A Review on Epoxy and Polyester Based Polymer Concrete and Exploration of Polyfurfuryl Alcohol as Polymer Concrete

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1. Introduction

Polymer concrete is monomers that are polymerized in situ in presence of other components. In situ polymerization takes place by heat, catalysts, or radiation. Monomer when polymerized can be used as the binder component and that does not require water to set or harden. Polymer concrete comprises polymeric binder, hardener, and the aggregate. The interactions among these components depend entirely on the chemical and physical reactions. Since late 70s, epoxy and acrylic polymer concrete have been used to replace traditional materials due to rapid curing and excellent bond to cement concrete [1–3]. Saljé et al. reported the comparative properties of machine tools prepared from polymer concrete and iron metal [4]. Due to high mechanical properties, there are reports on the use of polymer concrete components in machine tool [5, 6]. Methyl methacrylate, unsaturated polyester resin, epoxy resins, furan resins, polystyrene resins, urea formaldehyde resin, and blends of polyester/styrene are commonly explored as polymer concrete systems [7, 8]. The advantages of using polymeric resin are that it possesses high mechanical strengths, long durability, and resistance to chemical attack [9].

Polymer-impregnated concrete is another type of polymer concrete in which the hydraulic binder is totally substituted with a polymeric material. In polymer-impregnated concrete, the monomer penetrates the concrete matrix to a finite depth. Yet another category is polymer cement concrete which is a mixture of conventional hydraulic cement concrete and high molecular weight polymers. Polystyrene, polyacrylic, polyvinyl chloride, styrene-butadiene, and polyvinylidene chloride are the polymers that have been explored as polymer cement concrete. Based on the above introductory paragraph, it can be stated that polymer concrete differs from typical Portland cement concrete, polymer cement concrete, and polymer-impregnated concrete. Polymer cement concrete is extensively used as repair material.

The performances of polymeric concrete depend on different factors such as polymer properties, type of fillers and aggregates, curing temperature, and components dosage. The choice of particular type of resin depends upon factors like cost, desired properties, and chemical/weather resistance.
Curing temperature is related to thermoset resins which can be used as polymer concrete and there are several literatures available on curing temperature of thermoset polymers in the Journals of Polymer Chemistry and Material Chemistry.

Aggregates and fillers constitute about 75–80% volume of polymer concrete. The aggregates are normally inert in nature and can be dispersed throughout the polymer matrix. Based on dimensions, aggregates can be coarse aggregates (comprising material of more than 5 mm size) and fine aggregates (having size less than 5 mm). The aggregates used in polymeric concrete can be silicates [10], recycled polyethylene terephthalate [11], waste crushed stone, quartz, gravel, limestone, calcareous, granite, clay, and so forth [12]. The use of aggregates and fillers in natural fibre reinforced epoxy composites has been documented [13, 14]. In addition, there are reports related to the use of recycled concrete aggregates (RCA) [15]. RCA are available after demolition of old roads and buildings and if these are not used in proper way they are considered as waste. Near the aggregate, the filler is very important. Fillers are added to reduce the void content in aggregate mixture and thereby increase the strength of polymer concrete. Different types of fine materials can be used as fillers and they can be fly ash, silica fume, phosphogypsum, cinder, and so forth [16, 17]. The microfiller is fine powder with a particle size less than 80 microns so microfiller is slightly different from filler in terms of size.

Fly ash, a by-product of the coal burning in power plants, is used as filler because of its easy availability. Its usage in polymer concrete is reported to yield better mechanical properties as well as reduced water absorption. Addition of fly ash also improves the workability of fresh polymer concrete mix resulting in products with excellent surface finish [18]. It has been reported that for the fabrication of polymer concrete with fine aggregate one has to use higher cement dosage one. This is attributed to the large surface area of these materials [19–21]. Rebiz et al. reported the fabrication of polymer concrete by incorporating fly ash [22, 23]. It has been recommended by various researchers that the moisture content of the aggregate should not exceed from 0.1% to 0.5% for better mechanical properties in polymer concrete [24, 25].

In addition to the coarse and fine aggregates, microfillers as discussed above are added to the polymer concrete system mainly with an aim to fill the microvoids. Polymer concrete can also be reinforced with different kinds of synthetic and natural fibres for improving its mechanical properties [26]. A series of polymer concrete of different compositions using an optimized aggregate mix proportion having least void content is reported on the basis of mixture design concept of design of experiments [27].

Unsaturated polyester resins and epoxy resins are the most commonly used resin systems for polymer concrete because of their low cost, easy availability, and good mechanical properties [28]. The epoxy concrete has better properties than polyester concrete, but the properties of polyester concrete can be enhanced up to the same level by addition of microfillers [29]. Phenolic resin as polymer cement concrete is widely used. However, we are not discussing phenolic resin based concrete in this review paper. Furan resins are used as polymer concrete to a great extent in European countries [30]. But there are very little reports on the use of virgin or reinforced polyfurfuryl alcohol (PFA) as polymer concrete. This is attributed to the fact that the curing reactions of PFA from furfuryl alcohol are highly explosive in nature. But with a focus on biopolymer or bioresin in 21st century, it is important to rethink on the use of PFA as polymer concrete by controlling the explosive nature of curing reactions.

2. Epoxy Polymer and Biocomposites

Epoxy resins are prepared by the coupling reaction which contains at least two active hydrogen atoms with epichlorohydrin. Dehydrohalogenation takes place in the intermediate to form epoxy resin (see Scheme 1).

Almost all epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermoset networks for their uses by curing with cross-linkers. Amine functional compounds and carboxylic functional compounds are widely used to cure epoxy resins. The final properties of cured epoxy resins are dependent on the type of epoxy resins, curing agent, and curing process [31]. Researchers are trying to shorten the curing time of epoxy resin because short curing time will improve the efficiency of the process. In this respect, Zhang et al. had reported the preheating of mould and other additives used in epoxy resin during the fabrication of epoxy based material [32]. Glass transition temperature ($T_g$) of standard epoxy resin lies between 135 and 140°C while $T_g$ for high performance epoxy resin lies between 170 and 180°C. It has been reported by Kasemsiri et al. that there was presence of two-stage curing processes in cashew nut shell liquid incorporated epoxy resin instead of one stage conventional curing process [33]. It has been reported by Pan et al. that animated lignin increased the curing efficiency of epoxy resin due to presence of significant amount of reactive amino groups [34]. Johnston et al. had reported that use of...
microwave to cure epoxy resins did not affect $T_g$ and chemical properties of resulting epoxy resin. In fact, rate of curing increased over thermal curing when microwave was used as a source for curing [35].

Bio-composites based on epoxy polymer and natural fibres have generated wide research and engineering interest in the last decade. Natural fibre cannot be used directly as a reinforcement material but it has to be alkali treated so that lignin and other impurities could be removed [36]. Fiore et al. used sodium hydroxide treated kenaf fibres to produce kenaf fibre reinforced epoxy composites with higher moduli compared to neat epoxy resin [37]. Rrawi et al. developed bio-composites based on green epoxy resin and biodegradable bark cloth. Tensile and flexural properties of green epoxy resin were 33 MPa and 207 MPa, respectively [38]. Bisaria et al. fabricated jute fibre reinforced epoxy composites by taking jute fibre of different length (5, 10, 15, and 20 mm). They found the tensile and flexural properties to be maximum with 15–16 mm length of jute fibres [39]. With the advent of nanotechnology, researchers are also exploring nanocomposites with epoxy resin as a matrix and in one report; Schilde et al. had incorporated carbon nanotube (CNT) to fabricate CNT-epoxy composites [40].

3. Epoxy Polymer Concrete

The curing reaction in epoxy resin is exothermic in nature but is of small magnitude. Hence, it can be poured deeply in a mould, without overheating, during the preparation of epoxy based polymer concrete. Epoxy polymer concrete shows high physical strength and also good bonding to concrete and metal surfaces. Due to these properties, it can be used for many types of applications where heavy loads, high impact, and chemical exposure are present. Typical applications of epoxy polymer concrete include

(i) floor toppings,
(ii) trenches,
(iii) sumps,
(iv) rapid repair to deteriorated acid brick floors,
(v) precast polymer concrete shapes.

In this section, we will discuss the properties of epoxy polymer concrete as well as epoxy polymer cement concrete.

Epoxy polymer concrete has been prepared by using epoxy resin and silica fume as filler of different particle sizes and crushed aggregates of different dimensions (0.4 mm and 0.8 mm) [42]. The density of silica fume taken in the reported literatures varied between 2,100 and 2,250 kg/m$^3$. In addition to filler and aggregates, hardener had been added in the prepared epoxy polymer concrete. Compressive strength, flexural strength, and split tensile strength had been determined for epoxy polymer concrete with 0.4 and 0.8 mm of crushed aggregates. The compressive strengths for epoxy polymer concrete with 0.4 mm and 0.8 mm of aggregates were found to be 60 ± 9 MPa and 62 ± 4 MPa, respectively. The values of flexural strengths for epoxy polymer concrete with 0.4 mm of aggregates varied between 12.7 MPa and 9.32 MPa and the values of flexural strengths for 0.8 mm of aggregates varied between 17.57 MPa and 14.81 MPa. The values of split tensile strengths for 0.4 mm and 0.8 mm of aggregates were reported as 12.1 MPa and 7.67 MPa, respectively. It has been stated by the authors that the above mechanical properties were obtained by the use of 24% epoxy resin (weight of total sample). The above reported values indicated that aggregates with larger dimension reduce the compressive strength and split tensile strength of epoxy polymer concrete.

In another report, several epoxy polymer concrete specimens have been prepared utilizing 15% epoxy resin (weight of total sample) based on bisphenol A [43]. In the reported work, tetra-amine 3-ethylene had been used as a hardening agent and the ratio of resin: hardener was used was 2:1. The specific gravities of hardener and resin at 25°C were 1.07 and 1.18 g/cm$^3$, respectively. Fine, medium, and coarse silica powder, with average particle size of 50–60 μm, 600 μm, and 1100 μm, respectively, had been used as filler in the preparation of epoxy polymer concrete. Dolomite as an aggregate had been used with the particle size of less than 4.75 mm. The compressive strength of resulting epoxy polymer concrete was quite high (128.9 MPa) compared to value of 32.5 MPa for conventional concrete. Golestan et al. predicted that the maximum compactness of the aggregate and filler in the mixture was probably the reason for such a high value for epoxy polymer concrete. The highest value for flexural strength as reported was 22.5 MPa. Again this value was about 5-fold greater than the flexural strength of conventional concrete.

A new type of epoxy based polymer concrete with liquid type silicone rubber or tire waste powder had been explored for runway repair [44]. The mechanical performance of epoxy polymer concrete with tire waste powder was more than the silicone rubber. Elalaouie et al. reported that epoxy polymer concrete can also be used at higher temperature. They reported the mechanical and physical properties of epoxy polymer concrete exposed to temperature less than 250°C for 3 h [45]. When the epoxy polymer concrete was exposed to temperatures higher than 150°C, it showed a significant loss of strengths mainly due to the thermo-oxidative degradation of the epoxy polymer and to the debonding between aggregates and the binder. On the other hand, cement based concrete had lower mechanical properties compared to polymer concrete when they were exposed to high temperatures.

Haidar et al. fabricated an epoxy resin reinforced with a graded mixture of coarse and fine sands termed as micropolymer concrete (MPC) [46]. It has been reported that the MPC concrete designed with a polymer content of 9% showed the highest physical and mechanical characteristics such as strengths and rigidity. Also for the formation of MPC the amount of epoxy resin taken was slightly lower than for general epoxy polymer concrete.

Epoxy polymer concrete reinforced with natural fibres as well as synthetic fibres has been reported by Reis and Ferreira [47]. They used coconut, sugar cane bagasse, and banana fibres to fabricate epoxy based polymer concrete [13]. The flexural results from coconut fibre reinforced polymer concrete were higher than the others natural fibre polymer concrete and an increase was also observed when compared...
to unreinforced polymer concrete. Chopped carbon and glass fibres (6 mm long) reinforced epoxy polymer concrete had also been investigated by Reis and Ferreira [47]. Silica sand as an aggregate was mixed with epoxy resin. Authors had pretreated the glass fibres with silane to improve the adhesion between fibres and resin. The fracture toughness of carbon fibre reinforced polymer concrete increased up to 29% while glass fibre polymer concrete increased up to 13% when compared with epoxy nonreinforced polymer concrete.

Wastes are becoming integral part of our life. Wastes can be used to reinforce epoxy based polymer concrete. Fly ash and red mud solid waste were used in the preparation of polymer concrete so as to enhance the physical properties and mechanical strength of the polymer concrete [48]. For the preparation of composites about 8 to 12% ash, 12 to 25% red mud and 30–35% epoxy resin were used. About 10–15% filler in the form of silica powder was used. The casted polymer concrete with 35% resin, 25% fly ash, and 15% silica fume had been investigated for their flexural strength. The value of flexural strength as reported was 21.53 MPa. Marble waste was mixed with commercial epoxy resin to fabricate epoxy polymer concrete [49]. It has been observed that the incorporation of marble processing waste particles increased the 10% decomposition temperature of pure epoxy by 5–50°C. The composites reinforced with marble processing waste-pumice showed about 10% increase in elastic modulus, whereas the composites reinforced with marble processing waste-sepiolite or zeolite showed about 76.67–143.33% increase in elastic modulus over the pure epoxy matrix. Thus the mechanical properties of epoxy polymer concrete increased with the addition of marble based or clay based waste.

Epoxy resins are not only used as polymer concrete but they are also used as polymer cement concrete. Epoxy emulsion had been prepared by emulsifying epoxy resin, based on diglycidyl ether of bisphenol A, and amino-amide based hardener in water by using a nonionic surfactant so that it can be used as polymer cement concrete [50]. Epoxy polymer cement concrete specimens were prepared by varying the polymer cement ratio from 0% to 30% by mass of cement. The compressive strength of unmodified water cured mortar specimen increased from 39.5 MPa at 28 days to 45.0 MPa at 90 days of curing. It was observed that at both 28 and 90 days of compressive strengths of the mortar increased with polymer cement ratio. The flexural strength of the unmodified water cured mortar was 7.8 MPa. The flexural strength of air cured polymer modified mortars specimens was less than water cured unmodified mortar samples. However, for both polymer systems the flexural strength was better than that of the water cured control specimens at 30% polymer cement ratio. At 30% polymer cement ratio the flexural strength of epoxy modified mortar samples was about 10% higher than wet cured samples. This showed that the addition of polymer to cement mortar improved workability and increased flexural and compressive strengths. Also it has been stated that epoxy emulsion based mortar can be used for repair works in humid and industrial environments.

### 4. Polyester Polymer and Biocomposites

The curing reaction of polyester takes place in two stages. In the first stage at and above 100°C, the reactions of glycols with dibasic acid anhydrides, such as phthalic and maleic anhydrides, are carried out in presence of inert atmosphere. Since the 1st stage reaction is exothermic in nature the temperature of the reaction system increases to over 150°C. At this point, half of the esters condense into polymers with the evolution of water as by-product. Since the polyesterification reaction is reversible in nature, the removal of water in the latter part of the reaction process is essential:

\[
\text{OH-R-OH} + \text{HOOC-R’-COOH} \rightarrow \text{HO-\left(\text{R-OOC-R’-COO}\right)_n-R-OH} + \text{H}_2\text{O} \tag{1}
\]

Monitoring of curing reactions in polyesterification is done by differential scanning calorimetry (DSC) [51]. Researchers are also trying to fabricate polyesters from renewable resources. This will reduce the carbon footprint to large extent. Dai et al. synthesized three biobased unsaturated polyesters from itaconic acid and different diols derived from renewable resources [52].

Neat polyester resin shows tensile strength and tensile modulus as ~68 MPa and ~3.1 GPa. Flexural strength and flexural modulus of neat polyester resins are around 110 MPa and 3.44 GPa, respectively. Sodium hydroxide treated randomly oriented bamboo fibres reinforced polyester biocomposites with higher tensile and compressive strength compared with unreinforced polyester resin were fabricated by Manalo et al. [53]. Similarly alkali treated bagasse reinforced polyester biocomposites have been fabricated by Naguib et al. [54]. In this report, the cross-linking reaction was carried out by using methyl ethyl ketone peroxide as a catalyst and cobalt octoate as an accelerator. Jute fibre of 5-6 mm in length was utilized by Gopinath et al. to fabricate epoxy resin biocomposites [55]. Glass fibres are widely used as reinforcing agent for polyester based composites. Glass fibres reinforced polyester resin showed tensile strength and tensile modulus as ~110 MPa and 5.5 GPa, respectively. Flexural strength and flexural modulus of glass fibres reinforced polyester resin were around 193 MPa and 5.86 GPa, respectively. Blends of natural and synthetic fibres such as sisal-jute-glass fibres had been used to fabricate polyester composites [56]. Ojijo and Ray in his review paper reported about nanocomposites prepared from aliphatic polyesters and nanoclay [57].
5. Polyester Polymer Concrete

Polyester concrete has been used in constructions for more than 20 years. This type of polymer concrete can advantageously replace traditional Portland concrete in situations that require fast consolidation of the material. The construction material from polyester polymer concrete exhibits excellent chemical resistance and physical properties, such as high strength and relatively low shrinkage. The invention mentioned in US Patent 4371639A was directed to curable polymer concrete compositions, particularly suitable for articles of construction, comprising (1) a polyester composition, (2) an aggregate blend comprising sand as well as fly ash, and (3) an initiator [58]. These compositions are especially suitable for use in making pipe, bridge decks, dam spillways, building panels, and tank linings.

Polyester concrete is expensive and that is due to the fact that the aggregates used in the formulation of the need to be dried prior to their incorporation into the polymer matrix. Ignacio et al. used different curing systems (methacrylic acid and maleic anhydride) to test the hypothesis that the introduction of acid functionalities into unsaturated polyesters based on isophthalic acid could both restrict the detrimental effect of moisture in the curing process and also improve interfacial interactions even in polyester concrete containing wet aggregates [59]. Mechanical properties of the resulting polyester concrete were evaluated by compression tests. Results showed that methacrylic acid and maleic anhydride, when used as curing agents, led to the production of polyester concrete having higher mechanical properties in both dry and wet states than conventional polyester (based on isophthalic acid) concrete [59].

Polymer concrete mixes based on polyester resin as an organic binder, fly ash, and river sand as fine aggregates and granite as a coarse aggregate had been prepared by Varughese and Chaturvedi [18]. Fly ash had been used as a replacement for river sand, which was usually employed in the construction of ordinary cement concrete systems. Properties such as cure time, flexural strength, and resistance to water absorption had been studied by varying the level of fly ash. It has been noted by Varughese and Chaturvedi that fly ash can be used as a fine aggregate material for partially or fully replacing ordinary river sand in polymer concrete systems. At the higher level of fly ash, properties of polyester polymer concrete decreased by increasing the amount of resin in the mix. Cure time, strength, and resistance to water absorption of fly ash filled polymer concrete, using unsaturated polyester as the resin binder, could further be improved [18].

A porous polymer concrete has been developed by Korean scientists using unsaturated polyester resin as a binder, recycled aggregate as coarse aggregate, and fly ash and blast-furnace slag as filler for permeable pavement [60]. The mechanical properties of polymer concrete were investigated and it was reported to be more than 18 MPa. Hwang et al. replaced filler (calcium carbonate) and fine aggregate (river sand) with fly ash and rapid-cooled steel slag (RCSS), which were obtained from industrial by-products to fabricate polyester polymer concrete [61]. They were found to be effective for improving the strength characteristics and durability as well as the cost efficiency of polymer concrete. As reported, the developed product successfully reduced the demand for polymer binder by 21.3% compared to the conventional product, which in turn saved the total material costs by 18.5%. However, the use of RCSS showed performance degradation at an elevated temperature condition.

The effects of gamma radiation and the marble particle sizes on compressive properties of polymer concrete have been reported with an aim to develop polymer concrete with load bearing applications [62]. The results showed that the compressive strain and the elasticity modulus were dependent on the combination of the marble particle sizes and the applied radiation dose. The combination of medium and large particle sizes provided the highest elasticity modulus and also high radiation doses provoked higher numbers of dispersed particles per unit volume which provided more resistance to crack propagation [62]. It has been reported that the performance of polyester polymer concrete can be also improved by reinforcing polyester reinforced with steel and fibre reinforced polymer rears as well as waste glass powder [63, 64]. Recycled polyethylene terephthalate (PET) plastic waste has been used to prepare polymer concrete using an unsaturated polyester resin [11, 65]. It has been reported that the resins based on recycled PET could be used to produce good quality polymer concrete for precast applications such as utility components, transportation components, machine bases, and building components. Importantly, the use of recycled PET in polymer concrete helped in reducing the cost of the material.

A comparative study of the influence of thermal effects on flexural strength of two different binder formulations of polymer mortars had been reported. For this purpose, specimens of unsaturated polyester and epoxy polymer mortars were exposed to a large range of temperatures, between −20 and +100 °C, and tested afterwards in bending. The decrease in strength was clearly observed [21].

The effect of age on the compressive and flexural strength of recycled unsaturated polyester polymer concrete has been reported [66]. Recycled unsaturated polyester resin based polymer concrete achieved more than 80% of its 28-day strength in seven days. Due to high compressive strength, recycled unsaturated polyester resin based polymer concrete could be used in thinner sections of precast components. With the introduction of montmorillonite content (1% to 5%) the recycled unsaturated polyester polymer concrete compressive strength increased by about 12%. However, at 8% of montmorillonite the strength of specimens decreased.

The effect of temperature on the compressive and flexural strength of recycled unsaturated polyester polymer concrete has also been reported [66]. Recycled unsaturated polyester polymer concrete lost strength when temperature increased from 20 °C to 30 °C. Despite the loss in strength at high temperatures, recycled unsaturated polyester polymer concrete showed high compressive strength over Portland cement concrete.
Chemical resistance of polyester based polymer concrete was tested in seven different acid environments that represented those that often account for corrosive processes in industrial environments [67]. None of the compositions showed evidence of neither physical surface changes nor weight loss. There had been a decrease in the flexural strength of the samples exposed to corrosive agents and this effect was more pronounced in the compositions with lower filler concentrations. Scanning electron micrograph analyses also showed that the chemical attack occurred in the polymer matrix-aggregate interface. Gorninski et al. also compared mechanical properties of polymer concrete over Portland cement concrete [68].

6. Polyfurfuryl Alcohol

6.1. Background. PFA resin is a 100% biologically derived resin, which cures from furfuryl alcohol (FA) to form a thermoset polymer [69]. The manufacture of PFA starts with furfural obtained from the hydrolysis of agricultural waste rich in hemicellulose. The furfural is then reduced to FA which is polymerized to the PFA resin. FA monomers could be mixed with a novel aggregate system to yield polymer concrete of improved chemical and physical characteristics [70]. Furan polymers have found wide use in the formation of foundry cores in which small-sized aggregates (sand) were mixed. All large-sized aggregates had been excluded in the formulations of PFA based polymer concrete. There had been studies on polymer concrete systems utilizing furan polymers in the United States. It has been found that the performances of polymer concrete were significantly influenced by aggregate selection to produce furan polymer concrete with a range of compressive strengths varying from 5000 to 15,000 PSI. In epoxy and polyester based polymer concrete also, authors have used different sizes of aggregates and hence the selection of aggregates is important in the formulations of polymer concrete [18, 42].

The polymer concrete described in US Patent 4373058 was formed from a blend of FA monomer and an acidic hardener mixed with a mineral aggregate system. The FA monomer was polymerized in situ within the mixture to produce a highly cross-linked resinous polymer concrete in which the mineral aggregates were dispersed or bound within the polymer binder. Polymer concrete formed from furan polymers offered the broadest range of chemical resistance reported and were further advantageous for producing a usable concrete product because of the relatively low viscosity, ease of handling, mixing, consolidation, flow and finish, and rapid cure at ambient temperatures. Because of the advantageous raw material availability and cost performance relative to other organic binders furan based monomer have been utilized in polymer concrete.

Kukacka and Sugama developed a FA based polymer concrete for all-weather repair material for concrete and asphalt surfaces [71]. For this application, the following criteria were established:

(i) High strength at an age of one hour.

(ii) Placement of the materials possible during heavy precipitation over temperatures ranging from –32 to 52 °C.

(iii) The chemical constituents low in cost with long-term stability during storage.

A formulation consisting of FA monomer, \(\alpha,\alpha,\alpha\)-trichlorotoluene, pyridine, silane, zinc chloride, silica filler, and coarse aggregate met these above requirements.

6.2. Curing Reactions. The research in PFA resins started long ago but due to the highly exothermic reactions there are very few literatures related to PFA resins [72, 73]. Also PFA resins are mixed with phenol based thermoset resins to get modified resins [74]. The active catalysts for preparing PFA resins are sulphuric acid, sodium bisulphate, para-toluene sulphonic acid (PTSA), an alkane sulphonic acid having 2 to 14 carbon atoms, and para-toluene sulfonyl chloride. Under either Brønsted or Lewis acidic catalysis, FA polymerizes into PFA [75, 76]. Inert materials such as barium sulphate, silica, carbon, and asbestos have also been used with an active catalyst. It had been noted that once PTSA was added to FA, polymerization started which was slow in nature [77, 78]. An acid-curing condensation type resin, consisting of PFA or admixtures of PFA with other acid-curing resins, had also been used to process sand cores or moulds [79]. This product can be treated as first step towards the preparation of PFA based concrete. In this report, sulphur dioxide was introduced in the moulding composition together with the oxidizing agent which affected oxidation of the sulphur dioxide within the mould or core composition. The oxidizing agent was organic peroxide which was incorporated in the sand or introduced within the resins. In US4448234, the inventors used the same peroxide but different acid catalysts to prepare sand cores and moulds. The acids used were phosphoric acid, fluoroboric acid, or hydrofluoric acid [80]. The reaction scheme for the curing of PFA resins stated that in the first step the hydroxymethyl group of FA condensed on the C5 position of another furan ring leading to linear oligomers connected by methylene linkages [81]. In a second stage, these linear oligomers were cross-linked into branched black materials and they were demonstrated by NMR experiments [72].

Recently, a greener and more sustainable catalytic route was proposed in order to replace hazardous acidic catalysts [41]. Organically modified montmorillonite (Org-MMT) and, in comparison, sodium MMT (Na-MMT) were used to evaluate the catalytic effect on the FA polymerization to PFA. The octadecyl ammonium cation (ODA) was also used as homogeneous acidic catalyst to highlight the specific role of this interlayer cation present in Org-MMT. As reported in this paper, FA/Org-MMT polymerized more rapidly than FA/ODA but initiation of polymerization slightly shifted to higher temperature due to initial intercalation between MMT layers (Figure 1). The rheological and chemorheological behaviour of a PFA resin was studied by Domínguez and Madsen with an aim to design the curing process [82].
6.3. PFA Bioplastics/Composites. Recently, PFA had been combined with soy protein isolate (SPI) to fabricate bioplastics [83]. The bioplastics have been prepared physically by adsorbing water-insoluble PFA on SPI. In this method, a solution of PTSA monohydrate was added dropwise to FA at room temperature in order to catalyse the FA. SPI films were then immersed in the catalysed FA for different time intervals and after the designated time, the SPI films were removed and characterised.

The absorption of catalysed FA on SPI increased from 18% to 26% with the increase in immersion time of SPI from 24 to 60 h and this was due to hydrophilic nature of catalysed FA. In the next step, SPI films, with absorbed FA, were cured in an air oven for 2 h at 145–150°C to produce PFA adsorbed SPI films. The weight of PFA adsorbed on SPI film was dependent on the immersion time. Surface morphology showed the presence of physically adsorbed FA and PFA on the surface of SPI (Figures 2 and 3).

Flax fibre reinforced PFA biocomposites were also prepared by Kumar and Anandjiwala [84]. In this method PTSA was dissolved in FA. Prior to the use, the resins were kept for 10 days at low temperature (10–15°C) without disturbing to obtain partially cured and viscous PFA resin. 10 layers of woven flax fibre were dipped separately in PFA resins and stacked one above another. Flax fibre wetted with PFA resin was put in an air oven at 100°C for about 5 h to prepare the prepregs. After that, the prepregs were compression moulded at 170°C for 2 h to get the biocomposite samples of about 4 mm thickness. The ratio of PFA: fabric in cured biocomposites was 60:40. PFA/agave fibre biocomposites were also prepared by incorporating different weight fractions of microfibre into PFA matrix [85].

An organosilane-assisted synthesis of ordered mesoporous PFA-silica composites by employing TEOS, 3-(triethoxysilyl)furan and furfuryl alcohol as precursors and triblock copolymer F127 as a structure-directing agent via an EISA process has been reported [86]. Zarbin et al. reported the preparation of glassy carbon through the pyrolysis of PFA inside the pores of Vycor glass, which was used as a template [87]. The nanocomposites of glass/polymer were obtained. These nanocomposites were treated with HF to remove the silica fraction. The fabrication of bionanocomposites by incorporating cellulose whisker in PFA has been reported by Pranger and Tannenbaum [88].
Superhydrophobic films of PFA/multiwalled carbon nanotubes composites had been prepared by using fluorocarbon-modified MWNTs (MWNT-OCOC₆F₁₄), PFA, and PTFE [89]. The formed multiscale roughness structures and the lower surface energy in these nanocomposites played an important role in creating the superhydrophobic surfaces of PFA/MWNTs composites.

6.4. Mechanical Properties. The tensile strength and Young’s modulus of neat PFA had been reported to be 17 ± 2 MPa and 2.1 ± 1 GPa, respectively [78]. However elongation at break was too low [78]. To increase the elongation at break, soy protein isolate was incorporated in PFA to fabricate SPI-PFA film [83]. The mechanical performance of PFA absorbed/adsorbed soy protein films (at 65 ± 2% RH) showed a tensile strength of around 20 MPa and a Young’s modulus of 0.5 GPa.

Natural fibres such as flax and agave had been used to increase the mechanical properties of PFA based materials [84,85]. The behaviour of flax fibre reinforced PFA based biocomposites under tension was studied by performing tensile tests. In this case PFA showed tensile strength of 15.65 MPa and introduction of flax fibre had no effect on the tensile strength of the biocomposites as the value almost remained the same, that is, 15.53 MPa [84]. However, elongation at break increased with the introduction of flax fibre. There was a decrease in the tensile strength from 15.53 MPa to 10.07 MPa and further increase in elongation at break for the wet flax fibre reinforced PFA samples. Similar trend in mechanical properties was observed for agave reinforced PFA composites with different loadings of agave microfibres [85].

Neat PFA samples showed higher flexural strength of 60.2 MPa and flexural modulus of 3.2 GPa. Introduction of flax fibre decreased the flexural strength from 60.2 MPa to 23.2 MPa and also the modulus from 3.2 GPa to 2.4 GPa [84]. There was further decrease in the flexural modulus from 2.4 GPa to 2.2 GPa for the wet composite samples. Flexural properties also showed decreasing trend with increasing agave fibre loading in PFA [85]. Incorporation of flax fibre in PFA showed a decrease in the impact strength from 30.4 J m⁻¹ to 24.9 J m⁻¹ [84]. It further decreased to 14.8 J m⁻¹ for the wet biocomposite samples. The decrease in the tensile and flexural stress as well as impact energy for the wet samples was attributed to the water absorbing tendency of the flax fibre. In composites, migration of water through the polymer could lead to a disturbance of the fibre/polymer interface, reducing the overall strength of the composite. It had been reported that, in the case of flax reinforcement, this could be even more dramatic since flax tends to absorb rather large amounts of water when exposed to it.

6.5. Thermal Properties. PFA had inherently very high thermal stability with high char yield and $T_{\text{max}}$ ($T_{\text{max}}$ represents the temperature at which mass loss is maximum). PFA showed around 0.5% in mass loss at 200°C and for the dry biocomposite samples it increased to 5% (Figure 4). The increase in mass loss below 200°C was attributed to hydrophilic nature of flax fibre incorporated in PFA [84]. Similarly, it has been observed that PFA absorbed/adsorbed aryalted soy protein films showed higher thermal stability than native SPI films [83]. The SPI-PFA films exhibited two significant temperature range mass losses designated as $T_{\text{max 1}}$ in the temperature range 200–300°C and $T_{\text{max 2}}$ in the temperature range 300–400°C. First step mass loss was attributed to the loss of absorbed/adsorbed moisture. Second step mass loss was attributed to the degradation of the SPI materials in PFA.

Fire retardancy of PFA and flax fibre reinforced PFA have been evaluated by cone calorimeter [84]. Parameters typically available from the cone calorimeter experiment included the heat release rate (HRR) and especially its peak value (PHRR), total heat release (THR), volume of smoke produced, mass loss rate, time to ignition, and time to peak heat release rate. Flax fibres showed very low ignition time (5 sec). Introduction of PFA in flax fibre increased the ignition time from 5 sec to 105 sec. This showed that the thermal stability of natural fibre reinforced PFA materials increased.

6.6. Water Resistance. Neat PFA based plastics were completely water insoluble in nature. However, the incorporation of natural fibres in PFA based biocomposites showed water absorbing tendency due to hydrophilic nature of the fibres.
The PFA absorbed/adsorbed SPI films showed a maximum water uptake of 50% when immersed fully in water for 24 h with good dimensional stability. This was due to presence of water absorbing material, that is, SPI [83].

### 6.7. Products Available from Polysurfuryl Alcohol

The above literatures explore the possibility of PFA based bioplastics or natural fibre reinforced PFA materials in new-build and refurbished structures by replacing traditional fibre reinforced polymers and brick. The PFA based material will be low cost, lightweight, durable, and sustainable biocomposite or nanocomposite building systems based on panels, profiles, frames, and sandwich structures (Figure 5).

In one of the literatures, a comparison was made between cement roofing sheets reinforced with asbestos fibres, elephant grass, and sugar cane residue on the basis of some physical and mechanical properties and derived costs. The grass fibre sheets were shown to be the most attractive choice for roofing applications [90]. Many other natural fibres were also explored for the fabrication of biodegradable composites [91]. Biocomposites based panels from PFA and flax fibre had been successfully compression moulded by reinforcing PFA with 10 layers of woven flax fabric [84].
Kukacka et al. reported the preparation of water-compatible furfuryl alcohol polymer concrete containing 8% water by weight of aggregate with compressive strengths of \( >\sim 2000 \text{ psi} \) (\( >13.78 \text{ MPa} \)) at an age of 1 h at 24°C [92].

7. Conclusion and Future Directions

Concrete is the main component of the construction sector. Generally, a significant proportion of concrete is used in pavements, structural supports for buildings, and machinery. The formulations of concrete are based on a mixture of fine and coarse mineral aggregates and a paste of Portland cement and water. But the problem is that these resources are finite so after few hundred years one may not find Portland cement in abundance.

Another option is to use polymer concrete based on polyester and epoxy based thermoset resins. Rahman and Islam reported the use of epoxy resin for the preparation of polymer cement mortar and polymer mortar. The results showed the increase in the mechanical strength of both polymer cement mortar and polymer mortar with the addition of epoxy resin [93]. Latex modified concrete has also been reported by Jamshidi et al. [94]. The present review paper provides an insight of epoxy and polyester based polymer concrete with improved physical properties over conventional Portland cement concrete. It has been stated that this polymer concrete can be used for a wide variety of uses such as coatings, coverings, and repairs and for applications in heavy industrial environments in which strength, flexibility, and chemical resistance are required. It is well mentioned that compressive strength and flexural strength of polymer concrete are dependent upon the content of thermoset resin. However, the optimum thermoset resin content for a particular polymer concrete system is also dependent upon the nature of aggregate used in the system. Again, it is to be noted that both epoxy and polyester resins are synthetic in nature so the polymer concrete based on these two polymers is in the category of finite resources.

PFA based polymer concrete can be the answer for both the above points as it is obtained from renewable resources and can be used as polymer concrete over conventional Portland cement concrete. It has been reported that, for applications in heavy industrial environments, more chemically resistant polymer concrete is needed and then the possibility of the uses of furan based polymer concrete increases.

From the literature review the following points can be concluded:

(i) Flexural strength of natural fibre reinforced epoxy polymer concrete had been reported to be around 18 MPa. Incorporation of ash and red mud in epoxy and polyester resin showed flexural strength of 21.3 MPa and 18.5 MPa, respectively, and were better than Portland cement concrete.

(ii) The flexural strength and flexural modulus of natural fibre reinforced PFA composites were reported to be 50 ± 2 MPa and 2.2 ± 2 GPa which were comparable with that of natural fibre reinforced epoxy or polyester reinforced composites.

(iii) The compressive strength (13 ± 2 MPa) of PFA based polymer concrete was reported to be lower than that of epoxy polymer concrete (60 ± 10 MPa).

(iv) The biopolymer concrete had comparable mechanical properties as epoxy and polyester based polymer and also the sources of the raw materials were biobased and sustainable.

Lastly, we can state that biopolymer concrete will offer support structures and partitions with complete environmental validation. Figure 6 gives us the idea of formation of PFA based polymer concrete with rock-like structure or smooth structure depending on the rate of curing which is temperature dependent. One can successfully fabricate PFA based polymer concrete but polymer based concrete is expensive and the product suffers dimensional shrinkage after curing.

Competing Interests

The author declares that there are no competing interests.

References


