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Journal Pre-proof

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

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8 **Highlights**

- 9 • For biobased PFA and fibre reinforced PFA composites:
10 • Established the state of the art in synthesis, cure kinetics and manufacturing.
11 • Explained the limits of mechanical, thermal and moisture absorption properties.
12 • Provided guidance for applications and research direction for improvements.

13 **Abstract.**

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

26 **Keywords:** Biobased, Polyfurfuryl Alcohol resin (PFA); Fibre-reinforced Composites; Sustainability;
27 Properties; Green House Gas (GHG) emissions, Furan resin, Cure kinetic , Polymerization
28 ,Crosslinking

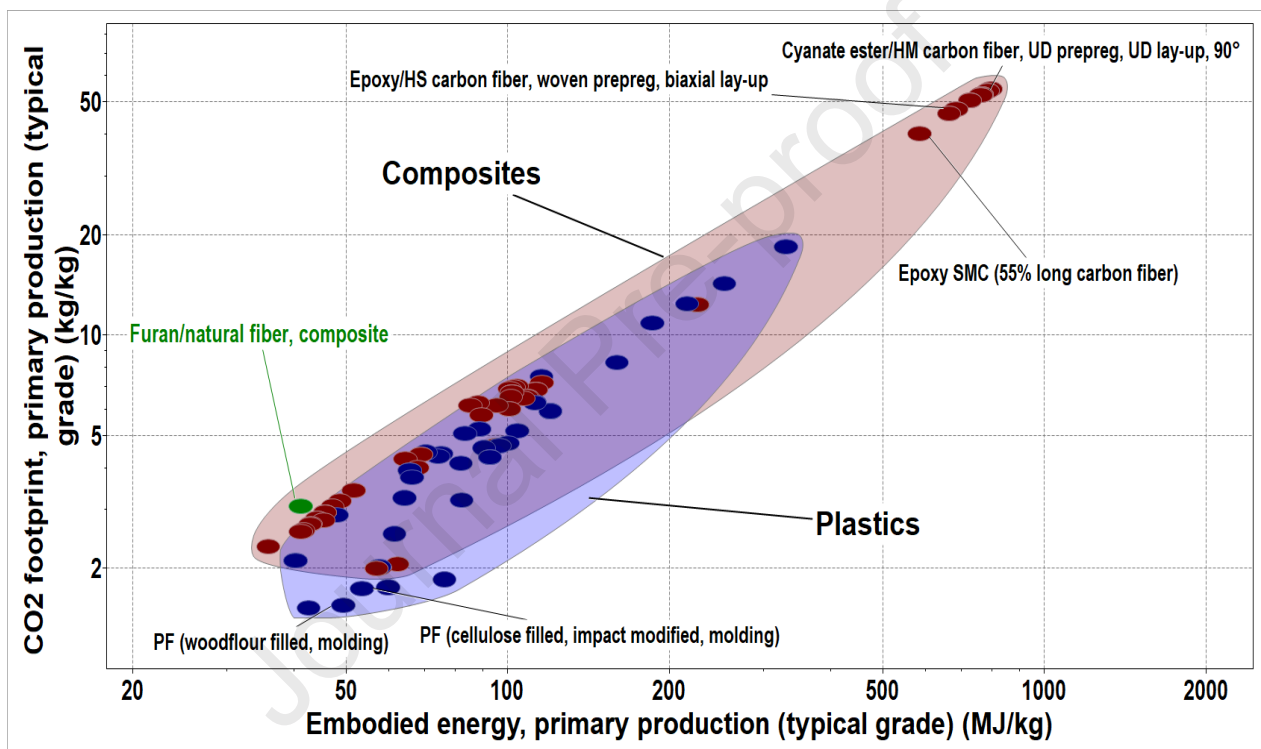
29 **1. Introduction.**

30 The development of advanced fibre-reinforced polymer FRPs has been marked by a series of
31 advancements in fibre and matrix materials, manufacturing processes, design techniques and exciting
32 applications. In fact, the year 2022 marks 50 years of first commercial application of carbon fibre in an
33 everyday product, the fishing pole by Toray industries. [1]. Over the years, the impressive properties
34 of fibre-reinforced polymer have led to an ever-increasing number of industries adopting these for
35 various applications. In general, petroleum based synthetic thermosets such as epoxies, phenolics, and
36 polyesters are reinforced with carbon or glass fibre reinforcements for most composite material
37 applications. According to a report by Witten and Mathes [2], the global production volume for
38 composites in 2021 was reported to be 12.1 million tonnes, with 52 kt of Carbon Fibre Reinforced
39 plastic (CFRP) produced in Europe alone. Estimated forecasts place global demand for Carbon Fibre
40 Reinforced Plastic (CFRP) at 200 kt to 285 kt between 2025 and the end of this decade [1,3]. This
41 inadvertently implies that large amounts of non-degradable petroleum-based polymers and composites
42 are continually manufactured globally, most of which are discarded as industrial waste products after
43 being used [4]. In fact, It is estimated that waste obtained from end-of-life components will reach up to
44 50 kt per year in 2030 [3]. In addition to the environmental challenges posed by end-of-life waste, the
45 petroleum-based polymers and polymeric composites also pose other environmental concerns such as
46 a high embodied energy and greater greenhouse gases (GHG) emissions. These are a consequence of
47 the highly energy intensive manufacturing process for the fibres as well as composites. Owing to these
48 environmental concerns and sustainability problems, this century has seen remarkable developments in
49 green materials in the field of polymer science through the development of bio-composites [5], as an
50 alternative to petroleum based composites, to mitigate this challenge. Additionally, the associated
51 benefit of a reduction in Green House Gas (GHG) emissions from the production of fully bio-based
52 composites potentially provides cost incentives from the perspective of carbon capture [6].

53 Over the last decade, the growth in the production and application of bio-composites in different
54 industries has experienced a tremendous increase. Bio-based composites are finding increasing use for
55 various applications within industries such as automotive, rail, sports goods, and aviation, amongst
56 others. This renewed interest stems from the need to find environmentally friendly and sustainable
57 alternatives to the prevailing petroleum-based composite products. According to a report by the Nova
58 Institute [7], an estimated 4.5 million tonnes of bio-based polymers were produced worldwide in 2022
59 . The report further projects an increase in the development of biobased polymer production capacities
60 to 9.3 million tonnes by 2027, indicating an average compound annual growth rate (CAGR) of about
61 14%. Sustainability, industrial ecology, eco-efficiency, and green chemistry are the fundamental and
62 ongoing drivers of this sector, spearheading the production of the next generation of materials, goods,
63 and processes. Recently, research, technological advancement and modifications of naturally existing
64 polymers, as well as the synthesis of novel new polymers from renewable monomers have rapidly
65 expanded [8]. One such area that has experienced rapid growth is the bio-resin sector. For example, the
66 global demand for furfuryl, which is a feedstock for many of these types of resins, was about 340,000
67 tonnes annually with an estimated value of USD 551 million in 2019 and is projected to reach USD 700
68 million in 2024, growing at a CAGR (Compound Annual Growth Rate) of 4.9% between 2019 and
69 2024. [9]. The continuous development and commercialization of bio-based resins are becoming
70 increasingly important and have enabled the expansion of bio composite applications in various
71 industries.

72 The PFA resin, also known as furan resin is one such biobased resin [10–13]. It is considered
73 as one of the fully bio-based resins, a dark brown organic polymer obtained by the acid-catalyzed
74 polymerization of furfuryl alcohol derived from renewable agricultural waste [8,14–19]. The resulting
75 highly crosslinked network forms a solid that possesses comparable mechanical properties to many
76 petroleum based thermosets as well as remarkable thermal and chemical resistance to acids, alkalis, and
77 solvents [20]. From an environmental point of view, the PFA resin has a remarkably lower GHG
78 emissions as measured in terms of CO₂ equivalent emission i.e. kg-CO₂-eq, compared to petroleum-
79 based resins [11,21,22]. Its eco-formulations can reduce up to 50% of CO combustion [23]. This is due

80 to its derivation from furfuryl alcohol, which has a global warming potential (in terms of kg-CO₂-eq)
 81 of 1.3, compared to the unsaturated polyester resin at 7.5 and epoxy at 6.5 [24]. A conceptual illustration
 82 of the environmental merit of the PFA resin can be seen in the evaluation of the dependence of CO₂
 83 footprint on the embodied energy of thermoset polymers and composite subsets within the material
 84 database of the ANSYS CES Granta EduPack 2022. The results show the Furan (PFA) flax composites
 85 with a CO₂ footprint primary production value range of 2.93-3.32 kg/kg to be among the lowest
 86 candidate materials with low primary production embodied energy, as shown in Figure 1.



87

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

91 In fact, a recent life cycle assessment examining end-of-life technologies for bio composite waste in
 92 aviation industry by Špela et al. [25] found that pyrolyzing 1 kg of basalt fibre/furan resin composites
 93 produced 0.394 kg of CO₂ equivalent emissions, while solvolyzing the same amount of material
 94 resulted in 0.467 kg of CO₂ equivalent emissions. In addition to the benefit of low GHG emissions and

95 low embodied energy, the bio-based polymers like PFA are also more sustainable as the feedstock is a
96 by-product of the food waste.

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

110 A review of the literature on the PFA resin reveals that tremendous work has been done on its
111 preparation, chemistry, kinetics, and characterization, particularly for non-composite applications.
112 Several authors [42,48,52–55] have reported on its precursor (furfural alcohol) and highlighted the furan
113 derived processes and its capabilities for a wide range of applications. However, a comprehensive
114 review aimed at cataloguing their mechanical, thermal, degradation behaviour and recent advancements
115 in fibre-reinforced applications is still lacking. Therefore, this paper aims to provide an in-depth analysis
116 of the PFA resin, with a focus on its applications in fibre-reinforced composites. It is intended to serve
117 as a useful reference for researchers and industry developers seeking to further advance widespread
118 utilization of eco-friendly PFA resin in high-performance composites for industrial application. In this
119 article, an overview of the polyfurfuryl alcohol resin is provided in Section 1, and this is aimed at
120 providing background on the resin and its applications. A brief historical background of the PFA resin,
121 its synthesis, structure and chemistry, cure kinetics, processing, and manufacture are discussed

122 extensively in Section 2. Section 3 presents a detailed review of the documented properties of the PFA
123 resin and its reinforced composites with a focus on mechanical, thermal, water absorption, and FST
124 properties. Lastly, applications employing the use of PFA composite are highlighted and discussed in
125 Section 4, with concluding remarks presenting suggestions for further development.

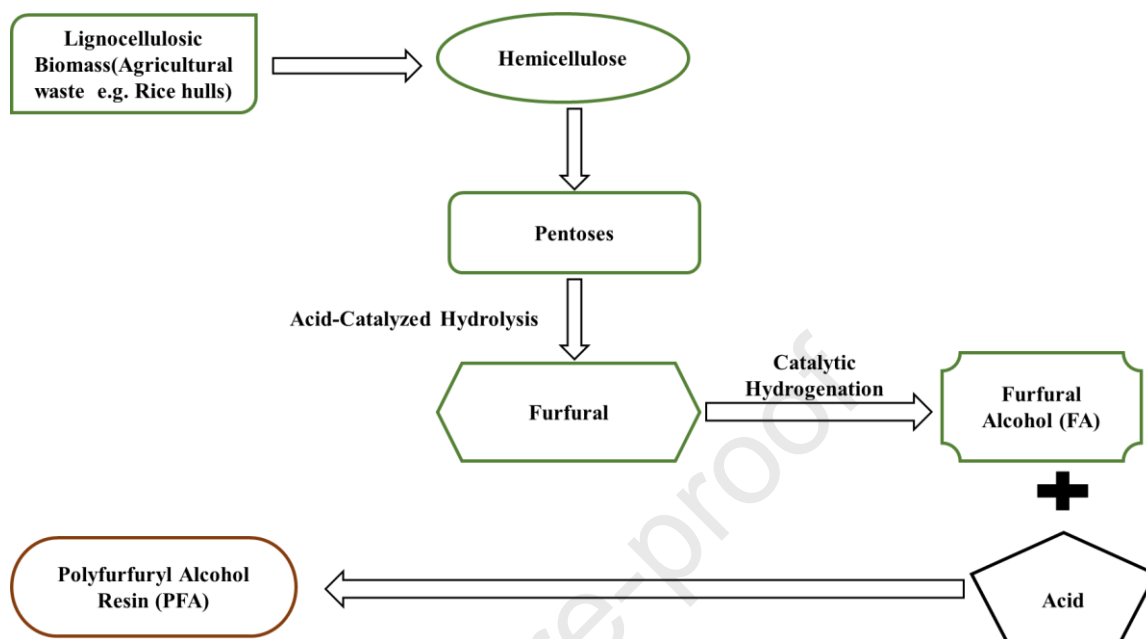
126 **2. Polyfurfuryl Alcohol Resin.**

127 Similar to conventional thermoset resins (Epoxy, Phenolic), PFA resin is a thermally cross-
128 linked polymer [56] However, it is bio-based because its main monomer, Furfuryl alcohol (FA), comes
129 from renewable resources such as agricultural waste, e.g., rice hull, sugarcane bagasse, and corn cob.
130 The early history of the development of PFA resin can be traced back to 1923, after the start of the
131 industrial production of furfural a year earlier [48]. Before that, however, Scottish chemist John
132 Stenhouse had discovered resin's ability to be produced from furfural in 1840 [48]. Iroegbu et al. [57]
133 reported the discovery of furfural by Johann Wolfgang Dberiner in 1832, while furfuryl alcohol, the
134 main precursor, was confirmed by studies by Limpricht et al. [58] identified according to the same
135 report. Despite these historical events, initial commercialization began in the early 1920s, with work to
136 commercialize furfural from corncobs initiated by LaForge and Mains of the Bureau of Chemistry [59]
137 [60]. Between 1920 and 1953, Peter and Dunlop at the Hull Research Facility of the Quaker Oats
138 Company significantly advanced the commercialization of furfuryl derivatives, which include the PFA
139 [55,57]. In 1970, it successively found its use in the aerospace industry [61]. Subsequently, it was further
140 researched and developed for various other applications and recently introduced into fibre-reinforced
141 applications.

142 **2.1 Synthesis of Polyfurfuryl Alcohol Resin.**

143 Various methods for synthesizing PFA resins have been published in numerous studies. The
144 pathway to the PFA resin manufacturing process begins with the extraction of furfural by acid-catalyzed
145 hydrolysis from pentosan-rich hemicellulose obtained from viable agricultural waste [60,62–66].
146 Conventionally, the extracted furfuryl is converted to furfuryl alcohol via a catalytic hydrogenation

147 reduction process [39,42,67–69]. Then, the furfural alcohol (FA) is converted by acid catalysis to obtain
 148 PFA resin. The entire process is illustrated in Figure 2.



149

150 **Figure 2.** Schematic of PFA manufacturing process.

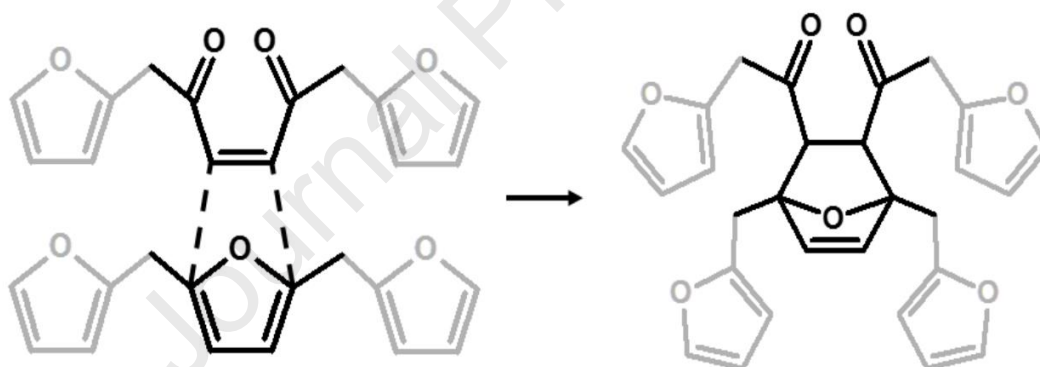
151 The furfural alcohol (FA) can be catalyzed by different types of acids. Studies show that either
 152 a strong or weak acid type can be used as a catalyst for the process. Some commonly used acid catalysts
 153 used for polymerization include mineral acids such as sulfuric acid [70], nitric acid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

163 The first step is the addition of acid to buffer-free hot furfuryl alcohol in an amount sufficient
164 to initiate and continue the reaction to establish the boiling point of the reacting mixture. This was
165 followed by continuing the reaction while boiling the furfuryl alcohol-water mixture until the
166 condensation reaction had progressed to the desired point. Next is the removal of the acid from the
167 system and lastly the distillation of the product to obtain a substantially anhydrous initial resin. The
168 process of this invention offered a solution to alleviate the explosive exothermic difficulties encountered
169 during the polymerization reaction process during synthesis. This technique was an inspiration for
170 numerous subsequent works. As suggested in recent literature, in most cases, the acid is dissolved in a
171 given volume of deionized water and gradually mixed with an aqueous solution of furfuryl alcohol (FA)
172 in a given weight ratio with vigorous stirring. The mixture is heated to the FA-water azeotrope
173 temperature for some time. Thereafter, the reaction mixture is cooled, and the pH is neutralized by the
174 addition of an alkali such as sodium hydroxide (NaOH). The resulting emulsion mixture is broken by a
175 saturated salt solution such as sodium chloride (NaCl) and then separated to remove the aqueous phase
176 and water. It is worth noting that the choice of processing time and temperature depends on the type of
177 acid used. Beyond the synthesis of the PFA resin for reinforced composites, studies have shown its
178 advancement for other advanced applications such as, resin modification [13,51,78–80], a precursor
179 for various materials including polymeric carbon beads used as adsorbent for volatile organic
180 compounds [81], carbon membranes for separation and purification applications [45], and as a
181 nanocomposites for sodium-ion battery cathode material [82]. In addition to the viscous liquid form,
182 Polyfurfuryl Alcohol PFA resin has also been synthesized as powder, flakes, film, and nanospheres
183 [81].

184 **2.2 Structure and Chemistry of Polyfurfuryl Alcohol Resin.**

185 A good amount of research has been done using various analytical techniques to understand the
186 polymerization chemistry involved in the synthesis and curing of PFA resin. The molecular structural
187 arrangement of the PFA resin contributes significantly to physical properties such as viscosity, bonding
188 (interaction), and thus to its processing (resinification, prepreg, and curing) and thermomechanical
189 properties, especially in fibre-reinforced applications. In fact, the mechanism of deepening and red-

190 shifting colour formation of the resin was suggested by Choura et al. [83] to involve a series of events
 191 of enhanced conjugation caused by linear condensations that produce oligomers that can undergo
 192 hydride-ion exchanges with the protonated chain ends of growing species, yielding methyl-terminated
 193 oligomers and carbenium ions in which the positive charge is shared by a methyne carbon atom and
 194 two adjacent furan rings. Despite initial assumptions that the exact molecular structure is difficult to
 195 determine due to the rapid three-dimensional crosslinking during polymerization [84], many studies
 196 have been conducted in an attempt to elucidate the molecular chemistry of the crosslinking mechanism.
 197 Tondi et al in [85] detailed a review of various scientific studies suggesting that the molecular structure
 198 arrangement be linear, ring-opening, α , β -unsaturated γ -lactons, Methylene bridge, conjugated or Diels-
 199 Alder. They further suggested a mechanism that encompasses the ring opening of some furanic rings,
 200 producing a double bond that promptly combines with the linear PFA to produce structure through
 201 Diels-Alder crosslinking, as shown in Figure 3.



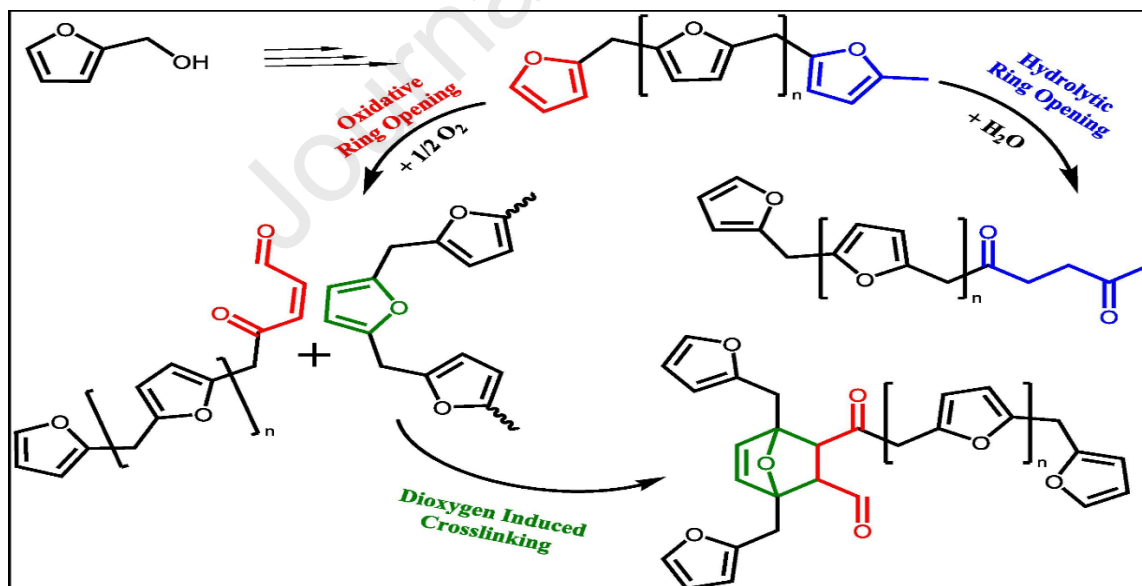
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203 **Figure 3.** Diels-Alder crosslinking reaction between linear and ring opened PFA structures [85].

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

207 Overall, the consensus remains that the cure chemistry of its thermoset nature indicates that the
 208 crosslinking mechanism, which occurs as a function of time and temperature, is a product of
 209 polymerization and primarily consists of two steps. The first consists of linear oligomer formation
 210 through polycondensation and the other composition of a structural network of ring-opening and Diels

211 arrangements leading to high branching density [48,87–89]. This was corroborated by Joshua et al, in
 212 [90] who found that Diels-Alder crosslinking and branching were prevalent in the polymerization of
 213 PFA resin. He attributed a significant influence on the viscosity of the resin to the chain-branching
 214 mechanism. These reactions explain the high crosslink density of PFA resin [19]. Recent studies by
 215 Delliere and Guigo [91,92] offer insight into functionalities provided by the side ring opening reaction
 216 that occurs during polymerization, which results in the formation of carbonyl moieties, and used to
 217 generate tough and ductile materials via the creation of Schiff-based macromolecular architectures,
 218 introducing the concept of degree of open structure (DOS). As a proof of concept, they reacted a flexible
 219 biobased amine (Priamine 1071) with the carbonyls of PFA resins to form Schiff bases and observed it
 220 is possible to change the macroscopic mechanical behaviour of the PFA, passing from a brittle material
 221 to a progressively more ductile material by increasing the stoichiometric ratio of amine. In a related
 222 study [93], they observed that the furan ring-opening process occurs predominantly on the terminal
 223 furans of PFA macromolecular chains. They also proposed two pathways for the opening of the furan
 224 ring, as shown in Figure 4.



225

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

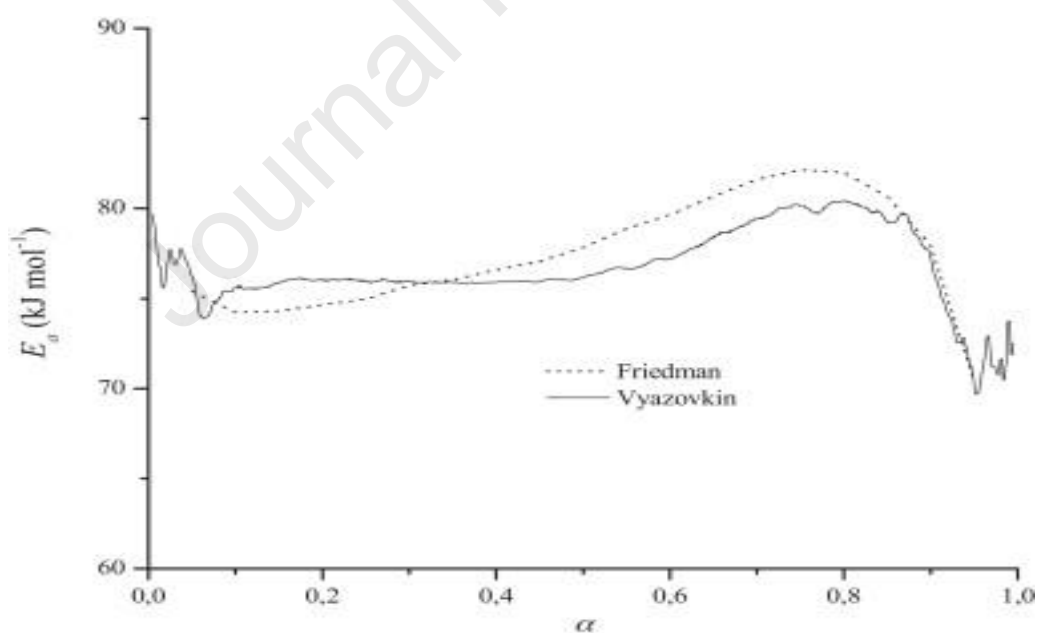
227 The first being a hydrolytic ring opening that produces levulinic-like species, while the second is an
 228 oxidative furan ring opening that produces conjugated aldehydes. With the latter being responsible for

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

244 **2.3 Cure kinetics Polyfurfuryl Alcohol Resins in Fibre-reinforced Application.**

245 Efficient processing of the bio-based PFA resin for various applications requires knowledge of
246 its processing conditions (curing temperatures, time and pressure). Therefore, the essence of
247 understanding its cure behaviour cannot be overstated. Researchers have employed various techniques
248 to understand the cure behaviour and evaluate the kinetics of PFA resin from different perspectives. For
249 example, Domínguez and Madsen [98] reported on the study of the PFA resin in which they employed
250 the model free kinetics method to study the curing process of the resin under vary amount of catalyst.
251 In their further research work, they [99] reported the determination of the gel point of the PFA resin by
252 rheological isothermal tests at different curing temperatures where they observed a reduction in the rate
253 of viscosity change when compared to the rate of viscosity change during the pre-gel stage. This
254 observation was further researched upon as the resin's rheological and chemorheological behaviour was
255 studied at pre-gel stage and reported in [14]. The study recorded the flow activation energy of the PFA

256 resin to be $63.396 \text{ kJ}\cdot\text{mol}^{-1}$ as calculated by Arrhenius model and found the flow activation energy to
 257 increases with a corresponding increase in the amount of catalyst. However, despite documenting a
 258 curing activation energy of $96 \text{ kJ}\cdot\text{mol}^{-1}$, they found no catalytic dependence on the curing activation
 259 energy. A related research by Domínguez et.al. [100] developed a new exponential model to study the
 260 chemorheological behaviour of bio-based polyfurfuryl alcohol (PFA) resin during the post-gel curing
 261 stage. The complete curing and polymerization complexity of the resin was also studied using
 262 chemorheological and isoconversional analysis by Guigo et al [101]. Vargas Scheubner and Guthausen
 263 [102] studied the polymerization of the resin through the influence of nanoparticles on the curing
 264 reaction kinetics. Further studies on the kinetics of the resin were carried out by Lopez De Vergara et
 265 al. [103] using a chemical characterization method to understand the mechanism responsible for the
 266 main reactions of the resins during curing. They observed that the Friedman and Vyazovkin
 267 isoconversional method yielded a similar curve profile as shown in Figure 5, the evolution of activation
 268 energy with the degree of conversion as the curing process progressed.



269

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

272 Sadler et al. [90] detailed the resin polymerization reactions and kinetics of the study from a
 273 molecular structure viewpoint. Regarding the manufacturing process, Imani and co-worker [104] and

274 [105] investigated its reaction kinetics to determine the resin's pot and shelf life, respectively.
275 Additional attempts have been made to characterize the PFA resin through kinetic studies by varying
276 catalyst type, quantity and filler effect [19] and [106]. Recent studies by Kemppainen *et al.* [107],
277 employed the use of reactive molecular dynamics (MD) modelling techniques to model the
278 polymerization of the PFA resin as well as to predict its mechanical properties. They found the predicted
279 mechanical properties of the polymerized resin to agree with the literature values. The outcome of such
280 studies has provided industrial manufacturers with the fundamentals of a window for selecting
281 parameters suitable for using the selected manufacturing process cycle in various applications,
282 including fibre reinforced composites. Despite the successes, it is worth noting that all previous research
283 studies were performed using synthesized neat resin alone, leaving the kinetic studies of fibre-reinforced
284 Polyfurfuryl alcohol-based prepreg largely unexplored. In this regards, our recent research [108]
285 addresses the gap in knowledge by providing an explanation of the curing mechanisms and
286 demonstrating the use of model-free kinetics to study the cure mechanism of biobased glass/PFA
287 prepreg. Our study determined the average activation energy for the cure reaction of the biobased
288 glass/polyfurfuryl prepreg to be 88.9 ± 4.9 kJ/mol. By utilizing validated models, we were able to
289 optimize the cure cycle for rapid curing under fills the gap and provides explanation of curing
290 mechanisms as well as demonstrates the use of model free kinetics to study the cure mechanism of the
291 biobased glass/PFA prepreg.

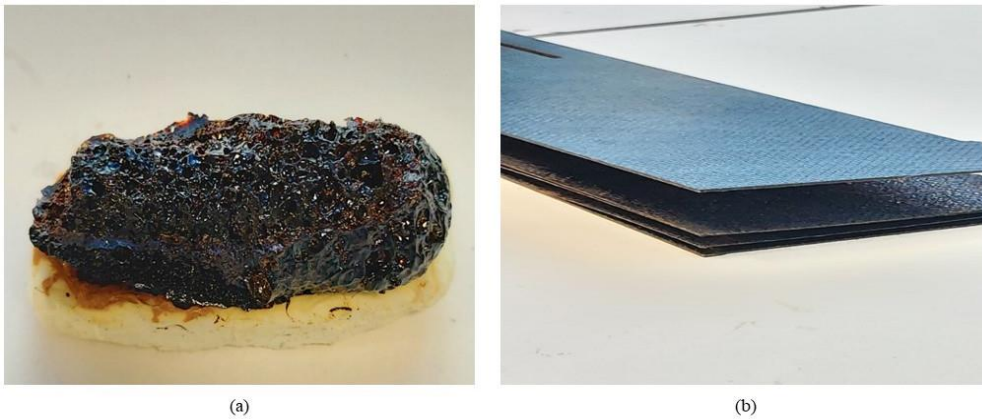
292 **2.4 Polyfurfuryl Alcohol Resin Processing and Fibre reinforced PFA Composites Manufacture.**

293 With the resin processing condition window determined via various kinetic methods, the
294 processing and manufacturing of fibre reinforced PFA composites with different manufacturing
295 processes is made possible. Conventional manufacturing techniques such as hand layup, autoclave
296 processing, resin transfer moulding (RTM), microwave processing and compression moulding are some
297 of the commonly used techniques in the manufacture of fibre reinforced PFA composites. Several types
298 of fibre have reportedly been used as reinforcements in the manufacture of PFA based composites. For
299 example, conventional fibre like glass fibre was used in the manufacture of PFA based composite for
300 comparative property studies with fibre reinforced phenolic composites by authors [15,50,109]. Natural

301 fibres such as abaca, flax, basalt, rayon and jute have also been reported as reinforcement for PFA based
302 composites for various investigative and comparative research studies [110–113]. PFA based materials,
303 like other thermosetting matrices for composites, requires a careful control of processing conditions to
304 monitor the viscosity achieved in the final composite, which is highly dependent on temperature and
305 polymer structure. Fibre wettability, bubble formation and growth, and composite consolidation are all
306 affected by the continuous transition of resin from a low-viscosity liquid monomer at the start to a solid
307 polymer at the end of the phase [114].

308 **2.4.1 Polyfurfuryl Alcohol Resin and Laminate Curing.**

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



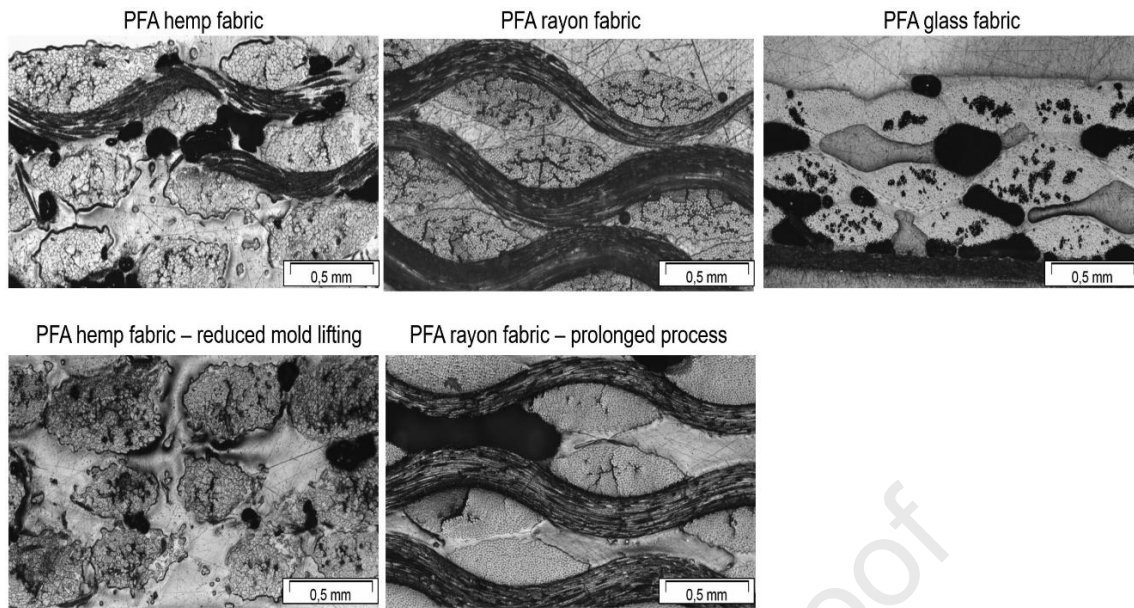
324

(a)

(b)

325 **Figure 6.** PFA laminate curing. (a) Bubble defects of an improperly cured PFA resin, (b) delamination
326 of an improperly cured PFA Prepreg.

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



339

340 **Figure 7.** Micrographs of PFA composites produced from fabric [119]

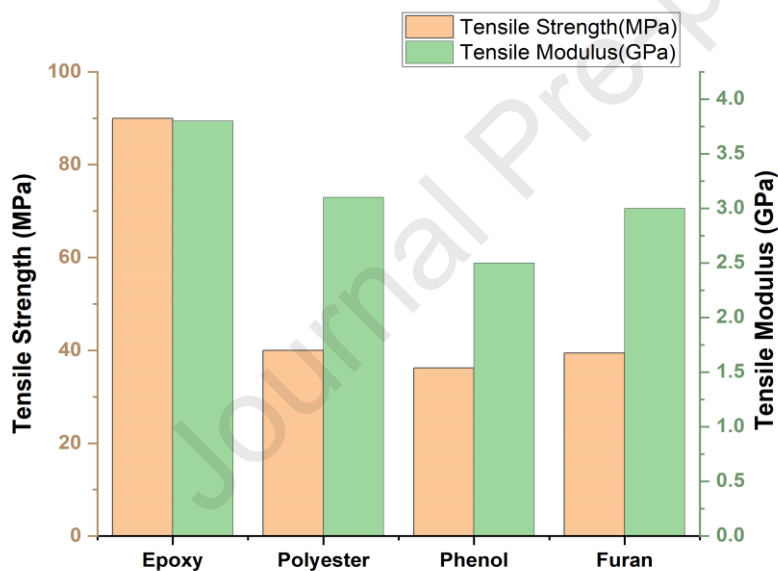
341 They discovered that the overall level of porosity is influenced by the water absorbance capacity of the
 342 reinforcing fibre and the effective transfer of water from the resin to the fibre, including the single fibre
 343 wetting and textile architecture. This revelation underscores how the hydrophilicity of natural fibres
 344 improves the processing and manufacturing of high-performance PFA composites. The study concludes
 345 that the porosity and morphology of PFA composites are more significantly influenced by material
 346 composition than by processing time and process control. Overall, a review of major studies reveals the
 347 cure processing temperature could range from 20°C to 180°C, and cure duration between 1 hour – 96
 348 hours, regardless of the manufacturing method employed [110,117,120–122].The lengthy
 349 manufacturing process cycle has been a significant drawback that has limited the industrial scaling up
 350 of its use for applications. Hence, the motivation for our previous research work [108] where we
 351 employed cure kinetic model to optimized the manufacturing cure cycle of a glass/prepreg leading to a
 352 50% reduction in curing time.

353 **3. Review of Properties of Polyfurfuryl Alcohol reinforced composite.**

354 **3.1 Mechanical Properties.**

355 The mechanical properties of PFA resin and its reinforced composites depend on the
 356 configuration of several factors. Some of these factors include curing conditions and parameters,

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

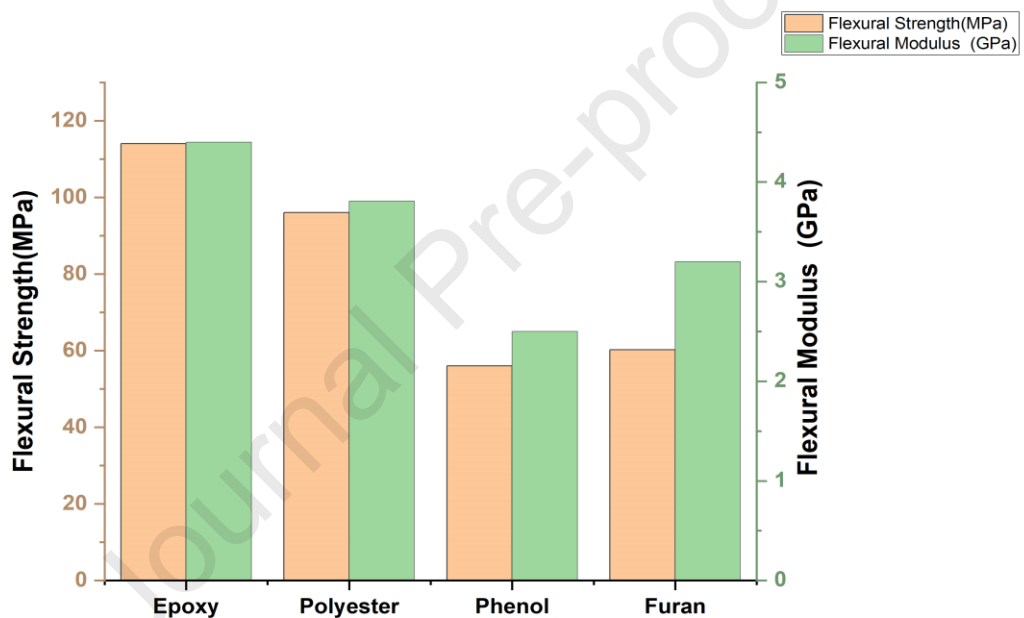


367

368 **Figure 8.** Tensile properties comparison between PFA resin and conventional resins. Data adapted from
 369 [124]

370 In the study of renewable resource green blends from PFA and lignin, Deka et al. [116]
 371 reported the flexural strength and modulus of the pristine resin to be 23 MPa and 1.9 GPa, respectively,
 372 while recording 15 Jm^{-2} as the impact strength found using the Izod test. The study found the effect of
 373 blending improved the properties of flexural strength, storage modulus, and glass transition

374 significantly. Similarly, Wang et al [125] documented 38.05 MPa, 2.2 GPa, and 2.50 kJ/m² as the
 375 respective values for the flexural strengths, flexural modulus, and impact energy of the neat PFA resin.
 376 They found the impact strengths, flexural strengths and moduli of a cured blend of furfuryl
 377 alcohol/epoxy/methyl-tetrahydro-phthalic anhydride blends with different ratios were found superior to
 378 the neat cured PFA resin [125,126]. A comparison of the PFA resin to conventional resins such as
 379 epoxies, polyester, and phenolics across literature as shown in Figure 9 reveals, the PFA resin exhibits
 380 comparable flexural properties enabling it to withstand substantial amount of bending stresses while
 381 maintaining structural integrity.

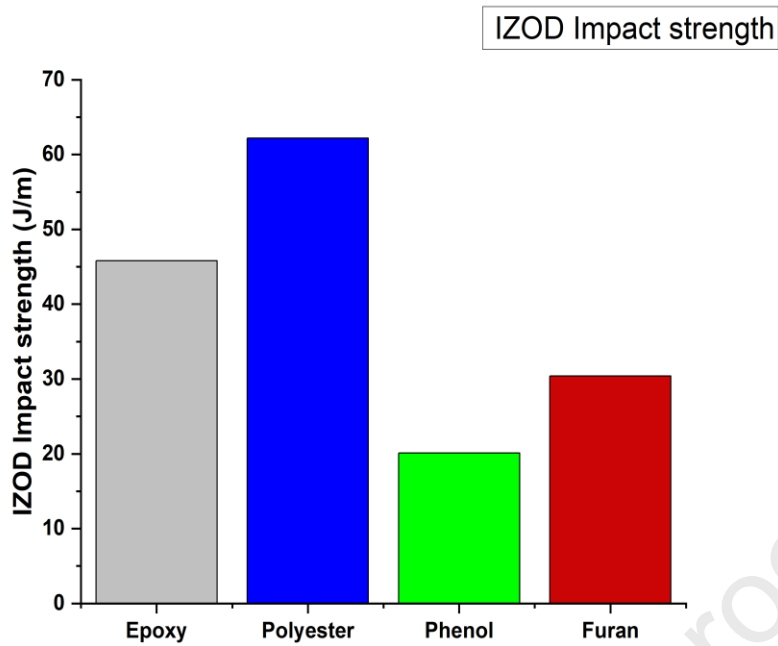


382

383 **Figure 9.** Flexural properties comparison between PFA resin and conventional resins. Data adapted from
 384 [113,127,128]

385 The addition of fibre reinforcement has proven to improve the mechanical properties of the PFA-based
 386 composite. For instance, Sharib et al. [122] found that incorporating 0.5% polylactic acid (PLA) fabric
 387 into PFA resin resulted in increase in tensile strength from 11.2 ± 1.1 MPa to 33.2 ± 3.5 MPa.
 388 Conversely, this addition caused a reduction in flexural strength, although the flexural modulus
 389 increased from 1.96 GPa to 3.37 GPa for the same weight percentage of PLA fabric in the PFA resin.
 390 Another study investigating the impact of alkali treatment on polyfurfuryl alcohol–flax fibre composites

391 [129] reported a 10% enhancement in flexural strength and modulus for flax fibre treated with 1.5%
392 and 2% NaOH in comparison to the cured pristine PFA resin. They attributed this to the bonding effect
393 of the fibre reinforcement with the matrix. In related a work on agave and sisal fibre - reinforced
394 polyfurfuryl alcohol composites belonging to the family of natural fibres by Motaung et al [130] sisal
395 and agave fibres were found to also improve the mechanical and thermal properties of the neat PFA
396 resin. They observed improvement in flexural strength of the natural fibre-reinforced composites which
397 also was attributed to the effective impregnation of the PFA matrix into the fibre enhancing the
398 interfacial bond strength. In addition, both fibre-reinforced composites were found to display quite
399 comparable thermo-mechanical properties. Similarly, studies on cork reinforced PFA composites were
400 investigated by comparing cork powder and cork granules, as observed by char et al. [131] where the
401 observed improvements in the thermomechanical and mechanical properties were attributed to good
402 adhesion between the PFA and the cork cells. Strong adhesion between fibres and the polymer matrix
403 is known to enhance impact resistance and toughness through several mechanisms in a composite
404 laminate. Although cured furan PFA resin itself is inherently brittle due to its highly crosslinked
405 structure, it has been shown to exhibit impact strength comparable to conventional resins. For instance,
406 Figure 10 presents a comparison across the literature of the Izod impact strength values of neat PFA
407 resin versus traditional epoxy, polyester, and phenolic systems. The PFA resin shows impact strengths
408 lower than the epoxy and polyester resins but higher than the phenolic resin.



409

410 **Figure 10.** Impact strength comparison between PFA resin and conventional resins. Data adapted from
 411 [132–135]

412 The impact behaviour of the hemp shives PFA based composites was also studied by Pernevan et al.
 413 [136], wherein they observed 3.47 and 4.42 kJ/m² as the Charpy impact strengths values for the hemp
 414 shives PFA based composites with 20% straw lignin and 20% flax lignin, respectively.

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

425 Table1. Mechanical properties of different fibre reinforced Polyfurfuryl Alcohol composites documented in the literature. VARTM = Vacuum-assisted resin
 426 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 140mins, 50°C for 45mins and 80°C for 45mins,80°C for ~18hrs (Post cure)	68 (%wt)	93 ± 8	7.2 ± 1.0	-	-	-	[109]
Flax Prepreg	VB	150°C for 15mins	60 (%wt)	64 ± 9.5	8.5 ± 0.8	-	-	-	[109]
2x2 Twill Flax Prepreg	VM	150°C for 20mins (5°C/min ramp)	-	34.9±1.84	6 ± 0.47	-	-	-	[138]
UD Flax	VM	150°C for 20mins (5°C/min ramp)	-	59 ± 4.3	10 ± 0.8	-	-	-	[138]
UD Flax Prepreg	CM	140°C for 20mins (5°C/min ramp)	-	211 ± 24	25.6 ± 1.9	-	-	-	[138]
2x2 Twill Flax Prepreg	CM	140°C for 20mins (5°C/min ramp)	-	69 ± 3	10.4 ± 0.4	-	-	-	[138]
Chopped Strand Mat Glass Fabric	VM	20°C for 150mins 50°C for 45mins 80°C for45 mins	44 (%wt)	103	7.7	4.7	110	-	[111]
Non-woven Mat Hemp	VM	150°C for 15mins	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 12h 50°C for 8h and 150°C for 7.8mins	73 (%vol)	324 ± 26	27.0 ± 0.6	-	-	39.7± 6.2	[139]

Glass non-crimp Fabric (± 45)	HL/CM	Room temperature for 12h 50°C for 8h and 150°C for 7.8mins	73 (%vol)	55.0 \pm 5	11.5 \pm 1.4	-	-	39.5 \pm 2.2	[139]
Flax non-crimp Fabric (0/90)	HL/CM	Room temperature for 12h 50°C for 8h and 150°C for 7.8mins	53 (%vol)	70 \pm 3	13.0 \pm 0.3	-	-	16.6 \pm 1.4	[139]
Flax non-crimp Fabric (± 45)	HL/CM	Room temperature for 12h 50°C for 8h and 150°C for 7.8mins	53 (%vol)	46 \pm 5	7.7 \pm 0.5	-	-	9.8 \pm 2.3	[139]
Flax non-woven Fabric	HL/CM	Room temperature for 12h 50°C for 8h and 150°C for 7.8mins	52 (%vol)	48 \pm 7	9.0 \pm 0.6	-	-	7.1 \pm 0.9	[139]
Kenaf Fibre	HL/CM	50-55°C for 30mins 60°C for 4h 80°C for 4h 100C for 1h (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	VART M	60°C at 4h (1°C/min ramp) 95°C for 4h (Post Cure)	31.5 (% vol)	41	5.6	~ 7	~ 80	~ 80	[123]
Glass Fabric	VART M	60°C at 4h (1°C/min ramp) 95°C for 4h (Post Cure)	44.6 (%vol)	850	36.5	~ 30	~ 850	~ 350	[123]
Woven Flax & Polyester Prepreg	CM	150°C for 7mins	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 12h 60°C for 12h 80°C for 6h. 110°C for 1h (Post Cure)	64 (%wt)	121	5.58	5.91	87.4	-	[110]

Rayon (Cordenka)	CM	40°C for 12h 60°C for 12h 80°C for 6h. 110°C for 1h (Post Cure)	51 (%wt)	77.2	4.32	6.96	95.4	-	[110]
Rayon (Cordenka)	CM	40°C for 12h 60°C for 12h 80°C for 6h. 110°C for 1h (Post Cure)	75 (%wt)	86.6	4.78	3.12	48.8	-	[110]
Plain weave Glass Fabric	CM	170 °C for 40mins	20-25(%wt)	-	-	-	267	24	[50]
UD Glass Fabric	HL	7 days	66.4 (% wt)	-	-	-	39.2	-	[89]
UD Carbon Fabric	HL	2 Weeks 3h Post cure	-	860 ± 110	93 ± 6	-	-	-	[142]
Basalt Fabric	HL/CM	80°C for 8h & 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 24h 100C for 24h (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]

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

443 So far, the mechanical properties of the PFA and its reinforced composite have only been
444 discussed in terms of their tensile, flexural, and impact capabilities. This is because other mechanical
445 properties like fracture toughness, off-axis, shear, and creep properties lack or have extremely little data
446 in the scientific literature. In spite of these limitations, attempts have been made to study other related
447 mechanical properties of fibre reinforced PFA composites, such as fatigue and load bearing behaviour.
448 Mak and Fam [145] published the results of a comparison study comparing the carbon/PFA resin and
449 carbon epoxy composites in terms of their fatigue life and stiffness degradation. Under quasi-tension
450 loading, they observed a 24% drop in strength and identical stiffness to that of carbon fibre reinforced
451 epoxy composite. Applying the Whitworth phenomenological model, the stiffness retention at the end
452 of life (2,000,000 cycles) was predicted to be 80% for epoxy-based CFRP and 65% for PFA-based
453 CFRP. Giannis et al. [109] also conducted fastener pull-through and bearing strength tests between

454 glass/polyester and glass /PFA, where they discovered no significant difference between the two
455 materials in terms of pull through load.

456 **3.2 Thermal Properties**

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

468 Guigo et al. [17] in a comparative study with a PFA Silica hybrid discovered that the
469 degradation of the resin involved several steps beginning with the chain scission at over 200°C. This
470 allows for the weakening of the chemical bonds leading to second and third decomposition steps that
471 occur at about 320°C. The thermal decomposition temperature, which corresponds to the 10% weight
472 loss was around 340°C. In a related study of the thermo-oxidative degradation of the Polyfurfuryl
473 Alcohol /plasticized lignin blend [147], it was found that the neat PFA exhibited better thermal stability
474 compared to the blend. It was found that the thermal stability of the PFA decreased with increasing
475 lignin content. Menager et al. [131] in agreement with other authors [74,88] confirmed a multi-step
476 degradation process of the PFA resin with a corresponding degradation temperature of 10% weight loss
477 is about 378 °C. Recently, a characterization study by Ma et al. [120] also found that the thermal stability
478 of PFA resin is improved with increasing modified hollow glass microsphere (HGM) content (0% to
479 20%) . The mass residual rate was also reported to have increased from 53% to 64.4%. For fibre-
480 reinforced PFA-based composites, their degradation behaviour has been compared to some

481 conventional composites. The degradation behaviour of the glass/PFA composite was reported to be
482 comparable with that of a glass/phenolic composite in a study by Ipakchi et al. [15]. Their study revealed
483 char yields of up to 77-85% for PFA samples measured at 800°C. For natural fibres such as kenaf bio
484 fibre, the degradation pattern has been reported to show a four-stage degradation pattern. The green
485 composite (kenaf/PFA) showed the same decomposition onset temperature as the neat PFA resin,
486 however, the maximum decomposition rate decreased from 468°C to 458°C with increasing fibre
487 content and a 45% retention of char residue. The decrease was attributed to an increase in the thermally
488 unstable non-cellulosic structure of the fibre composite [140]. Similarly, in [110], Talent and Wang
489 reported a 7% mass loss at 200°C in a study that addressed the thermal degradation of a unidirectional
490 Cordenka rayon/PFA composite. At a temperature of 275°C, the composite showed rapid mass loss
491 attributed to the degradation of the cellulosic structures of the unidirectional cordenka rayon (CR)
492 fibres. The degradation effect worsened as the per cent fibre weight in the composite increased.

493 **3.3 Water Absorption**

494 It is known that water absorption affects the physical, mechanical, and thermal properties of
495 fibre-reinforced composites [148,149]. For composite applications where exposure to the atmosphere
496 or wet conditions is required, evaluation of this property is very important. The PFA resin is known to
497 be inherently hydrophobic [41,102,130] and therefore, it can be expected to result in increased water
498 resistance of its composite. Menager et al. [131] noted this in their work on green composites with cork
499 residues, where they discovered that the hydrophobicity of PFA composites increases with a
500 corresponding increase in PFA content. The resin was also found to improve the moisture resistance of
501 the treated flax fibre in a study by Jia and Fiedler [53]. The study found that treated flax fibre absorbed
502 only 1.389% of its original weight in water over 10 days. Similarly, Pohl et al. [139] found that the non-
503 hygroscopic behaviour of glass/PFA composite explained its low water absorption rate of 2.4% after 72
504 hours compared to the high absorption rates of 21% and 36% observed for non-crimp flax/PFA and
505 non-woven flax/PFA, respectively. They proposed that the significant difference in water absorption
506 between flax-based composites is attributed to the swelling effect of fiber configuration. In a related
507 study on green composites [140], Deka et al. reported that the water uptake of the pure PFA resin at

508 saturation is 1.12%. Furthermore, Motaung et al. [118] found that the agave-reinforced PFA composite
509 absorbed more water than the sisal-reinforced PFA composite in their comparative investigation of
510 natural fibre reinforced polyfurfuryl alcohol composites. They attributed this to the reinforcement's
511 hemicellulose concentration level. Similarly, Foruzanmehr et al. [89] found the absorption rate of the
512 Glass reinforced bio-sourced furan composites to be 3.35 times higher than the Petro-based Glass/epoxy
513 composite. At saturation, moisture absorption was found to be higher in Glass reinforced bio-sourced
514 furan composites. However, they attributed this to the high porosity level of the glass/PFA. The effect
515 of which was evident in their interlaminar shear property, which showed a 13.1% increase in favour of
516 petro-based Glass/epoxy composite after 90 days. Relatedly, Sangregorio et al. [143] reported no
517 increase in mass of Jute/PFA over eight hours in their work, whereas a 25% increase in mass was
518 observed for Jute/Humins composite after half an hour attributing this to the low porosity level in the
519 PFA based composite in comparison to the humins-based composite.

520 Beyond investigating the water absorption behaviour of PFA-based composites, the evaluation
521 of their absorption behaviour in other fluids has also been studied. Giannis et al. [109] investigated and
522 compared the absorption behaviour of glass/PFA and flax/PFA composites to glass reinforced polyester
523 composites in various fluids such as motor oil, hydraulic oil, diesel oil, antifreeze, windscreen wash,
524 pesticide, and distilled water. The study observed that the glass reinforced polyester composites
525 exhibited the lowest absorption rate with less than 1% in most cases while both cases of the PFA-based
526 composite were reported to absorb a significant amount of fluids, with the Flax/PFA absorbing the most.
527 Additionally, they discovered that fluid immersion affected the surface properties of the glass reinforced
528 polyester composites and glass/PFA samples, resulting in a decrease in Barcol hardness. They also
529 evaluated the tensile properties of several composites following immersion in various fluids and found
530 that stiffness and strength decreased in all of the composites, with the effect of fluid exposure being
531 more detrimental on the Flax/PFA composites than on others. Relatedly, Eldridge and Fam [141]
532 conducted a study on the environmental aging effect on tensile properties of glass reinforced PFA
533 composite in comparison to glass reinforced epoxy composite. The study found that the glass-
534 reinforced PFA composite was more susceptible to salt water because it retained 80, 44, and 39% of its

535 original strength at 23°C, 40°C, and 55°C on exposure to water with a 3% salt concentration for up to
536 300 days, whereas the glass-reinforced epoxy composite retained 86, 72, and 61% of its strength under
537 the same temperatures and exposure conditions. Similarly, Mcswiggan and Fam [142] reported a
538 comparative research of the tensile property retention of aged carbon fibre reinforced PFA composites,
539 conventional carbon fibre reinforced epoxy, and carbon fibre reinforced epoxidized pine oil composite.
540 They recorded a tensile strength retention of 83, 81, and 82% for carbon fibre reinforced PFA
541 composites at 23°C, 40°C, and 50°C, respectively, after 240 days of exposure to salt water, compared
542 to 101, 90, and 95% for carbon fibre reinforced epoxy at the same temperature and exposure.

543 **3.4 Fire, Smoke and Toxicity Properties**

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

562 other authors have documented the fire, smoke, and toxicity (FST) performance of the PFA resin and
563 its reinforced composite in comparison to related composite materials. Table 2 below details some of
564 the results documented in the literature.

Journal Pre-proof

565 Table 3. 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/m²)	Peak of heat release rate (PHRR) (kW/m²)	Total smoke released (TSR) (m²/m²)	Maximum Average Rate of Heat Emission (MARHE) (KW/m²)	Specific extinction area (m²/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			36.8	19.8	[117]
Neat PFA resin	Cone calorimetry	98	30.9	682	15.3	154			[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]

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4. Applications Of Fibre Reinforced Polyfurfuryl Alcohol Composites

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The application of fibre reinforced PFA composites in various 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-minute 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.



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Figure 11. Examples of different fibre reinforced PFA based composite developed for applications (Images courtesy Cordis EU Research [153] and [154])

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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

587 rail industry, UK-based TRB Lightweight Structures Ltd. has developed and produced a railway
588 carriage carbon reinforced polymer (CFRP) sandwich panel door appropriate for subterranean rail
589 applications utilising a carbon fibre/PFA prepreg and recycled foam [155]. Bercella S.R.L., Element
590 Materials Technology, and Composite Evolution Ltd. collaborated on a project that saw the usage of
591 biobased fibre reinforced PFA composite for manufacturing cantilever seat supports that are positioned
592 on the wall of a train carriage rather than the floor [154].

593 **5. Concluding remarks**

594 This article has presented an extensive review of the PFA resin and its fibre-reinforced
595 composites. A review of existing studies on resin structure, chemistry, and cure kinetics was highlighted
596 and the fabrication of its reinforced composite was discussed, detailing the key challenges during the
597 curing process as well as some mitigation techniques found in the literature. In addition, the mechanical
598 and thermal properties of the resin and its common fibre-reinforced composites were reviewed,
599 highlighting that its mechanical properties are comparable to those of conventional matrices and their
600 composites, as posited by literature. Regardless of the fibre/PFA configuration, it is evident from the
601 review that the mechanical properties of the various composites are highly dependent on factors such
602 as curing conditions and parameters, manufacturing process, fibre type, fibre orientation, shape type
603 (fabric or fibre), and matrix modification, among others. The review also noted the excellent thermal
604 stability and fire response of PFA resin and its composites. Despite the thermal benefits and structural
605 potentials of reinforced PFA composites, it is clear from the literature that the major drawback of a
606 lengthy manufacturing process cycle has often prevented the industrial scaling up of their use for
607 applications. Therefore, there is a need for researchers to develop applicable techniques to aid in the
608 reduction of manufacturing process time without any detrimental effect on its mechanical or thermal
609 properties. Diverse techniques have been successfully employed to achieve a similar goal with
610 conventional resin and its composites. However, with the PFA resin and its composites, these same
611 techniques are directly inapplicable due to their unique curing nature. As a result, it does require an
612 adequate research study of its curing mechanism to enable process optimization for rapid
613 manufacturing. Despite the positives of biobased PFA resins, there is still much to be desired in some

614 key areas of research. These include the need to expand the research of its sustainability to include a
615 documented, data driven complete life cycle analysis from production to end of life. Also, from the
616 mechanical property standpoint, a lot more research is desired in evaluating its mechanical properties,
617 such as compressive properties, fracture toughness, shear properties, creep behaviour, and impact
618 damage analysis, as these properties of the PFA and its composites are still lacking. This review
619 highlights that the bio-based sustainable PFA composites are set to be an adequate replacement of
620 traditional petroleum based thermoset composites in many applications and this review provides the
621 researchers and manufacturers with a consolidated reference resource for future developmental
622 activities.

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Highlights

- For biobased PFA and fibre reinforced PFA composites:
- Established the state of the art in synthesis, cure kinetics and manufacturing.
- Explained the limits of mechanical, thermal and moisture absorption properties.
- Provided guidance for applications and research direction for improvements.

Journal Pre-proof

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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