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Brief History of Fiber Reinforced Polymers as Structural Material

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Abstract
Throughout history different kinds of composite materials were used for several reasons. Mixing components with different properties the emerging new material can show highly improved material characteristics. This article copes with Advanced Fiber Reinforced Polymer (FRP) as structural material. The trend of the utilization of FRP is continuously increasing not only in transportation or sport industry but also in building industry. Beside the traditionally used base materials new fiber and resin materials are still developing. This paper reviews the brief history of FRP and its often-used base materials. Material properties, advantages and disadvantages, production methods are also discussed.

Keywords
Fiber Reinforced Polymer (FRP), history

1 Introduction

Composites are the association of two or more components with significantly different physical or chemical properties that remain separate at the macroscopic level and remain distinct in the finished structure. Most of the composites can be separated into two main components; the disperse phase and the matrix. The disperse phase provides the loading capacity and other desired effects and is made from uniformly distributed parts, fibres, or particles. The matrix surrounds and holds together the disperse phase and protects it from environmental influences and mechanical damages. Well-designed composite structures behave better than the constituent materials on their own. This paper reviews the brief history of composites as structural material and its often-used base materials (Nagavally, 2016). In case of fiber reinforced plastic (FRP) material properties, advantages and disadvantages, production methods are discussed. Application fields of FRP are also listed including the state of this material in the Hungarian civil industry.

2 History of composites

Composites were used throughout history beginning with the first shelters, when people used wood and bush covered with mud for waterproofing. When the first walls were made, wattle was usually used as the primary load-bearing structure covered with mud. Also, adobe bricks were made for creating walls. They usually put grass or straws in the mud to make the bricks more durable (Macphail, 2008). Later, composite bows were created from animal tendons, silk and wood and bonded together with animal glue. Different geometrical versions created by different tribes like the Avarians, Chinese, Huns, Mongols, and Turkish (Horváth et al., 2006). These weapons were one of the most powerful ones in long-range combat until gunpowder was invented (Nagavally, 2016). In a broad sense concrete and reinforced concrete are also composite materials. In RC the steel bears the tensile forces, and the concrete around it bears the compressive stresses and provides a suitable medium for the steel, so the steel does not corrode until the concrete is damaged.

With time more composite materials evolved thanks to the development of the chemical industry. Advanced Fiber Reinforced Polymer (FRP) is a relatively new material, that is made from two main parts; the fibers which are generally made from carbon, aramid, or glass, or natural materials and the matrix, which is usually epoxy resin in the civil industry. Nowadays modern composites are used in several industries where lightweight durable

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materials needed, for example in aircraft and transportation industries, sports, construction, appliance among others. Composites are also used to create wind turbine blades. To sufficiently utilize wind energy, large wind turbine blades are needed, therefore light, durable structures are preferable, consequently composites are used (Ennis et al., 2019). Despite the obvious advantages of composites, synthetic fiber-based composites are hard to recycle so their environmental impact is high. Natural composites which are biologically degradable and recyclable are under development to make more environmentally friendly materials.

2.1 History of matrix materials

Until plastics were invented, glues and binders for composites came from animal and plant resins. At the beginning of the 20th century the first plastics were developed such as vinyl, polystyrene, and polyester, which were more resistant to loads and environmental effects than the natural resins. Although natural resins are still used in some industries such as in instrument manufacturing, plastic-based glues are more common these days. Comparing the most used resins in composite constructions epoxies are more resistant to cracking and peeling and less sensitive to chemical or environmental degradation and more expensive than polyesters, while polyesters are more fragile and usually used for temporary fixes or in low-stress situations. New bio-based, biodegradable resins with good mechanical properties also reached the market since sustainability has become a very important aspect in recent decades (Rajeshkumar et al., 2021). Short summary of the material properties of the most common resins can be seen in Table 1. Thermoplastic resins have a melting point above which whole polymer chain mobility occurs, whereas thermosetting resins cannot melt after curing. However, each resin has a glass transition temperature, above which the resin becomes brittle, and its mechanical properties gradually decrease. For each resin, there is also a maximum service air temperature above which its use is not recommended (Van de Velde and Kiekens, 2001).

2.1.1 Epoxy

In 1909 a Russian chemist, Prileschajew first discovered epoxy but it didn't make a breakthrough then. In 1934 Schlack from Germany made various materials among which there was the predecessor of epoxy resins. A new formula was invented by Dr. Sylvan Greenle from US and Dr. Pierre Castan from Switzerland around the same time. In 1938 Castan made a patent on low melting epoxy resins, which can be used in dental products, but it was not successful on the market. In 1943 Greenle made his first patent which contained a similar resin to the one made by Castan, but it had higher molecular weight for coatings, and this approach was successfully commercialized in the US (May, 1988). In 1946 at the Swiss Industries Fair the first epoxy adhesive was presented to the world and casting resin samples were offered to the electronic industry (Pham and Marks, 2004). In 1947 the first commercialized epoxy product was made in the US by the Davoe-Raynods Company. Epoxy resins have high toughness, good adhesion, and chemical resistance properties. They have been used widely in the surface coatings industry since then. In the 1940s Daniel Swern tried to approach epoxidation from a new angle, and he published a review on the subject in 1949 (May, 1988). In 1955 four epoxy resin making companies joined into a cross-licensing agreement and began to manufacture epoxy resins in the US. In the 1960s epoxies were developed further into multifunctional epoxies which can also be used at higher temperatures. In the late 1960s flame retardant epoxies were developed for electrical laminates and composite applications. In the 1970s Dow and Shell increased the chemical resistance of the epoxy resins further for corrosive chemicals like acids. These epoxies can be used in demanding environments such as in pipes, tanks, oil pans, and more recently in the construction of windmill blades. In the 1980s and 1990s new epoxy materials were invented to serve developments in the computer and electronic industry, where high performance resins with higher glass-transition and thermal decomposition temperatures and lower dielectric constants were demanded (Pham and Marx, 2004). Epoxies used nowadays have high tensile strength, have minimal shrinkage and provide hardness and resistance to heat and chemicals. Therefore, epoxies are widely used materials in modern composite industry. Epoxy resins are used in the electronics, packaging, recreation, building and construction, healthcare, transportation, aerospace industries, wind turbines, appliances and in other markets.

2.1.2 Vinyl esters

Various types of vinyl ester resins were developed in the 1950s. In 1965 they were commercially introduced by Shell Chemical Company as EPOCRYL® Resins. They provided better chemical resistance than the existing polyester resins at that time. They were used as adhesives, as electrical prepreg (impregnated tape) and in moulding.

Table 1 Short summary of the material properties of the most common resins used for FRP

	Thermoset resins			Thermoplastic resins	
	Epoxies	Unsaturated polyesters	Vinyl esters	Polyethylene (PE)	Polypropylene (PP)
Tensile strength [MPa]	55–130	34–105	73–81	4–78.6	26–41.4
Young modulus [GPa]	2.75–4.1	2.1–3.45	3–3.5	0.055–1.49	0.95–1.776
Elongation [%]	0–50	0.5–2.4	1.2–7.9	12–1000	15–700
Density [g/cm^3]	1.2–1.4	1.1–1.4	1.15–1.35	0.91–1.0	0.899–0.92
Flexural strength [MPa]	75.8–1890	53.8–265	40–1310	13.8–48.3	20–180
Glass transition temperature [°C]	1–285	–	119–200	(−133)–(−100)	(−23)–(−10)
Melting temperature [°C]	–	–	–	105–140	160–176
Maximum service temperature, air [°C]	25–250	71–200	98–300	70–120	65–125
Water absorption [%]	0.03–1.2	–	0.05–0.6	0.01–0.2	0.01–0.2
Coefficient of Thermal Expansion [10^{-5}/°C]	4.5–6.5	5.5–10	5–7.5	10–13	6.8–13.5
Advantages	Strong, good fatigue resistance; Resistant to peeling, cracking, corrosion, and damage from chemical and environmental degradation; Moisture resistant after curing; Good adhesion to many substrates; Low shrinkage during polymerization; Dimensional stability	Less expensive than epoxy; Considerable resistance to corrosion, chemical and environmental degradation; Some resistance to water absorption and shrinkage; Rapid curing	Less expensive than epoxy; Good wetting characteristics; Bonds well to glass fibers; Considerable resistance to corrosion, chemical and environmental degradation; Some resistance to water absorption and shrinkage; Stronger than polyesters	Good recyclability; it can be heated and remoulded; Moderate strength, stiffness, thermal stability, corrosion resistance, insulation property	Very good recyclability; it can be heated and remoulded; Moderate strength, stiffness, thermal stability, corrosion resistance, insulation property; Low processing temperature requirements
Disadvantages	Toxic volatiles during installation and burning; Not resistant to fire growth; Expensive; Not biodegradable; Not environmentally friendly; Not recyclable	Toxic volatiles during installation and burning; Not resistant to fire growth; More brittle than epoxy and vinyl esters; Not biodegradable; Not environmentally friendly; Not recyclable	Toxic volatiles during installation and burning; Incomplete curing affects the durability of FRP; More brittle than epoxy; Not resistant to fire growth; Protection from sunlight needed; Not biodegradable; Not environmentally friendly; Not recyclable	Medium operating temperature; Not resistant to fire; Not biodegradable; Not environmentally friendly; High density	
Manufacturing process for FRP	hand lay-up, prepreg lay-up, filament winding, resin transfer moulding, vacuum assisted resin transfer moulding, pultrusion, compression moulding, centrifugal casting	hand lay-up, spray-up, compression moulding, pultrusion, injection moulding, resin transfer moulding, casting	hand lay-up, filament winding, resin transfer moulding, vacuum assisted resin transfer moulding, pultrusion, compression moulding	hot pressing, compression moulding	hot pressing, compression moulding
References	ACI Committee 440 (2017); Asrafuzzaman et al. (2021); Bhatt et al. (2018); Hollaway and Teng (2008); MatWeb (n.d.); May (1988); Mullins et al. (2018); Lubin (1982); Pham and Marks (2004); Rosato et al. (1991); SpecialChem (n.d.); Van de Velde and Kiekens (2001)				

In 1966 Dow Chemical Company introduced Derakane® Resins which can be used for chemical resistant FRP applications. Furthermore, special ones are developed for solvent resistance and high service temperatures or to improve fire-retardancy. In 1977 Interplastic Corporation and Reichhold Chemical Company developed CoRezyn and Corrolite products. These have high chemical resistance and can be used in FRP applications made with casting, filament winding, flooring, pultrusion and hand lay-up. Fiber reinforced vinyl ester resins are used where chemical-resistant FRP needed. Pipes, ducts and storage tanks are some examples for application. Shrinkage of vinyl esters are smaller than of polyesters, but larger than epoxy resins. Additives can be used to develop strength and to reduce shrinkage in the material (Lubin, 1982).

2.1.3 Unsaturated polyesters

Carleton Ellis started to develop unsaturated polyester resins in the 1930s. He made a patent in 1936 which was granted in 1941. Unsaturated polyesters are used in the plastic industry since then. It is mostly used with reinforcing agents. It is also used in buttons, furniture castings, auto-body putty, and cultured marble. Different types of unsaturated polymers can be made; there are flexible, resilient, low-shrinkage, weather-resistant, chemical resistant, fire resistant and general resins (Lubin, 1982). They can be used in different fabricating methods like in hand lay-up, spray-up, preform moulding, centrifugal casting, pultrusion and filament winding, automatic injection moulding, etc. (Bhatt et al., 2018).

2.2 History of fibers

Natural fibers were used in everyday items throughout history for example jute, grass, flax, kenaf and hemp. In the beginning of the 20th century, synthetic fibers spread and become heavily researched. Glass, carbon, and aramid fibers were developed. Thanks to the decreased diameter which causes decrease in the internal material flaws, increased strength can be obtained from the same material. Therefore, these fiber materials have higher strength and stiffness than steel. On one side they are beneficial because they can have a long lifespan if placed in suitable environment, and protected well against the hazardous external effects, but at the same time they are toxic and difficult to recycle. Therefore, using natural fibers also can be beneficial. Natural fibers have the advantage to be obtained from sustainable roots. Waste materials from the textile industry, livestock, and agriculture can be used for fiber materials in composites. Therefore, obtaining natural fibers can be cheaper than synthetic fibers and have smaller or even negative carbon footprint (Khalid et al., 2021). Usually, they have low service life because they are sensitive to temperature, rain, and solar radiation. They have large scattering of their properties because of irregular geometry and heterogeneity (Rajeshkumar et al., 2021). Natural fibers can be addressed by chemical or physical treatments for better durability. It can be used together with other fibers to make a more easily predictable final composite from them (Asrafuzzaman et al., 2021). Short summary of the material properties of the most commonly used fibers can be seen in Table 2.

2.2.1 History of glass fibers

The first synthetic fiber was glass fiber which at first was used as an insulation which was made from melted basaltic rods. The diameters were varied in a large range; from 1 to 15 micron. The smaller diameter fibres (smaller than 3 micron) had some health concerns as they can be inhaled and can subside in the lungs. In the 1920s insulations from glass fibers were made from standard glass making raw materials in Newark, Ohio, USA. In the 1930s a process was developed for glass thermal insulations thus it became more commercially available and was able to compete with the other insulations available at the time. Later in 1932, Dale Kleist, a researcher for Owens-Illinois Company accidentally found a way to create glass fibers with compressed air metal layer guns during an experiment. Jack Thomas, another researcher in the research group, thought that this method could be used to make fiberglass insulation in a simple way. They used steam instead of compressed air. In 1933 they made their first commercial fiberglass thermal insulation with this method. In 1935 the first glass fiber reinforced polymers were made in the same plant in Newark, Ohio. In 1938, Owens-Corning was formed by the merger of Corning Glass and Owens-Illinois, and their main product was fiberglass. They developed glass fiber products further and presented fiberglass in 1939 to the world. In 1941, the first plant producing exclusively continuous glass fiber filaments was established in Ashton, Rhode Island, Ohio (Jones and Huff, 2018). Since then, fiberglass has continued to develop and is used in a variety of industries, particularly in aircraft manufacturing and wind turbines. There are different types of fiberglass; the most commonly used fibers are described below. The electrical conductivity of E-glass fibers is low; therefore, they can be used in places where transparency of magnetic

Table 2 Short summary of the material properties of the most commonly used fibers for FRP

	Inorganic fibers						Organic fibers		Plant based fibers		
	Glass		Carbon			Basalt	Aramid				
	E-glass	S-glass	General purpose	High/UH strength	High/UH modulus		General purpose	High performance	Coir	Flax	Hemp
Tensile strength [MPa]	1800–2680	3440–4140	2050–3790	3790–6200	1380–3100	3000–4840	3440–4140	3440–4140	220	800–1500	550–900
Young modulus [GPa]	69–72	86–90	220–240	220–240	340–690	79.3–91.3	69–83	110–124	6	60–80	70
Fracture strain [%]	4.5	5.4	1.2	1.4–1.5	0.2–0.5	3.15	2.5	1.6	15–25	1.2–1.6	1.6
Density [g/cm^3]	1.2–2.1		1.5–1.6			2.7	1.2–1.5		1.15	1.4–1.5	1.48
Production process	Melting (1200–1400 °C), stretching, cooling (room temperature)		Stabilization (200–300 °C), carbonization (800 °C), graphitization (1200 °C), surface treatment			Melting (1500–1700 °C), stretching	Dry-jet wet spinning process: solvent heating (80 °C), spinning (200 °C), stretching		Mechanical method	Water retting	Water retting/ Mechanical method
Fire resistance	Good		Good			Good	Good		Combustible		
Chemical durability	Good in acidic solutions, not in alkaline	Not in alkaline or acidic environment	Very good			Not in alkaline environment	Not in alkaline environment		Can lose mechanical properties by breakdown of lignin, hemicellulose, and cellulose		
Electrical resistivity	Nonconductive		Conductive			Nonconductive	Nonconductive		Nonconductive		
Advantages	Least expensive; Improved strain to failure; Small creep and relaxation		Good resistance to cyclic and sustained loads; Highly resistant to environmental degradation; Small creep and relaxation			Improved strain to failure; Low water absorption; Biodegradable; Available at a similar price as glass fibers; Good impact and heat tolerance	Highly resistant to fatigue; Improved stain to failure		Obtained from sustainable roots; Can be very cheap; from waste materials; Biodegradable; Production consumes low energy; Healthier working conditions, no skin irritation; Good thermal and acoustic insulating properties		
Disadvantages	Stress reduction in presence of moisture; Not biodegradable; Not environmentally friendly		Expensive; Brittle; Not biodegradable; Not environmentally friendly			Stress reduction in presence of moisture	Expensive; Can lose strength in presence of moisture; Can exhibit high creep and relaxation; Not biodegradable; Not environmentally friendly		Large scattering in physical properties; Heterogeneity; Low service life; Hydrophilic nature; Sensitive to moisture, temperature, environmental dampness, UV, and presence of different microorganisms; Limited heat and fire resistance; Limited fibre length		
References	ACI Committee 440 (2017); Ary Subagia et al. (2014); Asrafuzzaman et al. (2021); Dhand et al. (2015); Hollaway and Teng (2008); Hollaway (2010); Jones and Huff (2018); Khalid et al. (2021); Rajeshkumar et al. (2021); Rebouillat (2016); Wong et al. (2010)										

fields is required. The S-glass fibers have high strength. The AR-glass fibers have high chemical and corrosion resistance (Asrafuzzaman et al., 2021). A main advantage of glass fibers is that they are the cheapest of the synthetic fibers. All glass fibers are non-combustible and non-conductive, have low creep and relaxation, but are sensitive to moisture (Hollaway and Teng, 2008).

2.2.2 History of carbon fibers

In 1860, Sir Joseph Wilson Swan made carbon fibers by heating cotton fibers and used them in light bulbs. In 1879, Thomas Edison created the first electrically heated light bulbs, in which filaments were made from cellulose-based carbon fibers. These fibers had poor mechanical properties, so their use as a reinforcing material had not yet arisen. In the 1900s, filaments were later replaced by tungsten in light bulbs, and attention to carbon filaments waned for about fifty years. In 1958 carbon fibers were produced again by Roger Bacon with 20% carbon percentage. He applied higher pressures and was able to produce thin carbon fibers with better mechanical properties. These were discontinuous fibers of several cm length, 1–5-micron diameter, 20 GPa strength and 700 GPa Young's modulus. In 1959, Ford and Michelle used a new process; they made carbon fibers by heat treating rayon up to 3000 °C. In 1961 Akio Shindo used polyacrylonitrile (PAN) instead of rayon to produce carbon fibers. This method was only used in Japan until the 1970s. In 1963 W. Watt, L. N. Phillips, and W. Johnson developed a process that produced stronger carbon fibers than the previous process, but the technology was not advanced enough, and the fibers produced were too brittle. In 1970, the USA and Japan concluded a technology agreement on the PAN method used by Japan, so in the 1970s a wide variety of PAN-based carbon fibers with different mechanical properties and sizes were produced (Peijs et al., 2022). Carbon fibers are conductive, have low sensitivity to cyclic and sustained stresses, have small creep and relaxation and highly resistant to environmental degradation and not sensitive to moisture (Hollaway and Teng, 2008).

2.2.3 History of aramid fibers

Aromatic polyamide, shortly aramid fiber was introduced to the market in 1967 by DuPont. It was a meta-aramid fibre named Nomex which made a breakthrough in thermal and electrical insulations because they are nonconductive. Today, Nomex is used in protective clothing, such as for firefighters and racers, due to its high thermal stability, temperature and flame resistance. In 1973, chemist Stephanie Kwolek, a researcher at DuPoint, developed another aramid fiber with higher tensile strength and modulus of elasticity and named it Kevlar (Rebouillat, 2016). Kevlar aramid fibers are less brittle than glass or carbon fibers, making them easier to weave into fibers and highly resistant to static and dynamic fatigue. Powerful bulletproof vests can be made from them next to other protective gear like gloves and safety shoes. At elevated temperatures, they show more creep and relaxation, they are also sensitive to UV radiation, they can lose their strength due to moisture, so adequate protection is necessary in such an environment (Hollaway and Teng, 2008).

2.2.4 History of basalt fibers

In 1923 basalt fibers were discovered in America. It was used in military research during the World War II. For a while, this material received less attention than the above-mentioned fibers, but in recent decades, researchers have begun to deal with basalt fibers again due to their environmentally friendly properties. It is a natural inorganic fiber with tensile strength and modulus comparable to other synthetic fibers. It has high temperature resistance, improved strain to failure, good chemical resistance, and better impact tolerance compared to glass and carbon fibers. It is easy to process, and its price is comparable to glass fibers (Dhand et al., 2015).

2.3 History of Fiber Reinforced Polymers (FRPs)

Fiber reinforced polymers are made by putting fibers in compatible resins. The fibers may be short or long, continuous or discontinuous, and may be in different directions in the matrix. The type and the arrangement of the fibers in a structure depend on the requirements. In this paper laminated composites are highlighted. Laminated composites contain plies and the long fibers within a ply are in the same directions. Material properties become designable with properly choosing the number and the orientation of plies, and so the material can be totally fitted to the requirements. The fibers carry the loads while the resin helps in the stress distribution between the fibers. Better wetting of the fiber and the bond between the fiber and the adhesive result in better mechanical properties. The research of modern FRP was sponsored by the U.S. Air Force and the National Aeronautics and Space Administration (NASA) from the mind 1950's. Thus, the laboratory concept led to practical production in a very short time. It has been used in the production of aircraft and spacecraft since the 1970s. In other industries, where less durable FRP materials were also suitable, experimentation with the use of FRP began earlier. The three most used synthetic fibers are the GFRP from glass fibers, CFRP from carbon fibers and AFRP from aramid fibers. BFRP from basalt fibers and NFRP from natural fibers are also mentioned below. A brief summary of the properties of the most commonly used FRP materials is shown in Table 3. Table 4 summarizes the mechanical properties of fiber-reinforced polymers made from different fiber and resin materials.

2.3.1 History of GFRP

The first synthetic FRP was GFRP, developed in the mid-1930s, which established the use of FRP in various industries. The World War II brought GFRP from laboratory to production. It was used for airplanes because those airplanes needed lightweight materials. Researchers realized that this material is transparent to radio frequencies, so they started to use it to build Radomes (sheltering electronic radar equipment). In 1946 the first boat hull was made from this material (Nagavally, 2016). Pultrusion was first patented in 1951 to make fishing rods (Lubin, 1982). With pultrusion it become possible to produce composite profiles with constant cross-section. In 1957 Monsanto tried to make a basically all plastic house at Disneyland in Los Angeles. Despite being in an earthquake-prone area, the building's deflection and load-bearing capacity did not change over 10 years. In 1967, they wanted to demolish the scene from Disneyland, but during the demolition they encountered difficulties because the structure could withstand the impact of the wrecking ball, so a different technique had to be used. This has shown the possibilities of FRP products (Rosato et al., 1991). Today, GFRP is used in aerospace and wind turbines, among other industries such as electronics, construction, transportation, leisure, sports, and appliances (Hollaway and Teng, 2008).

2.3.2 History of CFRP

In terms of strength and modulus of elasticity, carbon fiber-reinforced polymers dominate the composites used today. However, the use of the first CFRP produced by Rolls Royce in 1963, called Hyfil, encountered difficulties due to its rigidity. Turbine blades were made for the RB221 jet engine, which did not pass the necessary tests because composite technologies were not advanced enough, as the blades were too fragile. After that, from 1970, the PAN method took a leading role in the production of composites, which has continued to develop over time, so that today FRP can replace metal in certain situations (Peijs et al., 2022). CFRP is used in sport, appliance, marine, transportation, and construction industries. Wind turbines and parts of airplanes can also be made of CFRP. In the case of wind turbines, it could be beneficial to use carbon-based FRP instead of GFRP, because CFRP is lighter, has better stiffness, strength and fatigue resistance per unit weight compared to GFRP, so they can make longer blades with the same weight, which means more energy production, but its cost is much higher than that of GFRP. In order to reduce the cost of CFRP-based wind turbines, there are different approaches to produce low-cost carbon fibers (LCCF) (Ennis et al., 2019).

2.3.3 History of AFRP

AFRP composites have been used since the 1970s. Due to its high heat resistance, modulus of elasticity, strength and tensile strength, this material can be used in a variety of ways. Because aramid fibers are not as brittle as carbon fibers, aramid fibers behave better when subjected to seismic or impact loads. There are also hybrid fabrics woven from carbon and aramid fibers to combine the high elastic modulus and stress of carbon fibers and the good properties of aramid fibers. The recreational, automotive, and structural industries also use aramid composites for various applications such as skis, hockey sticks, boat hulls, and concrete reinforcement. Aramid composites are also used in wind turbine blades and in aerospace technology for various structural components (Hollaway and Teng, 2008).

2.3.4 History of BFRP

In the 1980s and 1990s, basalt fibers were used in lined pipes, especially for the transport of hot fluids and abrasives, because of its resistance to heat, electromechanical corrosion, fungi and microorganisms. It is used in construction, aerospace, automobile, and electrical industries. It is a more environmentally friendly alternative to glass fibers, while its mechanical and durability properties are similar (Dhand et al., 2015). Basalt fibers are often used together with carbon fibers in hybrid applications. In this way, a cheaper material with lower strength but greater ductility can be produced. Different properties can be achieved with different layering methods (Ary Subagia et al., 2014).

2.3.5 History of NFRP

Before the WWII the automotive industry used natural fibers in combination with plastic, so they could make lighter parts than steel. The idea of making interior and exterior parts of cars from fiber-reinforced polymers is associated with Henry Ford. Ford's famous 1941 "soybean" car used natural fiber-based bioplastics to lighten the car's bodywork and minimize

Table 3 Short summary of the properties of the most commonly used FRP materials

	GFRP	CFRP	AFRP	BFRP	NFRP
Fire resistance	Not fire resistant	Not fire resistant	Not fire resistant	Not fire resistant	Not fire resistant
Conductivity	Nonconductive	Conductive	Nonconductive	Nonconductive	Nonconductive
General price	Less expensive	Expensive	Expensive	Less expensive	Not expensive; Sustainable fiber materials
Durability	Good	Very good	Very good	Good	Short service life; Sensitive to moisture, heat, fungus and microorganism attacks
Eco-friendliness	Not eco-friendly	Not eco-friendly	Not eco-friendly	More eco-friendly	More eco-friendly Burning of NF composites causes less danger in atmospheric impact
Biodegradability	Not biodegradable	Not biodegradable	Not biodegradable	Can be fully biodegradable if appropriate resin is used	Can be fully biodegradable if appropriate resin is used
Impact resistance	Good	Moderate	Very good	Good	Moderate
Strength	Good	High	Good	Good	Moderate
Moisture absorption	Matrix and fibre absorb moisture	Matrix absorbs moisture	Matrix and fibre absorb moisture	Matrix and fibre absorb moisture	Matrix and fibre absorb moisture
Moisture resistance	Sensitive to moisture	Not sensitive to moisture	Not sensitive to moisture	Sensitive to moisture	Sensitive to moisture
References	ACI Committee 440 (2017); Ary Subagia et al. (2014); Dhand et al. (2015); Hollaway and Teng (2008); Hollaway (2010); Khalid et al. (2021); Rajeshkumar et al. (2021)				

Table 4 Summary of the tensile properties of different fiber and resin materials

Fiber	Glass			Carbon			Kevlar		Basalt			Flax		
Resin	Epoxy	Poly-propylene	Polyester	Epoxy	Poly-propylene	Polyethylene	Epoxy	Poly-propylene	Polyester	Epoxy	Vinyl ester	Epoxy	Polyester	Poly-propylene
Tensile strength [MPa]	520–1400	40–90	60–85	1020–2080	32–37	12–30	700–1720	20–47	159	600–1500	1200–1310	115–383	85–277	31–54
Elastic modulus [GPa]	6.7–43	2–7.5	72	14–140	1–1.2	0.22–0.41	7–68	0.7–23	8.7	50–65	48–54	15–35	8.7–23.4	1.5–4
References	ACI Committee 440 (2017); Asrafuzzaman et al. (2021); Hallonet et al. (2019); Shakir Abbood et al. (2021); Wu et al. (2016)													

the use of steel due to metal shortages at the time. That year, he also made cars from fiberglass-based composites. Later during World War II, fiber-reinforced plastics served military purposes, and the idea of natural fiber-reinforced plastic cars was abandoned, but synthetic fiber-reinforced plastics were produced for other purposes. The production of car parts using natural fiber-reinforced polymers was revived in the 1990s and is still used today (Sathyaraj et al., 2021). Nowadays, natural fiber-reinforced plastics are used, for example, in wall panels, toys, furniture and packaging. They are also used in hybrid composites to make less expensive and more eco-friendly material (Khalid et al., 2021). Natural fiber materials and bioresins are being researched to produce more environmentally friendly and biodegradable composite materials. Until recyclable resins, bioresins and natural fibers effectively reach the market, the use of thermoplastic resins instead of thermosetting resins can be a potential solution to produce more recyclable products where less good material properties are also acceptable.

3 Manufacturing processes of FRP composites

Several manufacturing processes are used to produce FRP products, which are described below. Fig. 1 shows the different FRP manufacturing methods schematically.

3.1 Hand lay-up method

Resin and fibers or fiber mats are placed on a moulding tool layer by layer with hand and squeezed together with rollers. The layer numbers depend on the required final thickness. This is a time- and labour-intensive process, but any shape can be made with a proper mould.

3.2 Prepreg lay-up

It is a similar method to hand lay-up method. Preimpregnated resin fabrics are laid on the moulding and cured at room temperature. It is a faster method than hand lay-up method and it provides good fiber volume ratio. It costs a little more than the hand lay-up method.

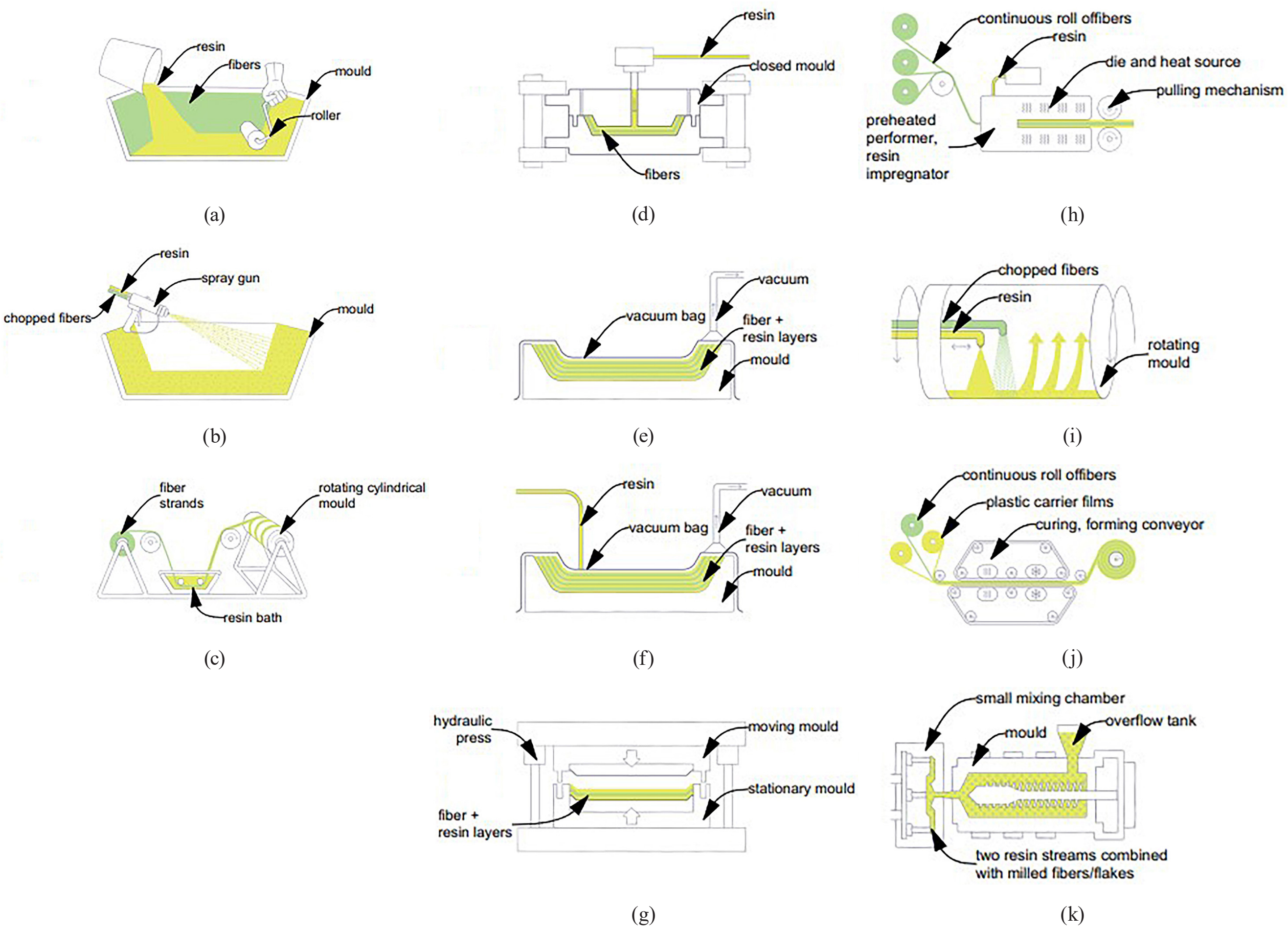

Fig. 1 Manufacturing processes of FRP composites (adapted from ACMA (n.d.)): Open moulding processes: (a) Hand lay-up, (b) Spray lay-up, (c) Filament winding, and Closed moulding processes: (d) Resin transfer moulding, (e) Vacuum bag moulding, (f) Vacuum assisted resin transfer moulding, (g) Compression moulding, (h) Pultrusion, (i) Centrifugal casing, (j) Continuous lamination, (k) Reinforced reaction injection moulding

3.3 Spray lay-up
Chopped fibers and resin are mixed in a spray gun and sprayed to the surface of an open or closed mould. Rollers are used for squeezing the material and remove entrapped air inside the material in case of open moulding. A sufficient percentage of resin is required to run the fibers, so the maximum fiber volume ratio and mechanical properties are limited.

3.4 Filament winding
It is used to make uniform cross sectioned cylindrical parts. The filaments are driven through a resin tank to a rotating cylinder until the desired thickness and length is reached. It is cured at room- or at an elevated temperature, after which the product is removed from the cylinder.

3.5 Resin transfer moulding
After the fabric is placed on a closed mould, resin is poured under high pressure to achieve the composite product. It can be used to make mass produced product parts.

3.6 Vacuum bag moulding
Two or more layers of fiber reinforcement bonded with resin placed on a fixed mould and covered with a vacuum bag and sealed by sealant tape. Vacuum is created to remove the trapped air bubbles and excess resin so a more compressed product can be made.

3.7 Vacuum assisted resin transfer moulding
It is a similar method to resin transfer moulding but instead of a two-part moulding tool one fixed and one flexible tool are used. The fabrics are placed on the mould and covered with a vacuum bag and sealed by sealant tape. The resin pumped in via a supply pipe and vacuum. With this process only one smooth surface is possible.

3.8 Compression moulding
There are two moulding components: a stationary bottom part and a moving top part. The moulded plastic (fibers and resin) is placed at the bottom mould, then the top mould gets a load from a hydraulic press. Excess material is removed to the overflow tank. Controlled pressure and temperature ensure the good quality of the products. It is used in mass producing.

3.9 Pultrusion
Continuous fibers are pulled through a resin tank and a preheated performer to get the desired cross-sectional shape. It then passes through a heating tool for final curing and is then cut to the desired length with a saw. It is used for mass production and making continuous cross-sections.

3.10 Centrifugal casting
From resin and chopped fibers, a centrifugal force generates cylindrical composite parts. It is good for mass producing cylindrical elements (Bhatt et al., 2018).

3.11 Continuous lamination
It's a highly automated process. Continuous roll of fibers placed between plastic carrier films and pulled through a conveyor, where forming rollers are used for forming at high temperatures, and then the product is cooled after hardening.

3.12 Reinforced reaction injection moulding
In a small mixing chamber, two streams of resin and milled fibers (usually glass) or flakes are mixed at high pressure and injected into the closed mould at relatively low pressure. This method has fast cycle time, low labor demand, low moulding pressure and low scrap rate. This process is widely used to produce automotive parts (ACMA, n.d.).

4 FRP in construction
During the Second world war GFRP system was used to build Radomes. This is the first known use of FRP to build a structure. In the following decades, attempts were made to use FRP without a proper understanding of the fundamentals of fabrication and the correct curing process. From the 1970s, FRP began to be considered as a building material, producing semi-load bearing and infill panels for houses and larger structures. They used manual lay-up method which we now call wet lay-up method. In the mid-1980s, the pultrusion technique made it possible to use FRP as a replacement for other construction materials, especially steel, in aggressive and hostile environments (Hollaway, 2010). Since then, the use of FRP in the construction industry has started to spread because of its good strength-to-weight ratio, corrosion resistance and designability (ACI Committee 440, 2015). Many bridge structures are made with FRP, which has a weight advantage over RC or steel structures (GangaRao, 2017). Thus, longer decks can be made, and the prefabricated structures can be transported to site in one piece by helicopter or disassembled and transported to site. In this way, buildings can be built in hard-to-reach and environmentally restrictive areas (Hollaway, 2010). However usually FRP is used in

hybrid systems to strengthen or rehabilitate bended structures for flexure, shear or to retrofit RC columns. This way FRPs can ideally be used in areas where it is exposed to tension forces, therefore buckles won't appear, also, hybrid systems can be more cost effective. Structure protection from chemical attacks also can be made from FRP thanks to their good chemical resistance (Mohammed et al, 2020). However, FRP behaves very brittle, and the resins are sensitive to high temperatures which should be considered in the time of design. Guidelines recommend that in case of fire the load bearing capacity of FRP systems should be decreased to zero (ACI Committee 440, 2017).

5 Environmental effects of FRP

The production and disposal of FRP can have a negative impact on the environment. However, efforts are being made to produce and dispose FRP in a more environmentally friendly manner.

5.1 Environmental challenges during FRP production

During the production of FRP, the biggest problem is the production of the constituent materials of FRP. Producing the synthetic fibers requires high temperatures (see in Table 2) and petroleum-based byproducts for precursors in case of carbon fiber production (Lee and Jain, 2009). Aramid fiber production needs sulfuric acid solvent during the spinning process which is a hazardous material (Rebouillat, 2016). It can cause severe irritation and burns to the skin. In case of inhalation headache, vomiting and nausea may occur (New Jersey Department of Health, 2016). The manufacturing process for glass and basalt fibers is similar, but basalt fibers are simpler to produce and do not require additional chemicals during production unlike glass fibers (Dhand et al., 2015). However, natural fibers are the most environmentally conscious choice, as they can be obtained from sustainable roots (Khalid et al., 2021). In the case of resin production, the goal nowadays is to replace fossil raw materials with renewable alternatives. Bio-based epoxy resins can be produced using natural/renewable precursor materials based on vegetable oils, lignin, or sugar, therefore their environmental impact can be decreased. However, these bio-based resins usually have lower glass transition temperature, less thermal stability and reduced mechanical properties (Agbo et al., 2023). Self-healing elastomers, nylon and long alkyl chain polyesters also can be produced from vegetable oils. In this way, a reduced carbon dioxide emission is achieved in terms of the life cycle of the resins, but it does not necessarily reduce the use of toxic chemicals as catalysts and reactors or solvents (Zhu et al., 2016).

5.2 Disposal of FRP materials after the end of their service life

Due to increasingly strict environmental protection efforts, one of the most important future aspects of FRP products is to become more environmentally friendly and more recyclable. The recycling of wind turbine blades is a hot topic these days due to their size and lifespan. The designed lifetime of wind turbines is around 20 years, and their length can be even 100 meters long (Jacoby, 2022). However, wind turbines represent less than 10% of the global composites industry, so recyclability should be considered in other industries where composite materials are used. Disposal method options known today are landfilling, cement coprocessing, thermal, chemical and mechanical recycling, high-voltage fragmentation, reuse and repurposing and designing for circularity. When landfilled, organic materials biodegrade with the release of volatile organic compounds. Cement coprocessing is a popular option for recycling GFRP materials, but it cannot be used for CFRP materials. Thermal recycling usually means high temperature (400–700 °C) processing in absence of oxygen. The fibers can be separated from the polymer matrix in this way. In the case of glass fibers, it may cause a decrease in strength, while in the case of carbon fibers, the mechanical properties remain almost unchanged, however, the surface of the fibers may become contaminated, so their bonding ability to the new matrix material is less good. Chemical recycling can mean solvolysis or thermolysis. The former uses a solvent and hydrolysis to dissolve the resin while the latter pyrolyze the polymer. Both methods can damage the glass fibers. During solvolysis, the water used, while in the case of thermolysis, the high temperature can damage the properties of the glass fibers. With mechanical recycling, the crushed composite material can be used in new composite products, where a shorter fiber length is sufficient. High-voltage fragmentation uses electrical pulses to break the composite material into fragments. It can produce longer fibers than mechanical recycling but requires more energy. Product parts can be refurbished and reused or sold to secondary markets or repurposed such as in playgrounds and benches. However, the best solution looking towards the future is to design more easily recyclable products. One option is to use thermoplastic resins because unlike thermosetting resins they can be heated and remoulded therefore the fibers can be obtained easily (Cooperman et al., 2021). Other options include the use of natural-based resins and fibers, and other more easily recyclable resin materials but these are still under research and development to provide better material properties (Jacoby, 2022).

6 FRP in Hungary

6.1 The history of fiber production in Hungary

There is one carbon fiber plant in Hungary which can be found in Nyergesújfalu. The factory building itself was built during the Second World War and produced rayon fibers from 1943. In the 1960s the factory started to produce polyamide based and polyacrylic nitrile fibers too. In 1995, during the privatization process, the company was bought by Zoltek Zrt. and the old products were gradually withdrawn from the company's product range. The company's primary goal was to cover the lowest price segment of the carbon fiber market. In 2014, the Japanese Toray Group acquired the entire Zoltek Zrt., including all of its plants. Nowadays, the company produces oxidized fiber and carbon fiber used in the production of aircraft brakes, as well as carbon fiber-reinforced pultruded sheets used to stiffen wind turbine blades from the produced polyacrylonitrile precursor (CNC Media, 2018). It also produces FRP products like prepregs and pultruded profiles (Zoltek Corporation, 2023). The production of natural fibers has a long history in Hungary. Several flax fiber mills were in Hungary, but the last one in Komárom was closed in 2019 due to the drastic price increase of raw materials (Hungaro-Len, n.d.). Hemp fiber production is running again in Nagylak under the name of Hungarohemp after the original factory was closed in 2009. Short basalt fibers are produced in Tapolca by Toplan Tapolcai Bazaltgyapot Kft. (Czigány, 2005) which was founded in 1989. In addition to these, natural fibers can be obtained from agriculture, such as straw, reed and corn fiber, as well as animal fibers.

6.2 The state of FRP in the Hungarian civil industry

Many researchers in our country deal with FRP materials. Common application topics include cars, airplanes, turbines and mechanical components, biodegradable implants, sports and leisure products and civil engineering applications. In addition, many publications have been published on the topic of recyclability of polymers and composites and degradable materials in recent decades (Czigány et al, 2005; Geier et al., 2022; Mezey and Czigány, 2007; Ronkay et al., 2021). In the civil industry a book was published on structures made entirely of composites (Kollár and Springer, 2003). This book includes the behavior, material properties and modelling of laminated composites, thin and sandwich plates, beams and shells made from composites. On the topic of structural reinforcement, several researchers have published articles on flexural strengthening with different FRP products (Balázs et al., 1999; Borosnyói, 2013). Some discusses the retrofitting of concrete columns (Csuka and Kollár, 2012). There are some national examples of strengthening reinforced concrete structures with FRP plates, strips, and bars since the 1990s. Examples to strengthen slabs, stairs, hanging corridors, beams, bridges, silos, crane track holders and slab opening boundaries were documented by Balázs et al. (1999). Recent examples are the Zugliget elementary school's expansion, and the rehabilitation of the Paris Courtyard in Budapest (Szabacsi, 2020; Varga, 2021).

7 Summary

Many types of materials became available in the market to make advanced fiber reinforced polymers in the last century. Composites are widely used materials in several industries especially in the transportation, aircraft and recreational industries. In recent decades, composites have also appeared in the Hungarian industry. A brief overview of mechanical properties, manufacturing methods and environmental effects of FRP and its base materials were discussed. We have briefly summarized the efforts of Hungarian researchers regarding the use of composites in the construction industry. Both international and Hungarian researchers place great emphasis on the development of more environmentally friendly options. This includes examining degradable materials from a mechanical and durability point of view, as well as striving for reusability. Effective recycling methods are also needed for existing products. The available methods which are used or under research were discussed above.

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