P, Carus M, Tweddle G, Ruiz P, Guzman D de, Ravenstijn J, et al. Bio-based building blocks and polymers - global capacities, production and trends 2022–2027. Germany: Hürth; 2023. <https://doi.org/10.52548/CMZD8323>.
- [8] Ahmad EEM, Luyt AS, Djoković V. Thermal and dynamic mechanical properties of bio-based poly(furfuryl alcohol)/sisal whiskers nanocomposites. *Polym Bull* 2013;70:1265–76. <https://doi.org/10.1007/s00289-012-0847-2>.
- [9] Rodriguez A, Racheb LY, Brijaldoc MH, Silvad LPC, Esteves LM. Common reactions of furfural to scalable process of residual biomass. *Cienc En Desarrollo* 2020:11.
- [10] Resch-fauster K, Džalto J, Anusic A, Mitschang P. High performance composites produced from polyfurfuryl alcohol : enhancing the process ability at short cycle times by applying hydrophilic. *ECCM18 - 18th. Eur. Conf. Compos. Mater.* 2018: 24–8.
- [11] Tumolva T, Kubouchi M, Aoki S, Sakai T. Evaluating the carbon storage potential of furan resin-based green composites. *ICCM Int Conf Compos Mater* 2011.
- [12] Domínguez JC, Madsen B. Development of new biomass-based furan/glass composites manufactured by the double-vacuum-bag technique. *J Compos Mater* 2015;49:2993–3003. <https://doi.org/10.1177/0021998314559060>.
- [13] Moazzen K, Zohuriaan-Mehr MJ, Jahanmardi R, Kabiri K. Toward poly(furfuryl alcohol) applications diversification: novel self-healing network and toughening epoxy–novolac resin. *J Appl Polym Sci* 2018;135:1–11. <https://doi.org/10.1002/app.45921>.
- [14] Domínguez JC, Madsen B. Chemorheological study of a polyfurfuryl alcohol resin system-Pre-gel curing stage. *Ind Crops Prod* 2014;52:321–8. <https://doi.org/10.1016/j.indcrop.2013.11.006>.
- [15] Ipakchi H, Shegeft A, Rezadoust AM, Zohuriaan-Mehr MJ, Kabiri K, Sajjadi S. Bio-resourced furan resin as a sustainable alternative to petroleum-based phenolic resin for making GFR polymer composites. *Iran Polym J (English Ed)* 2020;29: 287–99. <https://doi.org/10.1007/s13726-020-00793-w>.
- [16] Kumar R. A review on epoxy and polyester based polymer concrete and exploration of polyfurfuryl alcohol as polymer concrete. *J Polym* 2016:1–13. <https://doi.org/10.1155/2016/7249743>. 2016.
- [17] Guigo N, Mija A, Zavaglia R, Vincent L, Sbirrazzuoli N. New insights on the thermal degradation pathways of neat poly(furfuryl alcohol) and poly(furfuryl alcohol)/SiO₂ hybrid materials. *Polym Degrad Stabil* 2009;94:908–13. <https://doi.org/10.1016/j.polymdegradstab.2009.03.008>.
- [18] Zarbin AJG, Bertholdo R, Oliveira MAFC. Preparation, characterization and pyrolysis of poly(furfuryl alcohol)/porous silica glass nanocomposites: novel route to carbon template. *Carbon N Y* 2002;40:2413–22. [https://doi.org/10.1016/S0008-6223\(02\)00130-6](https://doi.org/10.1016/S0008-6223(02)00130-6).
- [19] Marefat Seyedlar R, Imani M, Mirabedini SM. Rheokinetics in curing process of polyfurfuryl alcohol: effect of homologous acid catalysts. *Iran Polym J (English Ed)* 2017;26:281–93. <https://doi.org/10.1007/s13726-017-0518-0>.

- [20] Marefat Seyedlar R, Imani M, Mirabedini SM. Bio-based furan coatings: adhesion, mechanical and thermal properties. *Polym Bull* 2020. <https://doi.org/10.1007/s00289-020-03124-4>.
- [21] Bachmann J, Hidalgo C, Bricout S. Environmental analysis of innovative sustainable composites with potential use in aviation sector—a life cycle assessment review. *Sci China Technol Sci* 2017;60:1301–17. <https://doi.org/10.1007/s11431-016-9094-y>.
- [22] Ramon E, Sguazzo C, Moreira PMGP. A review of recent research on bio-based epoxy systems for engineering applications and potentialities in the aviation sector. *Aerospace* 2018;5. <https://doi.org/10.3390/aerospace5040110>.
- [23] Fiore V, Scalici T, Di Bella G, Valenza A. A review on basalt fibre and its composites. *Composites Part B* 2015;74:74–94. <https://doi.org/10.1016/j.compositesb.2014.12.034>.
- [24] Mofidi A, Abila J, Ng JTM. Novel advanced composite bamboo structural members with bio-based and synthetic matrices for sustainable construction. *Sustain Times* 2020;12. <https://doi.org/10.3390/su12062485>.
- [25] Ferjan Š, Jovičić M, Lardiés Miazza N, Lighthart T, Harvey C, Fita S, et al. Sustainability assessment of the end-of-life technologies for biocomposite waste in the aviation industry. *Polymers* 2023;15:2689. <https://doi.org/10.3390/polym15122689>.
- [26] Chate GR, Patel GCM, Deshpande AS, Parappagoudar MB. Modeling and optimization of furan molding sand system using design of experiments and particle swarm optimization. *Proc Inst Mech Eng Part E J Process Mech Eng* 2018; 232:579–98. <https://doi.org/10.1177/0954408917728636>.
- [27] Holtzer M, Daňko R, Kmita A. Influence of a reclaimed sand addition to moulding sand with furan resin on its impact on the environment. *Water Air Soil Pollut* 2016;227. <https://doi.org/10.1007/s11270-015-2707-9>.
- [28] Holtzer M, Daňko R, Kmita A, Drożyński D, Kubecki M, Skrzyński M, et al. Environmental impact of the reclaimed sand addition to moulding sand with furan and phenol-formaldehyde resin—a comparison. *Materials* 2020;13:1–12. <https://doi.org/10.3390/ma13194395>.
- [29] Rivero G, Villanueva S, Manfredi LB. Furan resin as a replacement of phenolics: influence of the clay addition on its thermal degradation and fire behaviour. *Fire Mater* 2013. <https://doi.org/10.1002/fam.2209>.
- [30] Bobrowski A, Grabowska B. The impact of temperature on furan resin and binders structure Artur Bobrowski, Beata Grabowska. *Metall Foundry Eng* 2012;38:73. <https://doi.org/10.7494/mafe.2012.38.1.73>.
- [31] Katiyar R, Shobhit S. Studies on furan polymer concrete. *Int Res J Eng Technol* 2017;7:21–7. 04.
- [32] Muthukumar M, Mohan D. Studies on furan polymer concrete. *J Polym Res* 2005; 12:231–41. <https://doi.org/10.1007/s10965-004-3206-7>.
- [33] Mcswiggan C, Fam A. Bio-based resins for flexural strengthening of reinforced concrete beams with FRP sheets. *Construct Build Mater* 2017;131:618–29. <https://doi.org/10.1016/j.conbuildmat.2016.11.110>.
- [34] Ugrumov SA, Varankina GS, Katsadze VA. A method for manufacturing glued plywood based on furan resins. *Polym Sci - Ser D* 2019;12:398–400. <https://doi.org/10.1134/S1995421219040191>.
- [35] Pizzi A, Papadopoulos AN, Policardi F. Wood composites and their polymer binders. *Polymers* 2020;12. <https://doi.org/10.3390/POLYM12051115>.
- [36] Varodi AM, Beldean E, Timar MC. Furan Resin as potential substitute for phenol-formaldehyde resin in Plywood Manufacturing. *Bioresources* 2019;14:2727–39. <https://doi.org/10.15376/biores.14.2.2727-2739>.
- [37] Mokhothu TH, John MJ. Bio-based coatings for reducing water sorption in natural fibre reinforced composites. *Sci Rep* 2017;7:1–8. <https://doi.org/10.1038/s41598-017-13859-2>.
- [38] Rivero G, Fasce LA, Ceré SM, Manfredi LB. Furan resins as replacement of phenolic protective coatings: structural, mechanical and functional characterization. *Prog Org Coating* 2014;77:247–56. <https://doi.org/10.1016/j.porgcoat.2013.09.015>.
- [39] Marefat Seyedlar R, Imani M, Mirabedini SM. Bio-based furan coatings: adhesion, mechanical and thermal properties. *Polym Bull* 2021;78:577–99. <https://doi.org/10.1007/s00289-020-03124-4>.
- [40] Ruiz V, Pandolfo AG. High-frequency carbon supercapacitors from polyfurfuryl alcohol. *J Power Sources* 2011;196:7816–22. <https://doi.org/10.1016/j.jpowsour.2010.12.111>.
- [41] Vargas-Hernández MÁ, Sulbarán-Rangel B, Vázquez-Torres H. Non-isothermal curing kinetics of biocomposite from poly(furfuryl alcohol) and graphene oxide or reduced graphene oxide with different contents of oxygen-groups by DSC. *Thermochim Acta* 2020;684:178485. <https://doi.org/10.1016/j.tca.2019.178485>.
- [42] Gandini A, Belgacem MN. Furans in polymer chemistry. *Prog Polym Sci* 1997;22: 1203–379. [https://doi.org/10.1016/S0079-6700\(97\)00004-X](https://doi.org/10.1016/S0079-6700(97)00004-X).
- [43] Suárez-García F, Martínez-Alonso A, Tascón JMD, Ruffine L, Furdin G, Mareché JF, et al. Characterization of porous texture in composite adsorbents based on exfoliated graphite and polyfurfuryl alcohol. *Fuel Process Technol* 2002; 77–78:401–7. [https://doi.org/10.1016/S0378-3820\(02\)00088-7](https://doi.org/10.1016/S0378-3820(02)00088-7).
- [44] Burkett CL, Rajagopalan R, Marencic AP, Dronvajjala K, Foley HC. Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon. *Carbon N Y* 2006;44: 2957–63. <https://doi.org/10.1016/j.carbon.2006.05.029>.
- [45] Zaharopoulou A, Yannopoulos SN, Ioannides T. Carbon membranes prepared from poly (furfuryl alcohol–furfural) precursors: effect of FeCl₃ additive. *C — J Carbon Res* 2020;6:53. <https://doi.org/10.3390/c6030053>.
- [46] Pin JM, Misra M, Mohanty A. Green design of nanoporous materials and carbonaceous foams from polyfurfuryl alcohol and epoxidized linseed oil. *Mater Lett* 2017;196:238–41. <https://doi.org/10.1016/j.matlet.2017.03.058>.
- [47] Principe M, Martínez R, Ortiz P, Rieumont J. Furfuryl Alcohol Polymerization, Principe, *J Pol Cien e Tecnol. Polímeros - Ciência Tecnol* 2000;10:8–14. 2000.
- [48] Fink JK. *Reactive polymers: fundamentals and applications*. second ed. Elsevier Science & Technology Books; 2013.
- [49] Modica P Di, Gibson G, Kotsikos G, Hoydonckx H. Bio-resin for new bio-composite passive fire protection for off-shore application. *ICCM Int Conf Compos Mater* 2015. 2015-July.
- [50] Hans Hoydonckx IE, Monti M, Camino G, Di Monica P. Polyfurfuryl alcohol thermosets resins in fire resistant composite applications. 20th Int. Conf. Compos. Mater. Copenhagen 2015. 19-24th July 2015, Copenhagen.
- [51] Zolghadr M, Zohuriaan-Mehr MJ, Shakeri A, Salimi A. Epoxy resin modification by reactive bio-based furan derivatives: curing kinetics and mechanical properties. *Thermochim Acta* 2019;673:147–57. <https://doi.org/10.1016/j.tca.2019.01.025>.
- [52] Luckeneder P, Gavino J, Kuchernig R, Petuschnigg A, Tondi G. Sustainable phenolic fractions as basis for furfuryl alcohol-based co-polymers and their use as wood adhesives. *Polymers* 2016;8. <https://doi.org/10.3390/polym8110396>.
- [53] Jia Y, Fiedler B. Influence of furfuryl alcohol fiber pre-treatment on the moisture absorption and mechanical properties of flax fiber composites. *Fibers* 2018;6. <https://doi.org/10.3390/fib6030059>.
- [54] John MJ, Sabu T. Nanocomposites from furanic derivatives. *Nat. Polym.* 2012;2: 150–84. <https://doi.org/10.1039/9781849735315-00150>. Nanocomposites, vol. 2. 1st ed., Royal Society of Chemistry.
- [55] Eseyin AE, Steele PH. An overview of the applications of furfural and its derivatives. *Int J Adv Chem* 2015;3:42. <https://doi.org/10.14419/ijac.v3i2.5048>.
- [56] Wang H, Yao J. Use of Poly(furfuryl alcohol) in the fabrication of nanostructured carbons and nanocomposites. *Ind Eng Chem Res* 2006. <https://doi.org/10.1021/ie0602660>.
- [57] Iroegbu AO, Sadiku ER, Ray SS, Hamam Y. Sustainable chemicals: a brief survey of the furans. *Chem Africa* 2020;3:481–96. <https://doi.org/10.1007/s42250-020-00123-w>.
- [58] Limpricht H, Schwanert H. Ueber das Toluylenoxyd oder Desoxybenzoin, C₁₄H₁₂O. <https://doi.org/10.1002/jlac.18701.550106>; 1870.
- [59] Peters FN. The furans fifteen years of progress. *Ind Eng Chem* 1936;28:755–9. <https://doi.org/10.1021/ie50319a002>.
- [60] Sarika PR, Nancarrow P, Khansaheb A, Ibrahim T. Bio-based alternatives to phenol and formaldehyde for the production of resins. *Polymers* 2020;12:1–24. <https://doi.org/10.3390/polym12102237>.
- [61] Belgacem MN, Alessandro G. Furan-based adhesives. In: Pizzi A, Mittal KL, editors. *Handb. Adhes. Technol.* Second. New York: CRC Press; 2003. p. 615. <https://doi.org/10.1201/9780203912225>.
- [62] Corra Canos A, Iborra S, Veltz A. Chemical routes for the transformation of biomass into chemicals. *Chem Rev* 2007;107:2411–502. <https://doi.org/10.1021/cr050989d>.
- [63] Zheng T, Wang X, Lu C, Zhang X, Ji Y, Bai C, et al. Studies on curing kinetics and tensile properties of silica-filled phenolic amine/epoxy resin nanocomposite. *Polymers* 2019;11. <https://doi.org/10.3390/polym11040680>.
- [64] Machado G, Leon S, Santos F, Lourega R, Dullius J, Mollmann ME, et al. Literature review on furfural production from lignocellulosic biomass. *Nat Resour* 2016; 115–29. <https://doi.org/10.4236/nr.2016.73012>. 07.
- [65] AL-Rekabe JM, Saleh HM, Hanoosh WS. Synthesis, chemical resistance and thermal behavior of polyfurfural alcohol. *IOP Conf Ser Mater Sci Eng* 2020;928: 052015. <https://doi.org/10.1088/1757-899x/928/5/052015>.
- [66] Win DT. Furfural – gold from garbage. *AU J Technol* 2005;8:185–90.
- [67] Kim MG, Wasson L, Burris M, Wu Y, Watt C, Strickland RC. Furfuryl alcohol emulsion resins as co-binders for urea-formaldehyde resin-bonded particleboards. *Wood Fiber Sci* 1998;30:238–49.
- [68] Nanni G, Heredia-Guerrero JA, Paul UC, Dante S, Caputo G, Canale C, et al. Poly (furfuryl alcohol)-polycaprolactone blends. *Polymers* 2019;11:1–14. <https://doi.org/10.3390/POLYM11061069>.
- [69] Iroegbu AO, Hlangothi SP. Effects of the type of catalyst on the polymerisation mechanism of furfuryl alcohol and its resultant properties. *Chem Africa* 2018;1: 187–97. <https://doi.org/10.1007/s42250-018-0017-5>.
- [70] Oishi SS, Botelho EC, Rezende MC, Ferreira NG. Structural and surface functionality changes in reticulated vitreous carbon produced from poly(furfuryl alcohol) with sodium hydroxide additions. *Appl Surf Sci* 2017;394:87–97. <https://doi.org/10.1016/j.apsusc.2016.10.112>.
- [71] Origo FD, Ariseto JC, Seixas FL, Miyakawa W, Damião AJ, Oishi SS, et al. Acid catalyst influence on the polymerization time of polyfurfuryl alcohol and on the porosity of monolithic vitreous carbon. *J Appl Polym Sci* 2016;133:1–10. <https://doi.org/10.1002/app.43272>.
- [72] Mohajeri S, Vafayan M, Ghanbaralazadeh R, Pazokifard S, Zohuriaan Mehr MJ. Advanced isoconversional cure kinetic analysis of epoxy/poly(furfuryl alcohol) bio-resin system. *J Appl Polym Sci* 2017;134:1–10. <https://doi.org/10.1002/app.45432>.
- [73] Kumar R, Anandjiwala RD. Alternative fuels from waste cellulosic substrates and poly furfuryl alcohol. *Fuel* 2012;93:703–5. <https://doi.org/10.1016/j.fuel.2011.09.038>.
- [74] Bosq N, Guigo N, Vincent L, Sbirrazzuoli N. Thermomechanical behavior of a novel biobased poly(furfuryl alcohol)/silica nanocomposite elaborated by smart functionalization of silica nanoparticles. *Polym Degrad Stab* 2015;118:137–46. <https://doi.org/10.1016/j.polymdegradstab.2015.04.018>.
- [75] Mariscal R, Maireles-Torres P, Ojeda M, Sádaba I, López Granados M. Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energy Environ Sci* 2016;9:1144–89. <https://doi.org/10.1039/c5ee02666k>.

- [76] Kherroub DE, Belbachir M, Lamouri S. Study and optimization of the polymerization parameter of furfuryl alcohol by Algerian modified clay. *Arabian J Sci Eng* 2015;40:143–50. <https://doi.org/10.1007/s13369-014-1512-x>.
- [77] Purnal L, McWhorter J. Process of making furfuryl alcohol resin, US2471438A; 1949.
- [78] Mashouf Roudsari G, Misra M, Mohanty AK. A study of mechanical properties of biobased epoxy network: effect of addition of epoxidized soybean oil and poly (furfuryl alcohol). *J Appl Polym Sci* 2017;134:1–9. <https://doi.org/10.1002/app.44352>.
- [79] Hanifpour A, Miraghaie S, Zohuriaan-Mehr MJ, Behzadnasab M, Bahri-Laleh N. Poly(furfuryl alcohol) bioresin-modified LY5210 epoxy thermosets. *J Polym Res* 2019;26:1–9. <https://doi.org/10.1007/s10965-019-1876-4>.
- [80] Sharma M, Chopra EA. Comparative analysis of furan resin modified asphalt mix and conventional asphalt mix. *Int J Civ Eng Technol* 2019;10:1574–82.
- [81] Pophali A, Lee KM, Zhang L, Chuang YC, Ehm L, Cuiffo MA, et al. First synthesis of poly(furfuryl) alcohol precursor-based porous carbon beads as an efficient adsorbent for volatile organic compounds. *Chem Eng J* 2019;373:365–74. <https://doi.org/10.1016/j.cej.2019.05.029>.
- [82] Hu H, Bai Y, Miao C, Luo Z, Wang X. Polyfurfuryl alcohol assisted synthesis of Na₂FePO₄/C nanocomposites as cathode material of sodium ion batteries. *J Electroanal Chem* 2020;867:114187. <https://doi.org/10.1016/j.jelechem.2020.114187>.
- [83] Choura M, Belgacem NM, Gandini A. Acid-catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and cross-linking. *Macromolecules* 1996;29:3839–50. <https://doi.org/10.1021/ma951522f>.
- [84] Tondi G, Link M, Oo CW, Petuschnigg A. A simple approach to distinguish classic and formaldehyde-free tannin based rigid foams by ATR FT-IR. *J Spectrosc* 2015; 2015. <https://doi.org/10.1155/2015/902340>.
- [85] Tondi G, Cefarin N, Sepperer T, D'Amico F, Berger RJF, Musso M, et al. Understanding the polymerization of polyfurfuryl alcohol: ring opening and diels-alder reactions. *Polymers* 2019;11:1–15. <https://doi.org/10.3390/polym11122126>.
- [86] Kherroub DE, Belbachir M, Lamouri S. Synthesis of poly(furfuryl alcohol)/montmorillonite nanocomposites by direct in-situ polymerization. *Bull Mater Sci* 2015;38:57–63. <https://doi.org/10.1007/s12034-014-0818-3>.
- [87] Sommerauer L, Grzybek J, Elsaesser MS, Benisek A, Sepperer T, Dachs E, et al. Furfuryl alcohol and lactic acid blends: homo- or co-polymerization? *Polymers*, vol. 11. Basel; 2019. <https://doi.org/10.3390/polym11101533>.
- [88] Falco G, Guigo N, Vincent L, Sbirrazzuoli N. Opening furan for tailoring properties of bio-based poly(furfuryl alcohol) thermoset. *ChemSusChem* 2018;11: 1805–12. <https://doi.org/10.1002/cssc.201800620>.
- [89] Foruzanmehr M, Elkoun S, Fam A, Robert M. Degradation characteristics of new bio-resin based-fiber-reinforced polymers for external rehabilitation of structures. *J Compos Mater* 2016. <https://doi.org/10.1177/0021998315590262>.
- [90] Sadler JM, Yeh IC, Toulan FR, McAninch IM, Rinderspacher BC, La Scala JJ. Kinetics studies and characterization of poly(furfuryl alcohol) for use as bio-based furan novolacs. *J Appl Polym Sci* 2018;135:1–14. <https://doi.org/10.1002/app.46608>.
- [91] Dellièrè P, Guigo N. Monitoring the degree of carbonyl-based open structure in a furanic macromolecular system. *Macromolecules* 2022;55:1196–204. <https://doi.org/10.1021/acs.macromol.1c02098>.
- [92] Dellièrè P, Guigo N. Exploring new horizons for bio-based poly(furfuryl alcohol) by exploiting functionalities offered by side reactions. *ACS Macro Lett* 2022;11: 1202–6. <https://doi.org/10.1021/acsmacrolett.2c00427>.
- [93] Dellièrè P, Guigo N. Revealed pathways of furan ring opening and surface crosslinking in bio-based polyfurfuryl alcohol. *Eur Polym J* 2023;187:111869. <https://doi.org/10.1016/j.eurpolymj.2023.111869>.
- [94] D'Amico F, Musso ME, Berger RJF, Cefarin N, Birarda G, Tondi G, et al. Chemical constitution of polyfurfuryl alcohol investigated by FTIR and Resonant Raman spectroscopy. *Spectrochim Acta Part A Mol Biomol Spectrosc* 2021;262:120090. <https://doi.org/10.1016/j.saa.2021.120090>.
- [95] Quinquet L, Dellièrè P, Guigo N. Conditions to control furan ring opening during furfuryl alcohol polymerization. *Molecules* 2022;27:3212. <https://doi.org/10.3390/molecules27103212>.
- [96] Wang Z, Meng F, Li X, Zhang X, Hu W, Zhao G. Cure behaviors of furfuryl alcohol/epoxy/methyltetrahydrophthalic anhydride and their enhanced mechanical and anti-acid properties of basalt fiber reinforced composites. *Composites Part B* 2018;154:263–71. <https://doi.org/10.1016/j.compositesb.2018.08.011>.
- [97] He L, Li D, Dong D, Yao J, Huang Y, Wang H. Effects of polymerization conditions on the properties of poly(furfuryl alcohol) composite membranes. *J Appl Polym Sci* 2012;124:3383–91. <https://doi.org/10.1002/app.35356>.
- [98] Domínguez JC, Grivel JC, Madsen B. Study on the non-isothermal curing kinetics of a polyfurfuryl alcohol bioresin by DSC using different amounts of catalyst. *Thermochim Acta* 2012;529:29–35. <https://doi.org/10.1016/j.tca.2011.11.018>.
- [99] Domínguez JC, Madsen B. Determination of the gel point of a polyfurfuryl alcohol resin and characterization of its curing rheokinetics. *Proc. Risø Int. Symp. Mater. Sci.* 2013;34:209–16.
- [100] Domínguez JC, Oliet M, Alonso MV, Rodríguez F, Madsen B. An exponential chemorheological model for viscosity dependence on degree-of-cure of a polyfurfuryl alcohol resin during the post-gel curing stage. *IOP Conf Ser Mater Sci Eng* 2016;139. <https://doi.org/10.1088/1757-899X/139/1/012018>.
- [101] Guigo N, Mija A, Vincent L, Sbirrazzuoli N. Chemorheological analysis and model-free kinetics of acid catalyzed furfuryl alcohol polymerization. *Phys Chem Chem Phys* 2007;9:5359–66. <https://doi.org/10.1039/b707950h>.
- [102] Vargas MA, Scheubner M, Guthausen G. Reaction kinetics of polyfurfuryl alcohol bioresin and nanoparticles by 1H-NMR transverse relaxation measurements. *Polym Compos* 2018;39:3280–8. <https://doi.org/10.1002/pc.24342>.
- [103] Lopez De Vergara U, Sarrionandia M, Gondra K, Aurrekoetxea J. Polymerization and curing kinetics of furan resins under conventional and microwave heating. *Thermochim Acta* 2014;581:92–9. <https://doi.org/10.1016/j.tca.2014.02.017>.
- [104] Marefat Seyedar R, Imani M, Mirabedini SM. Curing of poly(furfuryl alcohol) resin catalyzed by a homologous series of dicarboxylic acid catalysts: kinetics and pot life. *J Appl Polym Sci* 2016;133. <https://doi.org/10.1002/app.44009>.
- [105] Behzadfar A, Imani M, Farahmandghavi F. Shelf-life of polyfurfuryl alcohol resin: an accelerated rheokinetics study. *Polym Bull* 2019;76:5903–18. <https://doi.org/10.1007/s00289-019-02692-4>.
- [106] Rivero G, Pettarin V, Vázquez A, Manfredi LB. Curing kinetics of a furan resin and its nanocomposites. *Thermochim Acta* 2011;516:79–87. <https://doi.org/10.1016/j.tca.2011.01.022>.
- [107] Kemppainen J, Gallegos I, Krieg AS, Gissinger JR, Wise KE, Kowalik M, et al. Evolution of glassy carbon derived from pyrolysis of furan resin. 2023. <https://doi.org/10.26434/chemrxiv-2023-gj6gd>. Cambridge.
- [108] Odiyí DC, Sharif T, Choudhry RS, Mallik S. Cure mechanism and kinetic prediction of bio-based glass/polyfurfuryl alcohol prepreg by model-free kinetics. *Thermochim Acta* 2022;708:179133. <https://doi.org/10.1016/j.tca.2021.179133>.
- [109] Giannis S, Arnold E, Hoydonckx HE, Weager B, Martin RH. Development of high performance bio-composite based on furan bio resin for vehicle panel. 13th Eur. Conf. Compos. Mater. 2008:1–10. Stockholm.
- [110] Talent M, Wang J. Unidirectional cordena fibre-reinforced furan resin full biocomposite: properties and influence of high fibre mass fraction. *J Compos* 2015;8. <https://doi.org/10.1155/2015/707151>. 2015.
- [111] Arnold E, Weager BM, Hoydonckx HE, Madsen B. Next generation sustainable composites : development and processing of furan-flax bio-composites. 17th int. Conf. Compos. Mater. Edinburgh: British Composite Society; 2009. p. 27–31.
- [112] López De Vergara U, Sarrionandia M, Gondra K, Aurrekoetxea J. Impact behaviour of basalt fibre reinforced furan composites cured under microwave and thermal conditions. *Composites Part B* 2014;66:156–61. <https://doi.org/10.1016/j.compositesb.2014.05.009>.
- [113] Kumar R, Anandjiwala RD. Compression-moulded flax fabric-reinforced polyfurfuryl alcohol bio-composites: Mechanical and thermal properties. *J Therm Anal Calorim* 2013;112:755–60. <https://doi.org/10.1007/s10973-012-2623-9>.
- [114] Carotenuto G, Nicolais L. Furfuryl alcohol-based resin as matrix for high performance composites. *Adv Compos Lett* 1998;7:105–9. <https://doi.org/10.1177/096369359800700402>.
- [115] Domínguez JC, Madsen B. Development of new biomass-based furan/glass composites manufactured by the double-vacuum-bag technique. *J Compos Mater* 2015;49:2993–3003. <https://doi.org/10.1177/0021998314559060>.
- [116] Deka H, Mohanty A, Misra M. Renewable-resource-based green blends from poly (furfuryl alcohol) bioresin and lignin. *Macromol Mater Eng* 2014;299:552–9. <https://doi.org/10.1002/mame.201300221>.
- [117] Rivero G, Villanueva S, Manfredi LB. Furan resin as a replacement of phenolics: influence of the clay addition on its thermal degradation and fire behaviour. *Fire Mater* 2014;38:683–94. <https://doi.org/10.1002/fam.2209Furan>.
- [118] Džalto J, Medina L, Mitschang P. Volumetric interaction and material characterization of flax/furan bio-composites. *KMUTNB Int J Appl Sci Technol* 2014;7:11–21. <https://doi.org/10.14416/j.ijast.2014.01.004>.
- [119] Resch-Fauster K, Džalto J, Anusic A, Mitschang P. Effect of the water absorptive capacity of reinforcing fibers on the process ability, morphology, and performance characteristics of composites produced from polyfurfuryl alcohol. *Adv Manuf Polym Compos Sci* 2018;4:13–23. <https://doi.org/10.1080/20550340.2018.1436234>.
- [120] Ma Y, Du Y, Zhao J, Yuan X, Hou X. Preparation and characterization of furan-matrix composites blended with modified hollow glass microsphere. *Polymers* 2020;12:1–12. <https://doi.org/10.3390/polym12071480>.
- [121] Kandola BK, Ebdon JR, Chowdhury KP. Flame retardance and physical properties of novel cured blends of unsaturated polyester and furan resins. *Polymers* 2015;7: 298–315. <https://doi.org/10.3390/polym7020298>.
- [122] Sharif M, Kumar R, Kumar KD. Poly(lactic acid) incorporated polyfurfuryl alcohol bioplastics: thermal, mechanical and curing studies. *J Therm Anal Calorim* 2018; 132:1593–600. <https://doi.org/10.1007/s10973-018-7087-0>.
- [123] Crossley R, Schubel P, Stevenson A. Furan matrix and flax fibre as a sustainable renewable composite: mechanical and fire-resistant properties in comparison to phenol, epoxy and polyester. *J Reinforc Plast Compos* 2014;33:58–68. <https://doi.org/10.1177/0731684413502108>.
- [124] Elejoste PA, Allue A, Ballesteros J, Neira S, Gómez-Alonso JL, Gondra K. Development and characterisation of sustainable prepreps with improved fire behaviour based on furan resin and basalt fibre reinforcement. *Polymers* 2022;14. <https://doi.org/10.3390/polym14091864>.
- [125] Wang Z, Cao N, He J, Du R, Liu Y, Zhao G. Mechanical and anticorrosion properties of furan/epoxy-based basalt fiber-reinforced composites. *J Appl Polym Sci* 2017;134:1–6. <https://doi.org/10.1002/app.44799>.
- [126] Wang Z, Meng F, Li X, Zhang X, Hu W, Zhao G. Cure behaviors of furfuryl alcohol/epoxy/methyltetrahydrophthalic anhydride and their enhanced mechanical and anti-acid properties of basalt fiber reinforced composites. *Composites Part B* 2018;154:263–71. <https://doi.org/10.1016/j.compositesb.2018.08.011>.
- [127] Abdul Khalil HPS, Firoozian P, Bakare IO, Akil HM, Noor AM. Exploring biomass based carbon black as filler in epoxy composites: flexural and thermal properties. *Mater Des* 2010;31:3419–25. <https://doi.org/10.1016/j.matdes.2010.01.044>.

- [128] St John NA, Brown JR. Flexural and interlaminar shear properties of glass-reinforced phenolic composites. *Compos Part A Appl Sci Manuf* 1998;29:939–46. [https://doi.org/10.1016/S1359-835X\(98\)00019-0](https://doi.org/10.1016/S1359-835X(98)00019-0).
- [129] Motaung TE, Mngomezulu ME, Hato MJ. Effects of alkali treatment on the poly (furfuryl) alcohol–flax fibre composites. *J Thermoplast Compos Mater* 2016;31:48–60. <https://doi.org/10.1177/0892705716679478>.
- [130] Motaung TE, Linganiso LZ, Kumar R, Anandjiwala RD. Agave and sisal fibre-reinforced polyfurfuryl alcohol composites. *J Thermoplast Compos Mater* 2017;30:1323–43. <https://doi.org/10.1177/0892705716632858>.
- [131] Menager C, Guigo N, Wu X, Vincent L, Sbirrazzuoli N. “Green” composites prepared from polyfurfuryl alcohol and cork residues: thermal and mechanical properties. *Compos Part A Appl Sci Manuf* 2019;124:105473. <https://doi.org/10.1016/j.compositesa.2019.105473>.
- [132] Saba N, Allothman OY, Almutairi Z, Jawaid M, Ghori W. Date palm reinforced epoxy composites: tensile, impact and morphological properties. *J Mater Res Technol* 2019;8:3959–69. <https://doi.org/10.1016/j.jmrt.2019.07.004>.
- [133] Araújo EM, Araújo KD, Pereira OD, Ribeiro PC, De Melo TJA. Fiberglass wastes/polyester resin composites: mechanical properties and water sorption. *Polimeros* 2006;16:332–5. <https://doi.org/10.1590/S0104-14282006000400014>.
- [134] da Silva CG, de Oliveira F, Frollini E. Sugarcane bagasse fibers treated and untreated: performance as reinforcement in phenolic-type matrices based on lignosulfonates. *Waste and Biomass Valorization* 2019;10:3515–24. <https://doi.org/10.1007/s12649-018-0365-z>.
- [135] Kumar R, Anandjiwala RD. Compression-moulded flax fabric-reinforced polyfurfuryl alcohol bio-composites: mechanical and thermal properties. *J Therm Anal Calorim* 2013;112:755–60. <https://doi.org/10.1007/s10973-012-2623-9>.
- [136] Pernevan MS, Maršavina L, Radu D, Popa M, Sirghie C. Considerations about the impact behavior of biocomposites based on polypropylene and furan resins reinforced with hemp shives. *J Nat Fibers* 2013;10:197–206. <https://doi.org/10.1080/15440478.2013.770723>.
- [137] Kandemir A, Longana ML, Hamerton I, Eichhorn SJ. Developing aligned discontinuous flax fibre composites: sustainable matrix selection and repair performance of vitrimers. *Composites Part B* 2022;243:110139. <https://doi.org/10.1016/j.compositesb.2022.110139>.
- [138] Crossley RJ, Schubel PJ, Stevenson A, Moreira M. Development and processing of a sustainable fully bio derived polyfurfuryl alcohol matrix flax. *ECCM15 - 15TH eur. Conf. Compos. Mater.* 2012. p. 24–8. Venice ,Italy.
- [139] Pohl T, Bierer M, Natter E, Madsen B, Hoydonckx H, Schledjewski R. Properties of compression moulded new fully biobased thermoset composites with aligned flax fibre textiles. *Plast, Rubber Compos* 2011;40:294–9. <https://doi.org/10.1179/1743289810Y.0000000017>.
- [140] Deka H, Misra M, Mohanty A. Renewable resource based “all green composites” from kenaf biofiber and poly(furfuryl alcohol) bioresin. *Ind Crops Prod* 2013;41:94–101. <https://doi.org/10.1016/j.indcrop.2012.03.037>.
- [141] Eldridge A, Fam A. Environmental aging effect on tensile properties of GFRP made of furfuryl alcohol bioresin compared to epoxy. *J Compos Construct* 2014;18. [https://doi.org/10.1061/\(ASCE\)CC.1943-5614](https://doi.org/10.1061/(ASCE)CC.1943-5614).
- [142] Mcswiggan C, Fam A. Tensile properties retention of aged carbon-FRP sheets made of fully and partially bio-based resins and conventional epoxy. *Polym Compos* 2016;39:2081–92. <https://doi.org/10.1002/pc>.
- [143] Sangregorio A, Muralidhara A, Guigo N, Marlair G, de Jong E, Sbirrazzuoli N. Natural fibre composites with furanic thermoset resins. Comparison between polyfurfuryl alcohol and humins from sugar conversion. *Compos Part C Open Access* 2021;4:100109. <https://doi.org/10.1016/j.jcomc.2021.100109>.
- [144] Fam A, Eldridge A, Misra M. Mechanical characteristics of glass fibre reinforced polymer made of furfuryl alcohol bio-resin. *Mater Struct Constr* 2014;47:1195–204. <https://doi.org/10.1617/s11527-013-0122-5>.
- [145] Mak K, Fam A. Fatigue performance of furfuryl alcohol resin fiber-reinforced polymer for structural rehabilitation. *J Compos Construct* 2020;24:1–12. [https://doi.org/10.1061/\(ASCE\)CC.1943-5614.0001018](https://doi.org/10.1061/(ASCE)CC.1943-5614.0001018).
- [146] Monti M, Hoydonckx H, Stappers F, Camino G. Thermal and combustion behavior of furan resin/silica nanocomposites. *Eur Polym J* 2015;67:561–9. <https://doi.org/10.1016/j.eurpolymj.2015.02.005>.
- [147] Guigo N, Mija A, Vincent L, Sbirrazzuoli N. Eco-friendly composite resins based on renewable biomass resources: polyfurfuryl alcohol/lignin thermosets. *Eur Polym J* 2010;46:1016–23. <https://doi.org/10.1016/j.eurpolymj.2010.02.010>.
- [148] Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R. Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: flax-fibres and glass-fibres. *Mater Des* 2011;32:788–95. <https://doi.org/10.1016/j.matdes.2010.07.024>.
- [149] Apolinario G, Jenny P, Corn S, Léger R, Bergeret A, Haudin JM. Effects of water ageing on the mechanical properties of flax and glass fibre composites: degradation and reversibility. *RILEM Bookseries* 2016;12:183–96. https://doi.org/10.1007/978-94-017-7515-1_14.
- [150] Glaskova-Kuzmina T, Dejus D, Jättnieks J, Kruuv PP, Lancere L, Kobenko S, et al. Flame-retardant and tensile properties of polyamide 12 processed by selective laser sintering. *J Compos Sci* 2022;6. <https://doi.org/10.3390/jcs6070185>.
- [151] Kandola B, Krishnan L. Fire performance evaluation of different resins for potential application in fire resistant structural marine composites. *Fire Saf Sci* 2014;11:769–80. <https://doi.org/10.3801/IAFSS.FSS.11-769>.
- [152] Eisenreich N. New classes of engineering composites materials from renewable resources. *Rep EU 6th Framew Program Integr* 2008:1–31.
- [153] Developing novel fire-resistant high performance composites. 2015. <https://cordis.europa.eu/project/id/246037/reporting>. [Accessed 10 May 2023].
- [154] Holmes M. Biocomposites take natural step forward: applications for biocomposites and the use of natural fiber reinforcements are increasing. *Reinforced Plastics* looks at a number of examples. *Reinforc Plast* 2019;63:194–201. <https://doi.org/10.1016/j.repl.2019.04.069>.
- [155] Iroegbu AO, Hlangothi SP. Furfuryl alcohol a versatile, eco-sustainable compound in perspective. *Chem Africa* 2019;2:223–39. <https://doi.org/10.1007/s42250-018-00036-9>.