Morphology and Mechanical Properties of Epoxy/Synthetic Fiber Composites

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Morphology and mechanical properties of epoxy/synthetic fiber composites

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Abstract

In this chapter, we provide an overview on the use of synthetic fibers for the production of performing epoxy composite materials. We choose to focus our effort on the description of works based on the utilization of carbon and glass fibers. Our decision is motivated by the diffusion of those fibers in plenty of key cutting edge applications and productions. Herein we report an introductive section where we describe the main features of carbon and glass fibers as well as those of epoxy. Afterwards, we discuss in detail the new discoveries in the field of synthetic fibers epoxy composites. Our aim is to guide the readers through the world of synthetic based epoxy materials enlightening the main and most relevant issues.

1.Introduction

Synthetic fibers are one the most revolutionary materials of the 20th century.. Since their discovery, synthetic fibers have attracted a great scientific and commercial interest for their outstanding properties and consequent wide range of applications.

As years went by, a new class of fibers gained worldwide attention: high performance fibers such as glass (GFs) and carbon (CFs) fibers. These materials have found their main application as reinforcement for the production of composites. Fiber reinforced composites are a large family that regroups materials that can be divided into four classes based on the host matrix: i) metal, ii) ceramic, iii) carbon/carbon and iv) polymer matrix.

Fibres containing polymer composites are the most widespread having a global marketplace of about 1 billion dollars.

Among the various polymeric matrices, epoxy resins are the most used thermoset polymeric host. Epoxy composites are one of the most extensively investigated fields of polymer and materials science due to the large and common use of epoxy and epoxy related materials in a wide range of real world applications. The use of epoxy matrix combined with fibrous fillers is a very attractive route to produce high performances composites materials.

GFs and CFs based epoxy materials are widely used by several strategic industries such as aeronautics and automotive.

Although the type of epoxy resin plays an unneglectable role, fibres are mainly accountable for all of the mechanical properties of the composites. However, the outstanding characteristics of the fibres can reinforce the whole composite only if a strong bonding between fibres and host material exist. Hence, the interaction between fibres and epoxy host is one of the key issues in the production of performing fibre based composites.

In this chapter, we overview GFs and CFs filled epoxy materials through an updated review of recent literature providing as well a comprehensive introduction on the essential information about the properties of both fibres and epoxy host.

2. Synthetic fibers epoxy composites: the materials

2.1 Carbon fibers

CFs are fibers with an average diameter ranging from 5 to 10 μm mainly composed by sp^2 carbon atoms as shown in figure 7.1.
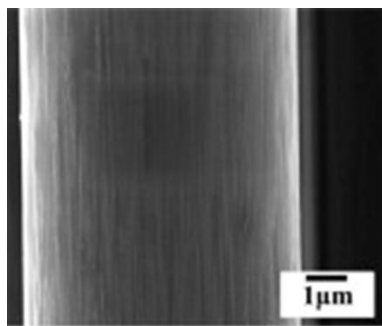

Figure 7.1: Scanning electron microscope image of an uncoated CF. Reprinted with permissions from Qui et al.[1].

Nowadays, they are mainly produced by using a polymeric precursor. Poly (acrylonitrile) (PAN) fibers represent the common choice with only around 10 wt.% of CF produced by using alternative feedstock such as biomass.

CFs are industrially produced by treating the precursors at high temperature to convert it into a carbonaceous structure. The procedure is usually a three stage process with a first step at around 300-350°C, the second at around 1000-3000°C and a final one for the surface oxidation. The first stage is called stabilization step and it is necessary to provide a rearrangement of CF bonding pattern. Dunham et al.[2] identified three main reactions occurring in this step: dehydrogenation, oxidation and cyclisation. After the first step, a partially carbonized structure

mainly made by a linear chain of pyridine moieties is formed accordingly with the original structure of PAN.

In the second stage, CF precursors are fully carbonized at temperatures ranging from 1000°C up to 3000°C in inert atmosphere under moderate pressure. In this stage, the heteroatoms such nitrogen and oxygen are removed from the carbon skeleton that start to rearrange itself in a graphitic like material. Several technologies have been used for this purpose ranging from tubular reactors to plasma processes.

Afterwards, CFs undergo to the last step that is an oxidation process to improve their adhesion properties by tuning their interphase chemistry. Oxidation can be achieved by immersion using watery solution of oxidating agents such as sodium hypochlorite or nitric acid, by using plasma treatment or by exposing the fibers to oxidating gases (i.e. air, oxygen, carbon dioxide ozone) in appropriate conditions of temperature and pressure.

High quality CFs produced by using PAN shows astonishing mechanical properties such as modulus of elasticity up to 531 GPa and a tensile strength up to 5600 MPa together with a high electrical and thermal conductivity.

The main drawback of CFs produced by using PAN is represented by their high cos but it was estimated that the CFs global market will reach up to 200 billion of dollar in 2022 due to the massive use in aerospace sector.

Several other CFs precursors have been investigated to simultaneously reduce the cost and the environmental impact. Recently, Mikkilä et al.[3] reported a comprehensive study on the use of both cellulose and lignin to produce good quality carbon fibers. Authors used the fibrous structure of cellulose and the aromatic content of the lignin to simulate the PAN precursor with quite remarkable results. Kubo et al.[4] blended lignin and polymers to improve the quality of the product but decreasing the cost price effectiveness of the use of natural feedstock. Kadla et al.[5] used only kraft lignin for the production of CFs proving that also amorphous wasted biopolymers could lead to the formation of CFs.

2.2 Glass fibers

GFs are a glass derived compound formed though stranding of silica-based or other formulation extruded into many fibers with a very small average diameter as shown in figure 2.
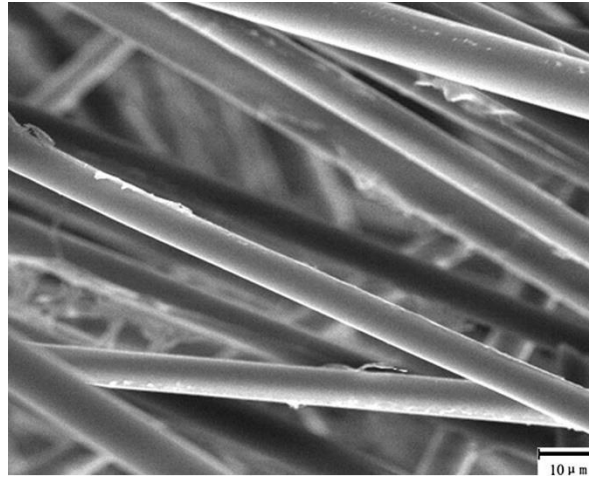
Figure 7.2: Scanning electron microscope caption of an uncoated GF. Reprinted with permissions from Di et al.[6].

There are two main types of GFs productive process: direct melt process and marble remelt process. Both of them are fed with solid form raw materials, silica and other inorganic oxides. Feedstock are mixed and melted together in a furnace at a temperature up to 1720°C. Afterwards for the marble process, the molten material is sheared and rolled into marbles and rapidly cooled. The blocks obtained could be easily remelted and extruded as fibers. On the contrary during the direct melt process, the molten feedstock in the furnace goes directly to the bushing for formation GFs. According to their compositions, GFs are classified as shown in Table 1.

Table 1: Composition of main GFs types.

	Composition [wt.%]									
	A	C	D	E	Advantex	ECR	AR	R	S-2	Quartz
SiO_2	63-72	64-68	72-75	52-56	59-62	54-62	55-75	56-60	64-66	>99.99
Al_2O_3	0-6	3-5	0-1	12-16	12-15	9-15	0-5	23-26	24-26	-
B_2O_3	0-6	4-6	21-24	5-10	<0.2	-	0-8	0-0.3	<0,05	-
CaO	6-10	11-15	0-1	16-25	20-24	17-25	1-10	8-15	0-0,2	-
MgO	0-4	2-4	-	0-5	1-4	0-4	-	4-7	0-4	-
ZnO	-	-	-	-	-	2-5	-	-	-	-
BaO	0-1	-	-	-	-	-	0-0.1	-	0-1	

Na$_2$O and K$_2$O	14-16	7-10	0-4	0-2	-	0-2	11-21	0-1	<0.3	-
TiO$_2$	0-0.6	-	-	0-0.8	-	0-4	0-12	0-0.3	-	-
Zr$_2$O$_3$	-	-		-	-	1-18	-	-	-	-
Li$_2$O	-	-	-	-	-	-	0-1.5	-	-	-
Fe$_2$O$_3$	0-0.5	0.8	0-0.3	0-0.4	-	0-0.8	0-5	0-0.5	0-0.1	-
F$_2$	0-0.4	-	-	0-1	-	-	-	0-0.1	-	-

GFs A are produced by using alkali-lime or soda lime glass and they are small sized. They can be boron doped and the maximum content of alkaline oxides is 0.8 wt.%.

GFs C contain calcium borosilicate which increases structural equilibrium in both basic or acidic corrosive environments.

GFs D contain a high percentage of boron, mainly as oxide, that leads to an enhancement of heat and thermal shock resistance. Furthermore, the presence of boron oxide decreases the dielectric constant making them suitable for the realization of optical cables.

GFs E are the most commonly used GFs and they are usually termed fiberglass. GFs E contain aluminum boron silicates and alkali oxide components such as aluminum oxide in concentration up to a maximum of 1 wt.%.

A GFs that was more recently made commercially available is the GFs Advantex produced since the early 1990s. Advantex are produced by using calcium aluminum silicates leading to a high content of calcium oxides. This induces a high corrosion resistance spreading GFs Advantex use in the oil and gas industry power plants, mining industry, and in marine applications as well as in wastewater and sewage systems.

GFs ECR are also called electronic GFs due to their lower electrical leakage rate and high surface resistance. They show a good waterproofing, high mechanical strength, electrical acidic and alkali corrosion resistance. They are boron oxide and fluorine free so they are more environmentally friendly than GFs E.

GFs AR, alkali resistant, were development targeting specifically concrete construction applications. GFs AR contain alkaline zirconium silicates and they are able to effectively prevent concrete cracking by improving strength and flexibility of concrete. Due to their

composition, they are very difficult to dissolve in any watery medium and they are practically not affected by pH changes.

Other GFs reported in Table 1 are quite close to the composition of GFs E-type glass fibers and they were developed for the aerospace and defense industries.

GFs S-2 are worth of a specific mention. They represent the top quality among GFs as they outperformed all the mechanical properties of GFs E as shown in Table 2. GFs S-2 are produced with a higher dense silica leading to the properties aforementioned.

Table 2: Comparison between mechanical properties of GFs E and GFs S-2.

	GFs-E	GFs S-2
Ultimate tensile strength [MPa]	521	4890
Elongation at Break [%]	4.8	5.7
Modulus of Elasticity [GPa]	72.3	89.6
Poisson Ratio	0.2	0.23
Shear Modulus [GPa]	30	35

2.3 Polymer based fibers

CFs and GFs are the most used but not the only fibrous materials for the production of epoxy based composites. Polymer based fibers (PBFs) represent the other great family of fibers currently available for the production of composites with improved properties. The most used materials for the production of these compounds are polyamides, polyesters, polyaniline and polysulfones PBFs classifications is tricky and properties dramatically change in each family with the change of molecular weight functionalization and preparation methodology. The great tuneability and the facile production of PBFs counterbalance the inferior performances compared with CFs and GFs. Furthermore, they could be used for the production of self-standing materials.

2.4 Epoxy resin

Epoxy resins are massively used for the production of reinforced plastics. Every year, worldwide market requires an increased amount of fibers containing composites for a lot of applications including automotiveand aerospace industry. Among thermoset polymeric matrix, epoxy resins represent a special class due to their impressive mechanical properties. Epoxy is generally composed by a diglycidyl ended prepolymer chain, an amine based hardener and additives to improve workability. One of the most common epoxy resin formulation is based on diglycidyl bisphenol, a monomer that reacts with the hardener accordingly to the scheme of figure 3.
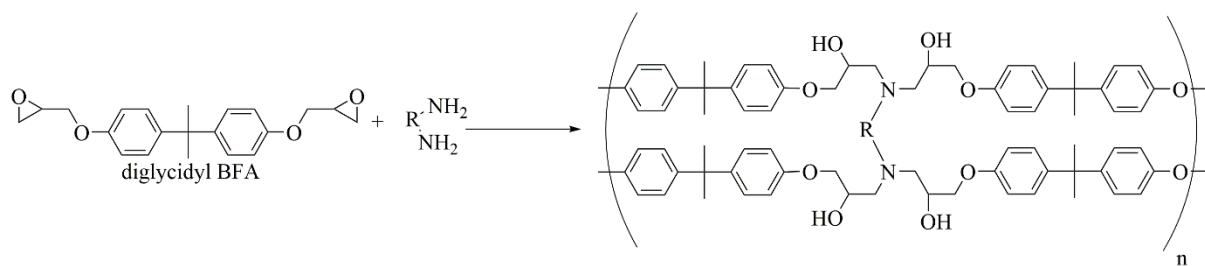

Figure 7.3: Schematic pathway for the polymerization of diglycidyl BFA based resin with amine curing agent.

Epoxy resin polymerization is a two-step process. During the first step low molecular weight chains having a poor reticulation are formed. This step is generally performed at room temperature. The second step is the most relevant and it is called curing step. During the curing the reticulation advance to completion and determines the final mechanical properties of the polymeric matrix. During the curing, the rheological properties of epoxy resin change accordingly to the increment in the reticulation degree. Epoxy matrix are generally resistant to corrosion and they are stable in a wide temperature range.

3. Synthetic fibers epoxy composites

Fibers reinforced epoxy composites have been used for decades for plenty of cutting edge applications where the mechanical properties of the filler paired to the stability of the epoxy matrix reached the optimum conditions for the application.

Several strategies have been applied to combine epoxy matrix with synthetic fibrous fillers ranging from longitudinal, woven mat, chopped ones. All were aimed to enhance the mechanical and tribological properties of the composites.

The main drawbacks in the production of fibers based epoxy composites are represented by brittleness and delamination. Synthetic fiber based epoxy composites brittleness is related to their high elastic modulus and low maximum elongation of the fibrous filler compared to those of the epoxy matrix. So, when fibers reach their failing point the polymer matrix is already beyond its limit. Accordingly, the composite undergoes a rapid crack propagation that can occur in three different modes. Mode I is due to stress orthogonal to the local plane of the crack surface, mode-II is related to the stress parallel to the crack surface but orthogonal to the crack front and mode-III is due to the stress parallel to the crack surface and to the crack front. For CFs and GFs containing epoxy composites the most relevant modes are I and II, due to the aforementioned mechanical properties. The delamination is the other key point that must be taken into account. It is due to the poor interphase bonding between the fibrous filler and the matrix. This create local weaknesses in bonding between fibers and matrix that under solicitation and aging lead to debonding.

The interactions occurring on the interphase region could be summarized by two main mechanisms. The first is represented by mechanical coupling or interlocking on microscale of the fibrous filler and polymeric matrix. The second one is based on physical interactions though both weak forces and direct covalent bonding between the fibers and the resin and the matrix. Both mechanical and physical interactions generate a complex region close to the surface of the fibrous fillers.

In the following subsection we present a comprehensive overview on the most remarkable results reached in the improvement of the properties of synthetic fibers containing epoxy composites taking into account the achievement and the remained unsolved issues.

3.1 Carbon fibers epoxy composites

CFs based epoxy materials have undergone extensive studies during past years. Commonly, purchased CFs are covered by a thin layer of a polymeric coating known as prepreg (pre-impregnated carbon fiber) material that retains the main features of neat CFs together with an improved workability.

Newcomb et al.[7] studied the time-temperature transformation diagram of a commercially CFs epoxy prepreg determining the gelation and vitrification behavior using small amplitude oscillatory shear and thermal analysis. Mphahlele et al.[8] studied the curing process by using differential scanning calorimetry and investigated the rheology of the system showing that a slow curing process leads to the best epoxy properties. Wu et al.[9] reported a study on the

interfacial improvement of CFs containing epoxy composites by tuning the content of curing agent during sizing process. Authors claimed to reach a maximum interfacial shear strength increment in the best conditions (15% stoichiometric curing agent in weight) of up to 30 %. Based on the deep knowledge of CFs behavior several authors improved their epoxy compositing by playing with many parameters.

Braided CFs improved significantly the toughness of epoxy composites, Tang et al.[10] comprehensively described the fracturing behavior of braided CFs epoxy composites aiming aerospace applications though explosive impact test. As clearly shown in figure 7.4 (b), CFs present in the surface ablation region were sheared off and pulled out. Furthermore, a damaged region was observed under the ablation layer (Figure 7.4 a). Fracture morphology observed in this region revealed that the epoxy matrix area between CFs showed crack growth traces similar to a "river pattern". This morphology was related to a brittle fracture and the direction of the river pattern was toward the direction of crack spreading. The fracture process showed that damage formation occurred by CF shearing off and epoxy flaking off under the ablation region together with the propagation of a macro-crack path along the sheaf interface under the ablation region.
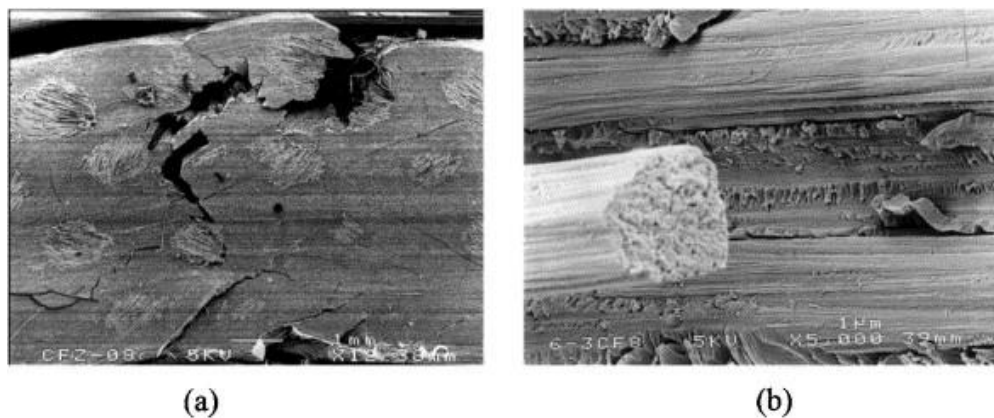

(a)   (b)

Figure 7.4: Scanning electron microscopic captures of CFs composites after failing under static loading: (a) zigzag cracks in cross-section of the specimens; (b) CF pull-out from the epoxy matrix as reported by [10].

Khan et al.[11] mixed CFs and GFs in different percentage enhancing the tensile strength up to 10 times and the epoxy glass transition from 71 °C of up to 110 °C. Bisht et al.[12] studied the role of 3-D network of carbon nanofillers in improving the mechanical properties of CFs epoxy laminated composite. Authors tested graphene flakes, nanodiamond and carbon nanotubes achieving an interlaminar and intralaminar mode I fracture toughness improvement of up to 260% and 5%, respectively by using a with 1:1:2 ratio of carbonaceous fillers.

Similarly, both tensile and interlaminar shear strength improved of up to 60% and 16%, respectively. This positive effect was induced by the high surface area of carbon fillers that induces an effective adhesion between matrix and CFs.

Hawal et al.[13] proved synergetic effect of rubber on the tensile and flexural properties of graphene added CFs based epoxy composite. Authors produced CFs epoxy composites containing from 0.1 wt.% to 0.3 wt.% of graphene and the same graphene based composites with an addition of natural rubber of up to 30 wt.%. The addition of 10 wt.% of rubber improved the tensile and flexural strength of the hybrid composite of up to 20 wt.% compared with the others. Srivastava et al.[14] coated CFs with graphene nanoplates and used them for the production of epoxy composites. Authors achieved a noticeable improvement of the flexural strength of the laminates due to the improvement of the interfacial properties of the CFs.

Sha et al.[15] used a different approach based on the low-temperature plasma assisted growth of vertical graphene plates on the CFs. Authors used a plasma-enhanced chemical vapour deposition operating at 400 °C. The presence of graphene nanoplates altered CFs surface roughness, wettability, tensile strength, and interfacial shear strength between CFs and epoxy matrix improving the mechanical properties of CFs reinforced composites through the development of a multifunctional hierarchical structure.

Li et al.[16] added reduced graphene oxide nanoplateletss (RGON) to CFs epoxy composites for evaluating not only the mechanical properties but also the electromagnetic shielding ones. Authors used unidirectional CFs mixed with the nanofiller to produce epoxy laminate composites. The addition of reduced graphene oxide improved both the mechanical properties and electromagnetic shielding effectiveness of the composites. Although a worsening in the flexural strength occurs, the addition of reduced graphene nanoplates improves the mechanical property and EMI shielding effectiveness of the composites without sacrificing their thermal properties.

Kim et al.[17] added graphene to highly loaded CFs epoxy composites and investigated the interactions between the fillers and the matrix. They achieved a 250% improvement of the interlaminar shear strength and of 140% of the fracture toughness. This was due to the $\pi-\pi$ interactions between graphene, CFs and epoxy resin that induced a good filler dispersion and crack bridging.

The interaction between nanostructured carbon, CFs and epoxy resin were deeply investigated by Wu et al.[18] by using poly ether amine binder and graphene oxide. The first stage of the process involved the chemical bonding of amine binder on the CFs surface. Afterwards, polar

residues of tailoring agent interact though hydrogen bonding and dipole interactions with graphene oxide. These interactions lead to an increment of interfacial shear strength by using covalent bonded CFs of up to 48% while the ionic interacting ones showed a total improvement of 38%. The mixed interactions dramatically decreased the properties of the material due to an un-effective interfacial modification of CFs.

Wu et al.[19] added not only graphene oxide but also nanozirconia to CFs based epoxy composites. Authors achieved an improvement of interfacial shear strength up to 42 % due to a more effective cracks deflection and energy dissipation due to an interfacial synergetic interactions of hydrogen bonding and π-π stacking.,

The simultaneous addition of nanosilica and the tailoring of epoxy matrix with silicon rubber was studied by Li and co-workers[20]. Authors claimed an increment in the tensile strength of epoxy composites by using a 5 wt. % of nanosilica of up to 49 % and a tensile strength improvement of up to 17 %. This was due to the combined ability of nanosilica and silicon rubber cooperating to transfer the stress from epoxy matrix to CFs.

Carbon nanotubes were also largely used for the CFs epoxy resin improvement as reported for example by Park et al.[21]. Authors modified single walled carbon nanotubes by oxidazing their surface using an ozone-treatment on the surface properties. The surface modified carbon nanotubes improved the interlaminar shear strength and fracture toughness up to 80% and 55% respectively.

Yao et al.[22] directly grow carbon nanotubes on CFs prior of the realization of composites by chemical vapor deposition technique. Authors improved interlaminar shear strength of up to 24% showing that the fracture surface morphology of the composites and the relative hardness modulus distribution at the interface was closely correlate with morphology of carbon nanotubes.

The carbon nanotubes improvement was also investigated by simulation approach by Reddy et al.[23] using 3-D finite element model achieving result in good agreement with experimental data.

The interfacial properties are a capital issue in CFs epoxy based materials and plenty of materials have been used such as carboxymethyl cellulose, polymeric films, amphiphilic molecules and hybrid formulations.

Modification of interfacial interaction between CFs and epoxy matrix drives the fracture process of CFs composites. As reported by Muralidhara et al.[24], CFs architecture marginally affected the mechanical properties of related epoxy composites. Substantial differences were not observed by using T700 or T800 CFs.

Cheng et al.[25] produced uniformly aligned polyethersulfone CFs simultaneously improving mode I and mode II fracture toughness. Data reported showed that polyethersulfone filaments were not dissolvable at the temperature of the resin infusion process but only during the curing process. Authors achieved an enhancement of up to 120% and 69% on mode I and II fracture toughness respectively. The fracture surface analysis enlightens that the interlaminar fracture toughness improvement was due to the interlaminar structures induced from the phase separation of polyethersulfone in epoxy resin. Additionally, authors observed an increment of the interlaminar shear strength and compression after impact of 18 and 43% respectively together with a limited enhancement of both tensile and flexural strength.

Wang et al.[26] investigated the effect of nylon microparticles on Mode-I interlaminar fracture toughness of CFs epoxy composites using both nylon 6 and 12. As clearly emerged from experimental data, the particle size is the driving force that regulates the toughness but only when the filler/epoxy matrix interfacial bonding is strong enough after the curing step. A good interfacial interaction allows the nylon particles to be plastically deformed while bridging the crack. Similarly, Quan et al.[27] observed an analogue behavior studying mode-II fractures in of aerospace-grade CFs containing epoxy using polyethyleneterephthalate, polyphenylenesulfide and polyamide-12.

The addition of polymeric additives could also improve the impact resistance as proved by using polyurethane and silane sized as additives. As proved by Salifu and co-workers[28] CFs based epoxy resin could compete with aluminium 3105-H18 performances in high velocity impacts response.

Zhang et al.[29] found a correlation between the CFs plane orientation and the dynamic impact loadings behavior of related composites. Showing that failure mode is ductile type one under higher strain rates. Marangonni et al.[30] studied the fatigue behavior of woven CFs showing the huge influence on the damage mechanisms and the fatigue life of waviness. This morphological feature deeply affected tension/compression and compression/compression loadings and only in less appreciable way the stiffness loss.

Hendlmeier et al.[31] studied the conductivity, current density, and sizings applied to CFs during manufacture and the related effect on the epoxy matrix adhesion. Authors explored the parameters for a large set of industrial CFs with an electrochemical oxidation treatment using ammonium hydrogen carbonate as electrolyte a conductivity value of the electrolytic medium varied between 8 and 24 μS/cm while current density ranged between 0.5 and 1.5 A/m^2. Afterwards, CFs were included into epoxy matrix and interphase properties were evaluated showing that oxidation degree did affect appreciably the electrochemical parameters but the

typology of residual functionalities induced an enhancement of interfacial properties.

Hiremath et al.[32] used low cost textile-grade CFs for the production of effective epoxy composites for the automotive sector. Ming et al.[33] developed a self-heating 3D printed continuous CFs containing epoxy mesh for wind turbine deicing application. Authors achieved the conductivity of up to 131 S/cm at 25 °C that reached 148 S/cm at 200 °C. Additionally, mesh reinforcement reduced the deicing time by 85%.

CFs based epoxy composites undergo an aging process. Behera et al.[34] evaluated the hygrothermal aging effect on both physical and mechanical properties of CFs epoxy material at high temperature and humidity. Authors immersed the laminates into water at 70 °C for more than 6 months. Afterwards, author observed that the moisture absorption follows a two-stage model where diffusion rate increased proportional to square root of immersion time followed by step of slowing down close to the saturation. a sluggish phase up to saturation. Aged materials mechanically failed due to the worsening of the bonding interaction between filler and matrix. A reduction of aging effect could be observed by adding an additive such graphene nanoplates or graphene aereogel as reported by Chiang et al.[35].

The increment of CFs use together with their aging have promoted several approaches to recycled CFs based epoxy composites under the principles of the circular economy[36]. Accordingly several studies tried to exploit the full potential of recycled CFs epoxy materials as filler for construction building or after the degradation of polymer matrix as filler for the production of new composites.

3.2 Glass fibers epoxy composites

GFs epoxy based composites are widely used in plenty of applications ranging from naval to aeronautic industries, insulation materials and lightweight components production. Joshi et al.[37] compared GFs with natural fibers production and applications showing that their log working life abundantly counterbalances the poor environmentally friendliness of their production.

The research work of Yang et al.[38] enlighten some key issues in the failure process of GFs containing epoxy composites by using IITRI method[39]. As shown in figure 7.5 (a), compressive loading resulted in the formation of a shear band during IITRI compression failure of the 0/90° non-crimp laminate. There was no relative displacement of the fibres across the failure and post-failure examination showed that the fracture band was oriented at 45° to the loading direction.

In figure 7.5 (b) IITRI compression failure in the plain weave fabric composite showed the appearance of interlaminar stresses due to local delamination together with a reduction of the local transverse support for the GFs and an overload in adjacent region of low waviness. In this case, a global microbuckling took place and delamination and global buckling could be ascribed to a bending failure due to interlaminar stresses failing leading to relatively low compressive strength.

Dense stitching GFs showed a different failure mode as shown in figure 7.5 (c). A typical failure mechanism for the densely stitched biaxial woven composite was observed with localized failure in the form of a kink band close to the crack initiation.
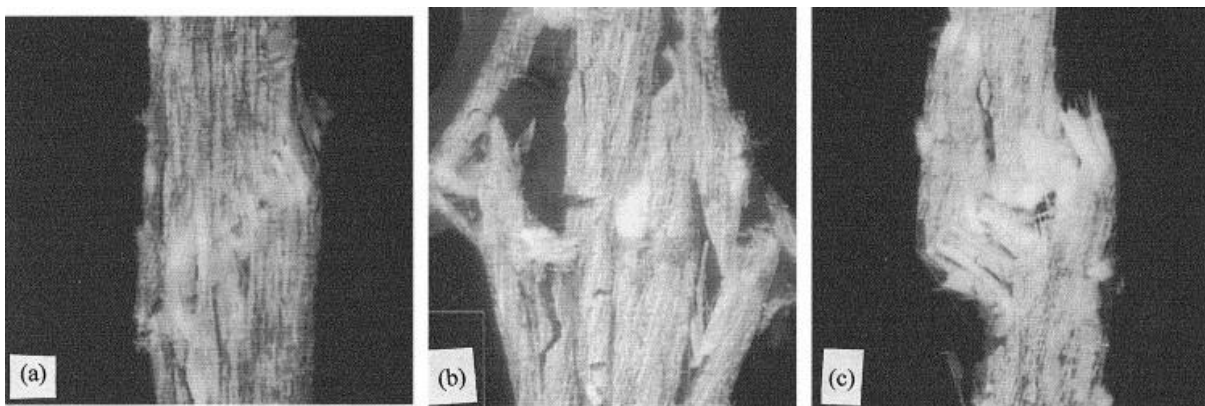

Figure 7.5: Compressive failure in: (a) non-crimp laminate composite; (b) unstitched woven composite; and (c) biaxial stitched (stitching lines 5 mm apart) woven composite as reported by Yang et al.[38].

Anjaneyulu et al.[40] studied the mechanical behavior of GFs-E epoxy composite laminates according to ASTM standards. Authors showed the linear relationship between the composites strength of composite and the GFs/matrix volume fractions. Furthermore, GFs orientation dramatically contribute to the tensile strength of epoxy composite. A more exhaustive study on the relation between GFs volume fraction and composites properties was reported by Swapnil et al.[41]. Authors investigated a GFs volume fraction of 40 v/v%, 50 v/v% and 60 v/v% in the total composition showing that the magnification of mechanical properties occurred for a volume fraction close to 50 v/v%. Minty et al.[42] evaluated the relevance of the hardener/epoxy precursor ratio on the interfacial strength GFs based composites. The interfacial shear strength, glass transition temperature, storage modulus and linear coefficient of thermal expansion were strongly related to the hardener/epoxy component ratio. Authors hypothesized that residual radial compressive interfacial stresses were influenced by the chemical bond network formed during the curing process. Similarly, Chakraverty et al.[43]

tested the thermo-mechanical response of GFs-E epoxy composites after a plasma treatment of GFs. Authors reported an improvement of the inter laminar shear strength due to the improvement of curing process after the surface treatment. A different approach was for the first time described by Sangermano et al.[44]. Authors reported the UV-crosslinking of aGFs reinforced epoxy composites. Authors established a radical induced cationic frontal polymerization with a very fast kinetic that preserved the good thermo-mechanical properties. Another modification to the GFs composites was reported by Sheinbaum et al.[45] that used a brominated epoxy derivatives. The addition of brominated material to a non-brominated matrix induced an increment in glass transition temperature, toughness, strength, and elongation. Authors hypothesized an energy dissipating mechanism based on rough fracture surfaces, due to high interfacial bonding between the epoxy matrix and GFs.

GFs/epoxy composites interfacial properties can be easily tailored by adding an additive to the epoxy resin as in the case of CFs. One of the most used additive class is represented by graphene and related materials. Ojha et al.[46] added graphene nanoplatelets to pultruded epoxy composites. Authors used unidirectional GFs pultruded by pulling the continuous GFs through the graphene containing epoxy resin. Authors observed an increment in ultimate tensile strength and the longitudinal modulus of up to 12% and 7% respectively by adding 0.1 wt.% graphene nanoplatelets. Prusty et al.[47] extensively studied the effect of graphene oxide loafing on GFs epoxy composites. Authors reported that the addition of graphene oxide up to 0.5wt.% induced a flexural strength improvement of up to 21%. This was due to the interface interactions between graphene oxide/GFs/epoxy matrix that altered the viscoelastic properties of the composites and failure mechanisms. About failure mechanisms and creep propagation, Ghosh et al.[48] published a very interesting computational study based on the use of time-temperature superposition principle to study the multi-layered graphene GFs epoxy composites. Flexural tests running in a temperature range from -196°C up to 110 °C showed that the best flexural performances could be achieved by using 0.1 wt.% graphene oxide. The computational approach evaluated in billions of year the time required for the naturally formation of cracks in the composites at 30°C. Domun et al.[49] proved that GFs epoxy matrix mixed with graphene nanoplates could resist to ballistic impact in a more effective way than common GFs epoxy composites dissipating up to 17% more energy.

Jena et al. [50] added together multi-layer graphene and nanosilica with a ratio close to 2 to GFs epoxy composites inducing an enhancement in flexural strength. Hua et al.[51] combined graphene oxide with carbon nanotubes increasing the transverse tensile strength of GFs epoxy

materials more than neat graphene oxide or carbon nanotubes addition. Anand et al.[52] studied the effect of neat and oxidized carbon nanotubes on creep propagation of laminated GFs epoxy materials in a temperature range from 50°C to 110°C. Authors clearly demonstrated the positive effect of surface modified carbon nanotubes. Similarly, Gaurav et al.[53] improved interlaminar strength of up to 41% GFs epoxy composites by adding carbon nanotubes modified by using arc discharged techniques.

The good dispersion of carbon nanotube is another key issue for the realization of improved GFs epoxy materials. Ismail et al.[54] evaluated this effect by using carbon nanotubes dispersed into watery media with different surfactants. Well dispersed carbon nanotubes could be used to detect the defects inside the GFs epoxy materials as demonstrated by the study of Slobodian et al.[55]. Authors use a carbon nanotubes buckypaper embedded in a polyurethane membrane to induce strain self-sensing property. This integrated sensor allowed a monitoring process due to the formation of micro-sized cracks pattern that altered its conductivity. The addition of carbon nanotubes to GFs epoxy materials improved also the microwave shield effect.

Carbon nanotubes could be combined with inorganic fillers such as nanoclays as reported by Sen et al.[56]. Authors improved the flexural modulus of up to 12% by using a carbon nanotube/nano clay ratio of 0.1 compared with GFs composites containing only the same amount of carbon nanotubes. Bozkurt et al.[57] used nanoclay up to 3 wt.% to improve GFs-S epoxy composites buckling loads, both axial and lateral, achieving an improvement of up to 9%. The improvement of flexural properties could magnified by using nanoclay and nanosilica simultaneously with a ratio of 2 and a total loading of 3 wt.% as reported by Nayak et al.[58]. These materials showed a good improvement of flexural strength but a decrement of glass transition.

Kumar et al.[59] combined GFs epoxy materials with cellulose nanocrystals increasing the storage modulus of up to 56%, the flexural modulus of up to 50%, the flexural strength 55%, the tensile modulus of up to14% and the tensile strength of up to 24%. These improvements were due to the strengthening of the interface interactions between GFs and epoxy matrix mediated by the presence of cellulose nanocrystals.

Plenty of nanofillers could be added to improve the interfacial interaction between epoxy resin and GFs such as fly ash, alumina, barium titanate nanoparticles, seashell maize, zinc oxide, carbon black and polymers.

Other studies have proved that the addition to epoxy matrix of compounds such as 2-Methylimidazole or encapsulated urea-formaldehyde formulation could lead to GFs epoxy composites with self-healing properties. Similar results could be achieved by treating the GFs fibers using silane and silane derivatives.

Silane treatment could also be used to improve the inter laminar shear strength of GFs composites as proved by Prakash et al.[60]. Authors treated GFs-E with a silane derivative, teh3-Aminopropyletrimethoxysilane. Surface treatment induced inter laminar shear strength improvement of up to 155 MPa by using a 20 v/v% of GFs-E.

The overall tuning of interfacial properties is aiming to improve the durability of the GFs epoxy materials. Mohamed et al.[61] evaluate the bending fatigue behavior of GFs epoxy composites correlating the properties of GFs with the outcomes.

GFs composites aging was studied under different conditions. Ahankari et al.[62] evaluate the accelerated aging effect of sea water on GFs epoxy coating used to insulate steel pipes. Authors reported a reduction of 43% of strength and 15% modulus after 40 days of immersion at 80°C in sea water proving that tough conditions could dramatically reduce the GFs composites performances.

Similarly, Fitriah et al.[63] studied the compressive behavior during hydrothermal ageing of GFs epoxy composite pipes from 60°C to 80°C for up to 1500h. Results showed that the mechanical properties of the composites decreased with the increment of aging temperature.

As for CFs, GFs epoxy composites could be recycled through thermochemical process. As reported by Hiremath et al.[32] recovered CFs are not up to mark compared with neat GFs. Accordingly, the authors proposed the addition of carbon nanotubes to the matrix to improve the mechanical properties of related composites.

3.3 Polymers-based fibers epoxy composites

Polyamides are the most diffuse PBFs due to the facile production and good mechanical properties of commercial materials such as Nylon type ones. Polyamides based epoxy composites have been deeply investigated for a wide range of application with a specific focus on compounds based on aromatic amines. In fact the ones containing aromatics amines are the most widespread due to high flame resistance and superior mechanical properties.

Aromatic poly(amide) fibers takes the generic name of aramid. The most known aramids are Kevlar™, Nomex™ and Twaron™ and they are used for production of bullet shield textiles. Generally, aramid fibres are relatively light with a density close to 1.4 g/cm3, stiff with a

Young's modulus up to 190 GPa and strong with tensile strength reaching of up to 3.6 GPa. Additionally, aramid fibres showed good resistance to both impact and abrasion damage.

As for textiles, the main application of aramid containing epoxy composites is represented by the anti-ballistic use as reported by Braga et al.[64]. Authors tested an aramid based epoxy multilayered armor by using high energy bullet 7.62 mm. The shielding material was realized by using several layers of epoxy composites and ceramic and compared with neat ceramic and neat army grade aramid (Kevlar®). Results clearly showed that epoxy composites met the requirements with comparable ballistic performance as the neat materials with a saving of up to 14% on the final cost-price. These good results were achieved by the unique stress absorption and subsequent deformation of the epoxy composite. As reported by Komai et al.[65], this is a crucial point. Authors studied the stress waveform and water absorption on the tension–tension fatigue fracture behavior on ±45° angle-ply laminates of aramid fibers based epoxy composite. Experiments run on dry samples showed a higher fatigue strength under negative pulse waveform than that under the positive pulse one. Fibers rotations on the longitudinal direction was evident by creep deformation caused by the cyclic loading superimposed on the maximum stress hold time inducing a decrement of the compliance and a simultaneous increment of the fatigue life under the negative pulse waveform. Authors observed a marked decrease of aramid/epoxy resin interfacial strength due to water impregnation that caused the swelling of the matrix with a decrement of the static tensile and fatigue strength. Moisture is not the only agent that could compromise the integrity of aramid based epoxy composites. Xu et al.[66] reported the damaging process of aramid composites by microwave irradiation. Authors used energy density ranging from $5.36 \ W/cm^2$ to $16.09 \ W/cm^2$ with exposure times from 2 min to 10 min studying several parameters such as equilibrium temperature, power thresholds and damage morphologies of quasi-isotropic laminates and unidirectional composites. Results reported clearly proved that quasi-isotropic laminates displayed a greater shielding to microwaves compared to unidirectional composites with same thickness. Furthermore, the quasi-isotropic materials showed a fast temperature increment with circular damaged regions in the region of maximum microwaves irradiation.

Laminate aramid based epoxy composites mechanical features could be improved by adding nanofillers into the epoxy matrix as above mentioned for both GFs and CFs. A more detailed study on aramid interaction with epoxy resin was reported by Qi et al.[67]. Authors evaluated the interaction between fibres and matrix by a model that took simultaneously into account the aramid skin and the core structure. Authors collected also an experimental set of data that

showed the splitting of aramid fibres above the fracture surfaces. The fiber fracture was caused by tensile splitting, which was a typical fracture characteristic of the aramid fibres independently from the loading conditions. By combining the empirical data with the model, authors proved that the failure mechanism was due to an extensive interfacial failure coupled with some skin fibrils detached from the bulk aramid fiber.

Accordingly to the relevance of interfacial interaction with epoxy resin, aramid fibres were modified in order to appropriately tailor the fiber surface. Liu et al.[68] modified aramid fibres by using ultrasonic treatment. Ultracavitation oxidized the aromatic moieties of aramid fibres promoting the creation of a solid network of hydrogen bonds in the composites. These additional interactions greatly improved the interlaminar resistance.

Similarly, Fan et al.[69] functionalized the fibres surface by plasma treatment. The low temperature plasma treatment on interfacial adhesion of aramid fiber type III reinforced epoxy composites was studied and optimized through statistical analysis by using orthogonal experiments. After plasma treatment, authors observed an improved interfacial shear strength together with single filament tensile stress decrement through single-fiber composite fragmentation tests. Authors reported that the observed behaviour was mainly due to i) rise in Van der Waals interactions due to increased surface area of post-treated fibres, ii) mechanical interlocking of the rough fibres surface with the epoxy matrix, iii) improved fibres surface wettability and iv) chemical bonding between oxygen-containing groups on the functionalized aramid and epoxy matrix.

Subsequently, the interfacial shear strength of aramid based epoxy composites increased of up to 38.1% compared with untreated based composite, reaching the value of 30.44 MPa together with a decrement of the tensile strength of up to 5.8%. These results were achieved by using a treatment power of 67.5 W for 11 min and a pressure of 2500 Pa.

The chemical modification of aramid was also performed through a multistep process as reported by Cheng et al.[70]. Firstly, a direct fluorination was used to generate aromatic C-F single bond on aromatic moieties by using fluorine at 100°C. Afterwards, a nucleophilic substitution reaction between the C-F and 3-aminopropyltriethoxysilane was induced to insert a silicon based residue on the surface of aramid. Then, ethoxy residue were hydrolysed directly on silicon producing a silicon tailored aramid fibres used for the realization of epoxy composites. Through this procedure the interfacial wettability of resin to fiber was modified

due to a surface energy increment of up to 25.01mN/m. This lead to an increment of interfacial shear strength up to 46.7 %.

Xing et al.[71] grafted aramid fibres in diethanolamine and epichlorohydrin promoting the formation of epoxy moieties directly bonded to aramid. Accordingly, authors observed that those sites acted as polymerization starter during epoxy resin curing. As a direct consequence of epoxylation, the resulting aramid based epoxy composites showed an increase of both interlaminar shear strength and flexural strength of composites up to 511 MPa and 479 MPa respectively.

Non aromatic polyamine fibres were used by Meshram and co-workers[72] to test the effect of combination between Nylon 6,6 and epoxy resin. Authors prepared the Nylon based composites by using a simple hand layup technique that consists in the application of the epoxy resin on Nylon fibres by using an handroller. The tensile test showed a remarkable effect of Nylon fibres that induced an improvement of ultimate tensile strength from 266 N to 1311, of Young's modulus from 3 MPa to 763 MPa and of yield stress from 4 MPa to 19 MPa. Simultaneously, authors observed a drastically decrement of maximum elongation from 1.2% to 0.5 %.

Palazzetti et al.[73] investigated the effect of electrospun Nylon 6,6 fibres on mode I and the mode II fracture mechanics of modified epoxy laminates. Authors produced specimens composed of twenty plies of woven carbon fibers/epoxy resin prepregs and inserted Nylon fibres mat in the mid-plane of beam shaped specimens Results clearly showed that NYLON fibres i) reduced maximum opening load that can be supported by stressed interface, ii) increased the absorbable mechanical energy during the overall test. Nonetheless, the presence of Nylon fibres did not affect the flexural modulus but enhanced the maximum value of the force that was required to initiate the longitudinal crack propagation. Furthermore, the presence of Nylon fibres induced a higher absorption of mechanical energy during interlaminar crack propagation. Considering the overall data set, authors concluded that the poly(amides) fibres enhanced composite delamination strength and damage tolerance due to a reduced damage progression sensitivity under mode I and mode II of fracture.

Moving on another class of polymers, polyesters were also considered as fibrous matrix for epoxy based composites. Among them poly(ethylene terephthalate) is one of the most used due to the good mechanical and chemical properties. Teh et al.[74] reported a very comprehensive study about the poly(ethylene terephthalate) fibres to toughen an intrinsically brittle epoxy

resin with high glass transition temperature. Authors achieved a strong fiber/epoxy matrix adhesion by tailoring poly(ethylene terephthalate) fibres surface though a treatment with NaOH. Compared with neat epoxy resin, the fracture toughness of poly(ethylene terephthalate) fibres based epoxy composites is almost doubled by using a fibres loading of only 1 wt.%. As shown in figure 7.6, the tailored poly(ethylene terephthalate) fibres presented a very high adhesion to the epoxy matrix without any appreciable debonding or delamination phenomena.
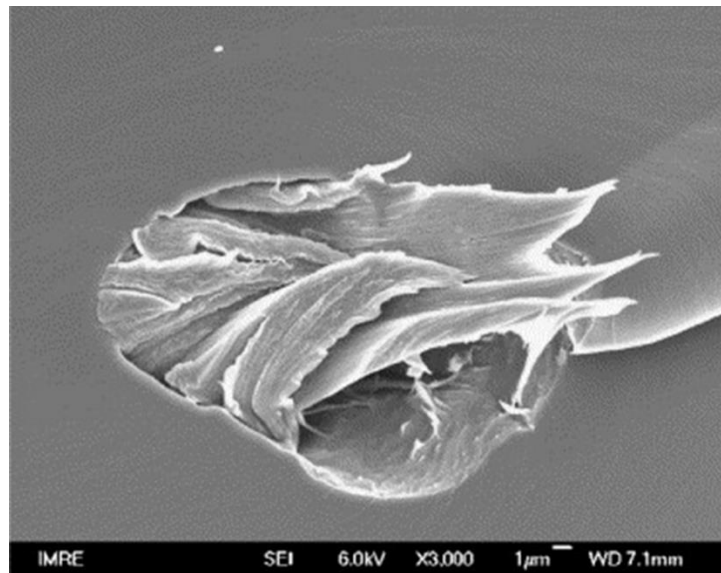

Figure 7.6: Scanning electron microscopic capture of poly(ethylene terephthalate) embedded into a brittle epoxy matric as reported by Teh et al.[74].

The last class of PBFs extensively used as fibrous component of epoxy composites is represented by polyolefins fibres.

Demir et al.[75] produced a composite mixing epoxy resin with electrospinned poly(styrene) fibres. The quasi-static and high strain rate compression stress vs strain curves of poly(styrene) fibres reinforced and neat epoxy resin showed the increment of both the elastic modulus and compression strength of the epoxy matrix after fibres addition. The increment of compressive strength of the poly(styrene) fibres based epoxy composites at high strain rate was the main feature of the strain rate sensitive compressive strength of the epoxy matrix. Conversely, the increment of strength at the quasi-static strain rate was mainly due to poly(styrene) fibres addition. The fracture surface of the specimens showed debonded fibres and a relatively flat fracture areas of the epoxy matrix with an evident strong interlocking on the nanometer-scale between the poly(styrene) fibres and the epoxy matrix. This was due to intrusions in the

porosities on the fibres surface that led to an improvement of the load transfer from matrix to fibres.

4.Conclusions and perspective on carbon and glass fibers epoxy composites

In this chapter, we established some key point̶s that can be used to better navigate the huge field of synthetic fibers composites reign:

i)   the interphase between CFs/GFs and epoxy matrix plays a crucial role in the production of tough long-life composites;

ii)   addition of nanofiller reduces the intrinsic brittleness of fibers-based composites;

iii)   surface tailoring of synthetic fibers promotes an improved interaction with the epoxy resin.

These points represent both the starting point and the final aim of the overall CFs and GFs research in the field of material sciences.

PBFs represent the other face of synthetic fibres based composites. Even if PBFs performances cannot reach CFs and GFs based materials properties, their affordability represents an unneglectable advance to spread their use in large markets around the world.

Furthermore, we believe that the future of the synthetic fibers will necessarily be encompassed in circular economy with an improved attention for the environmental impact of all production steps: from raw materials to productive plants, from ready to sell materials to end-of-life disposal.

References

[1] W. Qin, F. Vautard, L.T. Drzal, J. Yu, Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber–matrix interphase, Composites Part B: Engineering, 69 (2015) 335-341.
[2] M. Dunham, D. Edie, Model of stabilization for pan-based carbon fiber precursor bundles, Carbon, 30 (1992) 435-450.
[3] J. Mikkilä, M. Trogen, K.A. Koivu, J. Kontro, J. Kuuskeri, R. Maltari, Z. Dekere, M. Kemell, M.R. Mäkelä, P.A. Nousiainen, Fungal Treatment Modifies Kraft Lignin for Lignin- and Cellulose-Based Carbon Fiber Precursors, ACS omega, 5 (2020) 6130-6140.
[4] S. Kubo, J. Kadla, Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties, Journal of Polymers and the Environment, 13 (2005) 97-105.
[5] J. Kadla, S. Kubo, R. Venditti, R. Gilbert, A. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon, 40 (2002) 2913-2920.

[6] X. Di, Y. Gao, C. Bao, Y. Hu, Z.g. Xie, Optimization of glass fiber based core materials for vacuum insulation panels with laminated aluminum foils as envelopes, Vacuum, 97 (2013) 55-59.

[7] B.A. Newcomb, Time-Temperature-Transformation (TTT) diagram of a carbon fiber epoxy prepreg, Polymer Testing, 77 (2019) 105859.

[8] K. Mphahlele, S.S. Ray, A. Kolesnikov, Cure kinetics, morphology development, and rheology of a high-performance carbon-fiber-reinforced epoxy composite, Composites Part B: Engineering, 176 (2019) 107300.

[9] Q. Wu, R. Zhao, J. Zhu, F. Wang, Interfacial improvement of carbon fiber reinforced epoxy composites by tuning the content of curing agent in sizing agent, Applied Surface Science, 504 (2020) 144384.

[10] G. Tang, Y. Yan, X. Chen, J. Zhang, B. Xu, Z. Feng, Dynamic damage and fracture mechanism of three-dimensional braided carbon fiber/epoxy resin composites, Materials & Design, 22 (2001) 21-25.

[11] Z.I. Khan, A. Arsad, Z. Mohamad, U. Habib, M.A.A. Zaini, Comparative study on the enhancement of thermo-mechanical properties of carbon fiber and glass fiber reinforced epoxy composites, Materials Today: Proceedings, (2020).

[12] A. Bisht, K. Dasgupta, D. Lahiri, Investigating the role of 3D network of carbon nanofillers in improving the mechanical properties of carbon fiber epoxy laminated composite, Composites Part A: Applied Science and Manufacturing, 126 (2019) 105601.

[13] T.T. Hawal, M.S. Patil, R.M. Kulkarni, S.N. Nandurkar, Synergetic effect of rubber on the tensile and flexural properties of graphene based epoxy-carbon fiber hybrid nanocomposite, Materials Today: Proceedings, 27 (2020) 515-518.

[14] A.K. Srivastava, V. Gupta, C.S. Yerramalli, A. Singh, Flexural strength enhancement in carbon-fiber epoxy composites through graphene nano-platelets coating on fibers, Composites Part B: Engineering, 179 (2019) 107539.

[15] Z. Sha, Z. Han, S. Wu, F. Zhang, M.S. Islam, S.A. Brown, C.-H. Wang, Low-temperature plasma assisted growth of vertical graphene for enhancing carbon fibre/epoxy interfacial strength, Composites Science and Technology, 184 (2019) 107867.

[16] Y. Li, S.-t. Liu, J.-m. Sun, S. Li, J.-l. Chen, Y. Zhao, Effects of the oxygen content of reduced graphene oxide on the mechanical and electromagnetic interference shielding properties of carbon fiber/reduced graphene oxide-epoxy composites, New Carbon Materials, 34 (2019) 489-498.

[17] J. Kim, J. Cha, B. Chung, S. Ryu, S.H. Hong, Fabrication and mechanical properties of carbon fiber/epoxy nanocomposites containing high loadings of noncovalently functionalized graphene nanoplatelets, Composites Science and Technology, 192 (2020) 108101.

[18] Q. Wu, J. He, F. Wang, X. Yang, J. Zhu, Comparative study on effects of covalent-covalent, covalent-ionic and ionic-ionic bonding of carbon fibers with polyether amine/GO on the interfacial adhesion of epoxy composites, Applied Surface Science, 532 (2020) 147359.

[19] Q. Wu, R. Zhao, T. Xi, X. Yang, J. Zhu, Comparative study on effects of epoxy sizing involving ZrO2 and GO on interfacial shear strength of carbon fiber/epoxy composites through one and two steps dipping routes, Composites Part A: Applied Science and Manufacturing, 134 (2020) 105909.

[20] S. Li, D. Chen, C. Gao, Y. Yuan, H. Wang, X. Liu, B. Hu, J. Ma, M. Liu, Z. Wu, Epoxy-functionalized polysiloxane/Nano-SiO2 synergistic reinforcement in cryogenic mechanical properties of epoxy and carbon fiber reinforced epoxy laminate, Composites Science and Technology, 198 (2020) 108292.

[21] S.-J. Park, S.-J. Park, Effect of ozone-treated single-walled carbon nanotubes on interfacial properties and fracture toughness of carbon fiber-reinforced epoxy composites, Composites Part A: Applied Science and Manufacturing, 137 (2020) 105937.

[22] Z. Yao, C. Wang, R. Lu, S. Su, J. Qin, Y. Wang, Z. Ma, H. Wei, Q. Wang, Fracture investigation of functionalized carbon nanotubes-grown carbon fiber fabrics/epoxy composites, Composites Science and Technology, 195 (2020) 108161.

[23] B.R. Reddy, K. Ramji, Modeling and Evaluation of Effective Elastic Properties of Carbon Nanotubes Reinforced Carbon Fiber/Epoxy Multiscale Composites, Materials Today: Proceedings, 21 (2020) 1099-1103.

[24] B. Muralidhara, S.P. Kumaresh Babu, B. Suresha, The effect of fiber architecture on the mechanical properties of carbon/epoxy composites, Materials Today: Proceedings, 22 (2020) 1755-1764.

[25] C. Cheng, Z. Chen, Z. Huang, C. Zhang, R. Tusiime, J. Zhou, Z. Sun, Y. Liu, M. Yu, H. Zhang, Simultaneously improving mode I and mode II fracture toughness of the carbon fiber/epoxy composite laminates via interleaved with uniformly aligned PES fiber webs, Composites Part A: Applied Science and Manufacturing, 129 (2020) 105696.

[26] W.-T. Wang, H. Yu, K. Potter, B.C. Kim, Effect of the characteristics of nylon microparticles on Mode-I interlaminar fracture toughness of carbon-fibre/epoxy composites, Composites Part A: Applied Science and Manufacturing, 138 (2020) 106073.

[27] D. Quan, F. Bologna, G. Scarselli, A. Ivanković, N. Murphy, Mode-II fracture behaviour of aerospace-grade carbon fibre/epoxy composites interleaved with thermoplastic veils, Composites Science and Technology, 191 (2020) 108065.

[28] S. Salifu, D. Desai, O. Ogunbiyi, R. Sadiku, O. Adesina, O. Adesina, Comparative study of high velocity impact response of aluminium 3105-H18 and carbon fibre-epoxy composite double hat bumper beams, Materials Today: Proceedings, (2020).

[29] Z. Zhang, S. Hou, Y. Mao, L. He, X. Han, Rate-related study on the ply orientation of carbon fiber reinforced epoxy composite laminates, International Journal of Mechanical Sciences, 188 (2020) 105968.

[30] L. Maragoni, G. Modenato, N. De Rossi, L. Vescovi, M. Quaresimin, Effect of fibre waviness on the compressive fatigue behavior of woven carbon/epoxy laminates, Composites Part B: Engineering, 199 (2020) 108282.

[31] A. Hendlmeier, F. Stojcevski, R. Alexander, S. Gupta, L.C. Henderson, Examining conductivity, current density, and sizings applied to carbon fibers during manufacture and their effect on fiber-to-matrix adhesion in epoxy polymers, Composites Part B: Engineering, 179 (2019) 107494.

[32] M.M. Hiremath, B.N.V.S. Ganesh Gupta K, R.K. Prusty, B.C. Ray, Mechanical and thermal performance of recycled glass fiber reinforced epoxy composites embedded with carbon nanotubes, Materials Today: Proceedings, (2020).

[33] Y. Ming, Y. Duan, S. Zhang, Y. Zhu, B. Wang, Self-heating 3D printed continuous carbon fiber/epoxy mesh and its application in wind turbine deicing, Polymer Testing, 82 (2020) 106309.

[34] A. Behera, M.M. Thawre, A. Ballal, Hygrothermal aging effect on physical and mechanical properties of carbon fiber/epoxy cross-ply composite laminate, Materials Today: Proceedings, 28 (2020) 940-943.

[35] C.-L. Chiang, H.-Y. Chou, M.-Y. Shen, Effect of environmental aging on mechanical properties of graphene nanoplatelet/nanocarbon aerogel hybrid-reinforced epoxy/carbon fiber composite laminates, Composites Part A: Applied Science and Manufacturing, 130 (2020) 105718.

[36] S. Naqvi, H.M. Prabhakara, E. Bramer, W. Dierkes, R. Akkerman, G. Brem, A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using

pyrolysis towards a circular economy, Resources, conservation and recycling, 136 (2018) 118-129.

[37] S.V. Joshi, L.T. Drzal, A.K. Mohanty, S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites?, Composites Part A: Applied Science and Manufacturing, 35 (2004) 371-376.

[38] B. Yang, V. Kozey, S. Adanur, S. Kumar, Bending, compression, and shear behavior of woven glass fiber–epoxy composites, Composites Part B: Engineering, 31 (2000) 715-721.

[39] T.A. Bogetti, J.W. Gillespie Jr, R.B. Pipes, Evaluation of the IITRI compression test method for stiffness and strength determination, Composites Science and Technology, 32 (1988) 57-76.

[40] J. Anjaneyulu, M. Moizuddin, P. Chandra kumar, Evaluation of mechanical behaviour of Glass fibre-epoxy composite laminates, Materials Today: Proceedings, 22 (2020) 2899-2905.

[41] A.S. Swapnil, B. SatheSandip, P. ChaudhariBapu, S.J. Vishal, Experimental Investigation of Mechanical Properties of Glass Fibre/Epoxy Composites with variable volume fraction, Materials Today: Proceedings, 4 (2017) 9487-9490.

[42] R.F. Minty, L. Yang, J.L. Thomason, The influence of hardener-to-epoxy ratio on the interfacial strength in glass fibre reinforced epoxy composites, Composites Part A: Applied Science and Manufacturing, 112 (2018) 64-70.

[43] A.P. Chakraverty, D. Parida, S. Dash, M. Parida, S. Beura, U.K. Mohanty, Thermo-mechanical response of post-plasma irradiated E-glass fibre/epoxy composite, Materials Today: Proceedings, (2020).

[44] M. Sangermano, A. D'Anna, C. Marro, N. Klikovits, R. Liska, UV-activated frontal polymerization of glass fibre reinforced epoxy composites, Composites Part B: Engineering, 143 (2018) 168-171.

[45] M. Sheinbaum, L. Sheinbaum, O. Weizman, H. Dodiuk, S. Kenig, Toughening and enhancing mechanical and thermal properties of adhesives and glass-fiber reinforced epoxy composites by brominated epoxy, Composites Part B: Engineering, 165 (2019) 604-612.

[46] M. Ojha, P.K. Penumakala, G.V. Marrivada, P.K. Chaganti, A.K. Gupta, Processing Of Glass Fiber Pultruded Composites Using Graphene Nanoplatelets Modified Epoxy Matrix, Materials Today: Proceedings, 18 (2019) 3298-3304.

[47] R.K. Prusty, S.K. Ghosh, D.K. Rathore, B.C. Ray, Reinforcement effect of graphene oxide in glass fibre/epoxy composites at in-situ elevated temperature environments: An emphasis on graphene oxide content, Composites Part A: Applied Science and Manufacturing, 95 (2017) 40-53.

[48] S.K. Ghosh, P. Rajesh, B. Srikavya, D.K. Rathore, R.K. Prusty, B.C. Ray, Creep behaviour prediction of multi-layer graphene embedded glass fiber/epoxy composites using time-temperature superposition principle, Composites Part A: Applied Science and Manufacturing, 107 (2018) 507-518.

[49] N. Domun, C. Kaboglu, K.R. Paton, J.P. Dear, J. Liu, B.R.K. Blackman, G. Liaghat, H. Hadavinia, Ballistic impact behaviour of glass fibre reinforced polymer composite with 1D/2D nanomodified epoxy matrices, Composites Part B: Engineering, 167 (2019) 497-506.

[50] A. Jena, Shubham, R.K. Prusty, B.C. Ray, Mechanical and thermal behaviour of multi-layer graphene and nanosilica reinforced glass Fiber/Epoxy composites, Materials Today: Proceedings, (2020).

[51] Y. Hua, F. Li, Y. Liu, G.-W. Huang, H.-M. Xiao, Y.-Q. Li, N. Hu, S.-Y. Fu, Positive synergistic effect of graphene oxide/carbon nanotube hybrid coating on glass fiber/epoxy interfacial normal bond strength, Composites Science and Technology, 149 (2017) 294-304.

[52] A. Anand, P. Banerjee, D. Sahoo, D.K. Rathore, R.K. Prusty, B.C. Ray, Effects of temperature and load on the creep performance of CNT reinforced laminated glass fiber/epoxy composites, International Journal of Mechanical Sciences, 150 (2019) 539-547.

[53] A. Gaurav, K.K. Singh, Ilss improvement of quasi-isotropic glass fiber reinforced epoxy laminate enhanced with arc discharged multi-walled carbon nanotubes, Materials Today: Proceedings, 5 (2018) 8638-8644.

[54] N.H. Ismail, J.O. Akindoyo, M. Mariatti, Solvent mediated dispersion of carbon nanotubes for glass fibre surface modification – Suspensions stability and its effects on mechanical, interlaminar and dynamic mechanical properties of modified glass fibre reinforced epoxy laminates, Composites Part A: Applied Science and Manufacturing, 139 (2020) 106091.

[55] P. Slobodian, S. Lloret Pertegás, P. Riha, J. Matyas, R. Olejnik, R. Schledjewski, M. Kovar, Glass fiber/epoxy composites with integrated layer of carbon nanotubes for deformation detection, Composites Science and Technology, 156 (2018) 61-69.

[56] B. Sen, A.O. Fulmali, B.N.V.S.G. Gupta K, R.K. Prusty, B.C. Ray, A study of the effect of carbon nanotube/nanoclay binary nanoparticle reinforcement on glass fibre/epoxy composites, Materials Today: Proceedings, 26 (2020) 2026-2031.

[57] Ö.Y. Bozkurt, M. Bulut, A. Erkliğ, W.A. Faydh, Axial and lateral buckling analysis of fiber reinforced S-glass/epoxy composites containing nano-clay particles, Composites Part B: Engineering, 158 (2019) 82-91.

[58] B.A. Nayak, Shubham, R.K. Prusty, B.C. Ray, Effect of nanosilica and nanoclay reinforcement on flexural and thermal properties of glass fiber/epoxy composites, Materials Today: Proceedings, (2020).

[59] S. Kumar, B.G. Falzon, J. Kun, E. Wilson, G. Graninger, S.C. Hawkins, High performance multiscale glass fibre epoxy composites integrated with cellulose nanocrystals for advanced structural applications, Composites Part A: Applied Science and Manufacturing, 131 (2020) 105801.

[60] V.R. Arun prakash, A. Rajadurai, Inter laminar shear strength behavior of acid, base and silane treated E-glass fibre epoxy resin composites on drilling process, Defence Technology, 13 (2017) 40-46.

[61] Y.S. Mohamed, H.A. El-Gamal, M.N. Abouelwafa, W.A. Al-Tabey, Static and fatigue characterizations of fiber glass/epoxy tubes exposed to internal pressure and/or bending moment, Alexandria Engineering Journal, 58 (2019) 1247-1256.

[62] S. Ahankari, A. Patil, Sea Water Effect on Mechanical Performance of Steel Pipes Rehabilitated with Glass Fiber Reinforced Epoxy Composites, Materials Today: Proceedings, 22 (2020) 2490-2498.

[63] S.N. Fitriah, M.S. Abdul Majid, M.J.M. Ridzuan, R. Daud, A.G. Gibson, T.A. Assaleh, Influence of hydrothermal ageing on the compressive behaviour of glass fibre/epoxy composite pipes, Composite Structures, 159 (2017) 350-360.

[64] F.d.O. Braga, T.L. Milanezi, S.N. Monteiro, L.H.L. Louro, A.V. Gomes, É.P. Lima, Ballistic comparison between epoxy-ramie and epoxy-aramid composites in Multilayered Armor Systems, Journal of Materials Research and Technology, 7 (2018) 541-549.

[65] K. Komai, K. Minoshima, K. Tanaka, T. Tokura, Effects of stress waveform and water absorption on the fatigue strength of angle-ply aramid fiber/epoxy composites, International Journal of Fatigue, 24 (2002) 339-348.

[66] X. Xu, B. Zhang, L. Xing, K. Liu, M. Bai, D. Liu, Characterization and analysis of the thermal damages of aramid/epoxy composite laminates induced by the dielectric heating effect of microwaves, Composite Structures, 200 (2018) 371-379.

[67] G. Qi, B. Zhang, S. Du, Y. Yu, Estimation of aramid fiber/epoxy interfacial properties by fiber bundle tests and multiscale modeling considering the fiber skin/core structure, Composite Structures, 167 (2017) 1-10.

[68] L. Liu, Y.D. Huang, Z.Q. Zhang, Z.X. Jiang, L.N. Wu, Ultrasonic treatment of aramid fiber surface and its effect on the interface of aramid/epoxy composites, Applied Surface Science, 254 (2008) 2594-2599.

[69] W. Fan, H. Tian, H. Wang, T. Zhang, X. Yang, Y. Yu, X. Meng, X. Yu, L. Yuan, B. Xu, S. Wang, Enhanced interfacial adhesion of aramid fiber III reinforced epoxy composites via low temperature plasma treatment, Polymer Testing, 72 (2018) 147-156.

[70] Z. Cheng, B. Li, J. Huang, T. Chen, Y. Liu, X. Wang, X. Liu, Covalent modification of Aramid fibers' surface via direct fluorination to enhance composite interfacial properties, Materials & Design, 106 (2016) 216-225.

[71] L. Xing, L. Liu, F. Xie, Y. Huang, Mutual irradiation grafting on indigenous aramid fiber-3 in diethanolamine and epichlorohydrin and its effect on interfacially reinforced epoxy composite, Applied Surface Science, 375 (2016) 65-73.

[72] P. Meshram, S. Sahu, M. Zahid Ansari, S. Mukherjee, Study on mechanical properties of epoxy and nylon/epoxy composite, Materials Today: Proceedings, 5 (2018) 5925-5932.

[73] R. Palazzetti, A. Zucchelli, C. Gualandi, M.L. Focarete, L. Donati, G. Minak, S. Ramakrishna, Influence of electrospun Nylon 6,6 nanofibrous mats on the interlaminar properties of Gr–epoxy composite laminates, Composite Structures, 94 (2012) 571-579.

[74] S.F. Teh, T. Liu, L. Wang, C. He, Fracture behaviour of poly(ethylene terephthalate) fiber toughened epoxy composites, Composites Part A: Applied Science and Manufacturing, 36 (2005) 1167-1173.

[75] M.M. Demir, N. Horzum, A. Taşdemirci, K. Turan, M. Güden, Mechanical Interlocking between Porous Electrospun Polystyrene Fibers and an Epoxy Matrix, ACS Applied Materials & Interfaces, 6 (2014) 21901-21905.