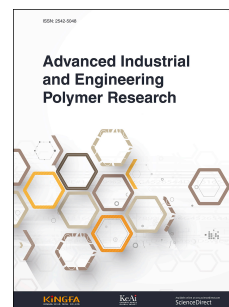


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Recycling of thermosetting composites for wind blade application

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Contribution for the special issue “Recycling of Polymer Blends and Composites” (Part 2)
Advanced Industrial and Engineering Polymer Research

Recycling of thermosetting composites for wind blade application

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Abstract

It is well known that wind energy could represent a promising solution to the continuous increase of energy demand in the modern society. At the end of 2016 the European wind power amounted to 153.7 GW, distributed on 77000 wind turbines and corresponding to the 10.4% of the electrical energy supplied. Considering the EU program to increase the renewable energy share to 27% by 2030, the key role of the wind energy in the next decade is clear. As the number of wind towers that will be dismantled in the next years will continuously increase, the development of sustainable practices to dispose of these plants at the end of their life is of utmost importance. Some parts of these turbines (tower, foundations, generator and gear box) are constituted by materials having elevated recycling rates, while the blades, that are nowadays made up of thermosetting fiber reinforced polymers, are very difficult to be recycled, because of the nature of the materials involved and their complex composition.

Therefore, the aim of this review is to present the state of the art in composite wind blades recycling. In the first chapter, some general concepts about wind energy and composite wind blades are presented. The second section of the work is devoted to the analysis of the most important methods for recycling composite laminates. In the third chapter, a presentation of the recycling processes directly applied on waste composite blades is reported. Considering the actual difficulties in composite blades recycling, particular attention is devoted in the fourth chapter to innovative solutions to develop composite structures with improved recyclability, with some examples of modified thermosetting composites, innovative thermoplastic laminates and composites reinforced with natural fibers. The key aspects of composite wind blades recycling and the future perspectives are summarized in the last section.

Keywords: wind turbines, wind blades, composites, fibers, recycling.

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List of acronyms

Description	Acronym
Addition–fragmentation chain transfer	AFT
Anionic polyamide 6	APA6
Anionic polylactam 12	APLC12
Bulk moulding compound	BMC
Carbon fiber reinforced plastic	CFRP
Carbon fiber	CF
Covalent adaptable network	CAN
Cyclic butylene terephthalate	CBT
Dimethyl sulphoxide	DMSO
Diglycidyl ether of bisphenol-A	DGEBA
Degradable epoxy-ended hyperbranched polyester	DEHP
Fiber reinforced polymer	FRP
Fluidized bed process	FBP
Fused deposition modeling	FDM
Gas chromatography/mass spectroscopy	GC/MS
Glass fiber	GF
Glass fiber reinforced plastic	GFRP
Hemiaminal dynamic covalent network	HDCN
High density polyethylene	HDPE
Horizontal axis wind turbine	HAWT
Interfacial shear strength	IFSS
Life cycle assessment	LCA
Low density polyethylene	LDPE
Natural fiber reinforced composite	NFRC
Polyamide 12	PA12
Polybutylene terephthalate	PBT
Polyether ether ketone	PEEK
Polyethylene terephthalate	PET
Polyhexahydrotriazine	PHT
Polylactic acid	PLA
Polymer matrix composite	PMC
Polypropylene	PP

Recycled carbon fiber	rCF
Recycled carbon fiber reinforced polymer	rCFRP
Recycled glass fiber	rGF
Resin transfer molding	RTM
Thermoset hyperbranched polymer	HER-HT _n
Transesterification	TE
Trithiocarbonate	TTC
Scanning electron microscope	SEM
Sheet moulding compound	SMC
Shredded composite	SC
Unidirectional laminate	UD
Vertical axis wind turbine	VAWT
Vacuum resin infusion moulding	VRIM
Virgin carbon fiber	vCF
Wind turbine	WT

1. Composite materials for wind turbines

Wind energy is nowadays one of the energy sources with the fastest growth rate and it can thus represent a valuable and economically sustainable solution to the problems of the shortage of fossil fuels and of the climate change [1]. Basing on recent IRENA's report, in the last twenty years the worldwide wind power installed (both onshore and offshore) increased from 7.5 GW in 1997 to 564 GW by 2018. The global wind energy produced doubled between 2009 and 2013, and it represented the 16% of the renewable energy share in 2016 [2]. Even if the greatest part of the wind energy is produced in rural areas outside the cities, where wind flows are not disturbed or blocked, wind technology can give also an important contribution to the sustainable development of metropolitan areas, as wind towers do not produce toxic gas emissions during their service life [3].

Generally speaking, wind is the air flow produced by the non homogeneous heating of the earth's surface by the sun [4]. The wind power (P) that could be theoretically exploited by a wind turbine (WT) is expressed by Equations (1-3):

$$P = \frac{1}{2} d A V^3 \quad (1)$$

$$A = \pi r^2 \quad \text{for horizontal axis wind turbines (HAWT)} \quad (2)$$

$$A = dh \quad \text{for vertical axis wind turbines (VAWT)} \quad (3)$$

in which d is the density of the air (about 1.229 kg/m^3 at sea level), A is the swept area of the wind turbine, V is the velocity of wind, r is the radius (i.e. the length of the turbine's blades), d is the rotor diameter and h is the height of the turbine. It is thus evident that P increases with the cube of the wind speed, and it is thus clear that the annual distribution of the wind speed (and its direction) in a certain location is probably the most significant project parameter [5]. However, the amount of wind energy that can be converted in usable energy is considerably lower. Theoretically speaking, the maximum efficiency of a wind turbine rotor exploiting the lift force (i.e. perpendicular to the direction of the wind) is 59.3%, and it represents the 'Betz limit'. Wind plants based on the drag force (i.e. parallel to the direction of the wind) have an even lower theoretical efficiency (about 29.6%) [6]. As reported in Equations (2) and (3), WTs can be classified in horizontal axis wind turbines (HAWTs) or a vertical axis wind turbines (VAWTs). HAWTs are nowadays the preferred turbine design, especially for big size wind projects, but small scale VAWTs have been also recently installed in urban areas, as they are characterized by lower noise levels and allow the production of energy also in

locations with discontinuous and turbulent winds. In Figure 1(a-b) is reported a representative scheme of HAWT and VAWT wind generators. Regardless to the diameter of the WT, today the greatest part of the generators is based on the Danish three-bladed rotor scheme, and large-scale power production is covered by plants having a nominal power in the range 1-3 MW [7,8].

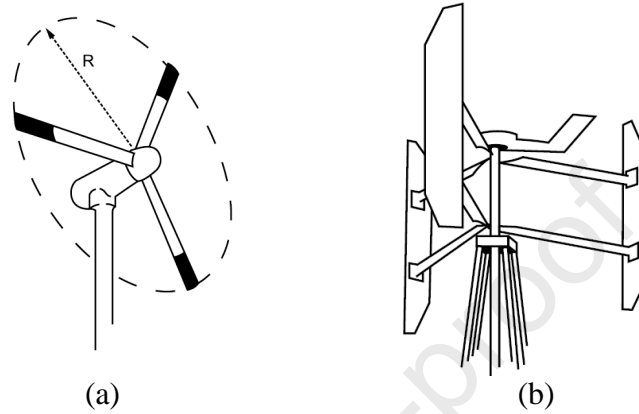


Figure 1. Representative scheme of (a) horizontal axis wind turbine (HAWT) and (b) vertical axis wind turbine (VAWT) [8].

In Table 1 a classification of the wind turbines on the basis of their size, together with their applications fields, is summarized. It is evident that wind plants are rather expensive, and the economical investments on these plants are noticeably influenced by scale economies. As the specific cost of WTs strongly decreases with the plant size, high power wind towers are less expensive than small size wind generators [9,10].

Table 1. Size classification of wind turbines (adapted from [9,10])

type	nominal power (kW)	swept area (m ²)	specific cost (\$/kW)	application field
micro	<1.5	up to 7.5	3900-12500	small battery charging, streetlights and road signs
small	1.5 to 15	7.5 to 75	2130-11250	residential or small commercial buildings
small-medium	15 to 100	75 to 500	4000-6250	multifamily apartment or commercial buildings
large	>100	>500	1200-5000	large buildings or grid supply to wholesale market

As WTs do not produce gas emissions during their service life, wind energy is considered one of the cleanest renewable energy sources. In comparison with power plants based on fossil fuels, wind generators have considerably reduced CO, SO_x, NO_x and particulate emissions

[11]. Unlike traditional fossil fuel resources, wind energy is practically inexhaustible. On the other hand, the specific productivity of wind power plants is rather limited, and considerable energy amounts are required for the manufacturing and the assembly of the different WT parts. Given a certain lifetime for a wind energy project, it is important to determine its energy intensity (i.e. energy spent for the production/energy produced) and the relative energy payback time (i.e. the time required for the turbine to produce an energy amount equal to that consumed in the production of the WT). Generally speaking, small-scale wind turbines are more energy intensive and have thus longer energy payback periods (between 2.4 and 4.8 years). On the contrary, big scale wind projects are characterized by very limited energy payback periods (from eight months to about one year) [12]. Therefore, it can be seen that the energetic payback time is very short with respect to the expected lifetime of a wind turbine (between 20 and 30 years). There are many aspects that influence the public perception of wind turbines in the metropolitan areas, like noise levels, avian impacts, city aesthetics and public safety. A detailed analysis of these points can be found in the work of Hyams et al. [3], but it is out of the main scope of the present review.

The problems encountered in the design of rotor blades of WTs are similar to those faced by aeronautical engineers [13,14]. The first wind blade turbine constituted by glass fibre reinforced plastic (GFRP) was designed by U. Hütter in 1958. At that time, rotor blades were generally constructed by using steel, aluminium, and wood. Nowadays, the primary structure of wind blades is entirely made up of composite materials, while wood is sometimes utilized in some small-size plants. Composite materials are widely applied in WT blades for their better mechanical performances and easy manufacturing [15-25], coupled with the possibility to tailor/modify both the stiffness and the strength changing the orientation of the reinforcing fibers [13]. HWATs blades are generally manufactured by using glass fiber and carbon fiber reinforced plastics (CFRPs). As it can be immediately seen in the mechanical properties chart reported in Table 2, the specific strength of unidirectional (UD) GFRPs (fiber volume fraction $V_f = 0.5$) and CFRPs ($V_f = 0.6$) is significantly higher than that of steel, and also the absolute strength of CFRPs is superior than that of steel. However, it has to be also considered that the mechanical resistance of FRPs is strongly affected by several factors, such as the intrinsic mechanical properties of the constituents, the interfacial adhesion conditions, the adopted processing conditions, etc.

Table 2. Comparison of the mechanical properties of different structural materials (adapted from [13]).

material	density (kg/m ³)	elastic modulus (GPa)	tensile strength (MPa)	specific stiffness*	specific strength*
mild steel	7800	210	350	1.0	1.0
high-strength steel	7800	210	900	1.0	2.6
GFRP (UD, $V_f = 0.5$)	1840	38	600	0.8	7.3
CFRP (UD, $V_f = 0.6$)	1500	130	1675	3.2	25.0
wood/epoxy laminate	660	17	70	1.0	2.4

*specific values were normalized with respect to mild steel

From the data reported in Table 2 it is evident that polymer composites are characterized by a superior specific strength, but the most interesting advantage in their use is probably the superior fatigue resistance. From the S_N/N fatigue curves reported Figure 2, where S_N is the applied fatigue stress amplitude for a certain number of fatigue cycles (N), it is evident that fiber reinforced plastics (both CFRP and GFRP) show a higher fatigue resistance with respect to steel, that shows a fatigue behaviour similar to that of wood/epoxy laminates. If the fatigue performance of these materials is considered in terms of specific strength (i.e. per unit weight), the advantage in the use of composite materials is further enhanced.

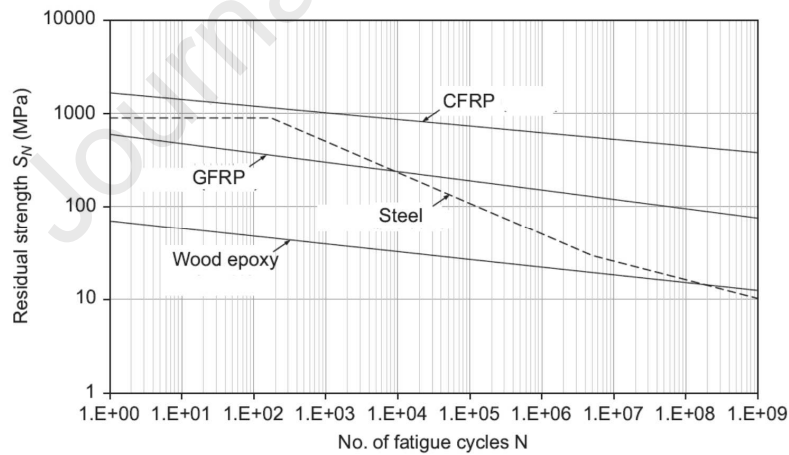


Figure 2. Fatigue curves for blade materials (adapted from [13]).

The elevated stress at break values of GFRPs and CFRPs are due to the mechanical properties of the reinforcing fibers that, because of their limited thickness, present a lower flaws concentration with respect to the corresponding bulk materials. The limited density of glass and carbon fibers with respect to the metals is also responsible for their elevated specific stiffness and strength [26]. GFRPs are generally produced by using an epoxy or polyester (or less commonly vinylester) thermosetting matrix, while for the manufacturing of CFRPs only

epoxy resin is utilized. With traditional hand layup technique, it is possible to produce GFRPs having fiber concentration of 30%-40%, while adopting vacuum resin infusion moulding (VRIM) a V_f around 50% can be reached. Carbon fibers have a smaller diameter and therefore they are harder to be infused than glass fibers. For this reason, CFRP are generally produced by using 'prepregs' [27], i.e. fiber plies pre-impregnated with liquid epoxy resin, that can be heated after the stacking operations to perform the crosslinking reaction [13]. In the case of CFRPs, it is possible to obtain a fiber concentration higher than 60 vol%.

As already said, nowadays the primary structure of HAWT blades is generally constituted by fiber reinforced polymers, without the insertion of metal parts. In Figure 3 a section of a typical composite blade, together with the indication of its main structural components, is presented. A complete description of the different cross-sections of the rotor blades for WTs can be found in the book of Hau [14]. The spar caps are generally constituted by UD glass fiber reinforced laminates, with the fibers oriented parallelly to the blade long axis. They are located in the thickest section of the blade, and their thickness decreases along the blade, because the flapwise bending moment decreases in radial direction. Due to their elevated cost, carbon fibers are utilized only in blades with a length higher than 50 m. In order to support the combination of flapwise, edgewise, and torsional stresses near the blade root, in this zone the section is thickened with the use of multi-axial composites. In order to support flapwise shear stresses and to provide shape stability, shear web skins constituted by $\pm 45^\circ$ biaxial GFRP are utilized, while the core could be a stiff polyurethane or polyvinylchloride foam (also balsa wood is sometimes utilized). Blade skins are formed by a sandwich construction, composed by a $\pm 45^\circ$ biaxial GFRP on a lightweight core. The two halves of the blades are generally bonded together with an epoxy adhesive put at the leading and trailing edges and on the shear web surfaces. Some blades with large dimensions are now moulded in a single piece, forming thus a continuous shell at the leading edge.

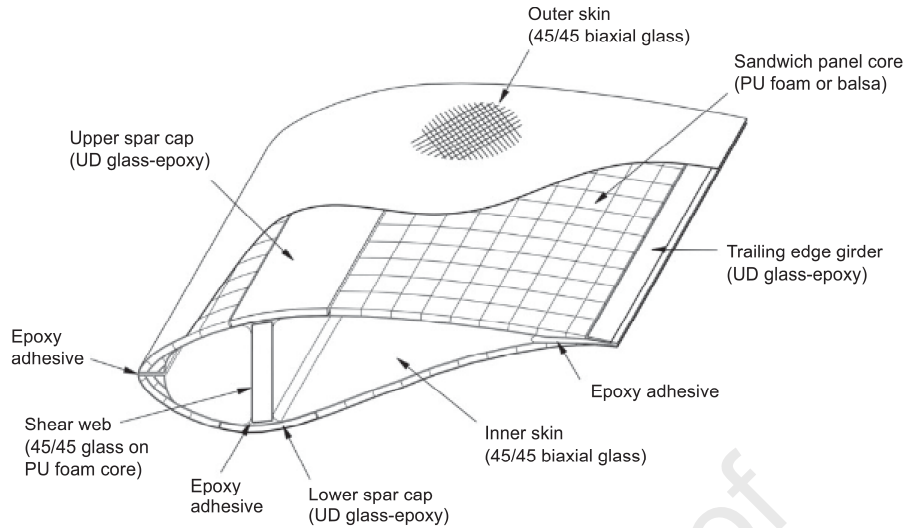


Figure 3. Structure of a typical composite blade. The design shown is based on a thick profile, with unidirectional glass-epoxy spar caps and a single shear web [13].

2. Recycling of composite materials

As reported in Chapter 1, composite materials are endowed with unique and versatile properties with respect to more traditional materials (like metals). For as concerns their environmental attributes, the end of life scenario of composites should be analyzed in a different way with respect to commodity materials, as they are generally characterized by a longer service life, typical of structural components [7]. In the last years the interest towards CFRPs has been strongly increased, especially in industrial, sport and automotive field. Therefore, the global consumption of carbon fibers (CFs) in 2011 amounted to about 46000 t, with an expected growth rate for the next years of the 13% [28,29]. The recent EU policy on waste treatment (EU 1999/31/EC and EU 2000/53/EC regulations) tends to strongly limit the negative environmental impact of waste, transforming the waste in new resources. In this sense, landfilling is the least favourable option, as the waste is not recovered and thus it does not have any value. Moreover composite materials, thanks to their elevated durability, are characterized by a very limited degradation rate in the landfilling site [7]. Nevertheless, nowadays the greatest part of the CFRP waste is landfilled, with negative environmental, economic and even legal consequences [30]. On the other hand, the effectiveness of incineration with energy recovery is strongly dependent by the composition of the composites. For instance, the organic and flammable content within GFRPs and sheet moulding (SMC) is rather limited, and the amount of recoverable energy through incineration

from these materials is thus rather limited, while CFRPs are characterized by an elevated calorific value [7].

Nowadays recycling and/or reuse of composite waste is probably the best choice on the basis of the recent EU directives, while landfilling is the last option [29]. Considering the intrinsic energy intensive nature of CFRPs, these materials are ideal candidates for the application of different recycling approaches. From the chart reported in Figure 4, it can be noticed that the embodied energy related to the production of 1 kg of CFRP is about 500 MJ/kg, that is 2.5 times higher than that of Al (200 MJ/kg) and an order of magnitude higher than that of steel [31]. The environmental impact of GFRPs, even if lower than that of CFRPs, is comparable to that of aluminium and much higher than that of steel. From the same chart, it can be understood that the greatest part of the embodied energy in CRFPs is related to the production of carbon fibers and not to the polymer matrix (generally an epoxy resin). It is well known that CFs are generally produced through a high temperature treatment of different organic precursors (polyacrylonitrile, pitch, etc.), and this leads to an elevated environmental impact [32]. For instance, it was recently demonstrated that CFs recovered from waste laminates through pyrolysis have an overall energy consumption equal to 5-10% of the energy needed to produce virgin CFs.

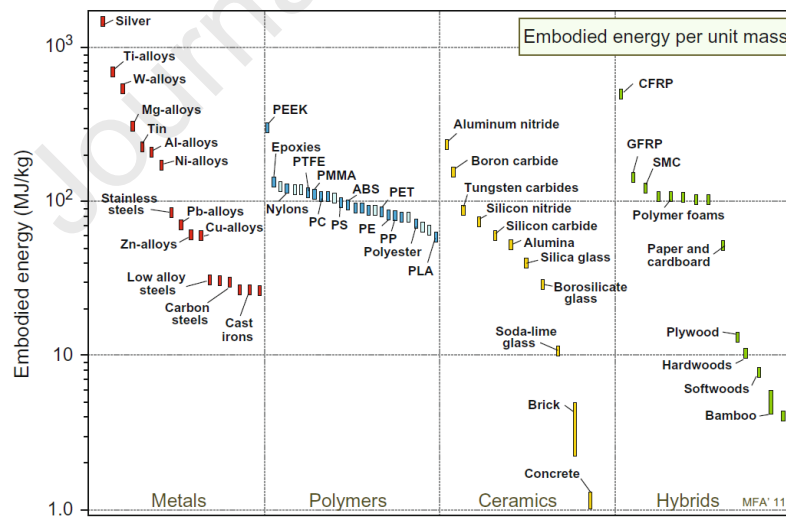


Figure 4. Values of embodied energy per unit mass of different materials [31].

Recycling of composite materials presents some intrinsic difficulties, mainly related to the following issues [27]:

- fiber reinforced polymers (FRPs) have a complex composition, because of the presence of the polymer matrix, the reinforcements and the fillers

- in most cases the matrix is constituted by a thermosetting resin (like epoxy), that cannot be re-melted and re-moulded
- composite materials are very often combined with other materials (metal parts, honeycomb structures etc.).

Considering the importance of closing the life cycle loop of FRPs (especially in the automotive industry), different recycling approaches have been considered. As reported in Figure 5, recycling techniques can be classified as mechanical or thermo-chemical methods.

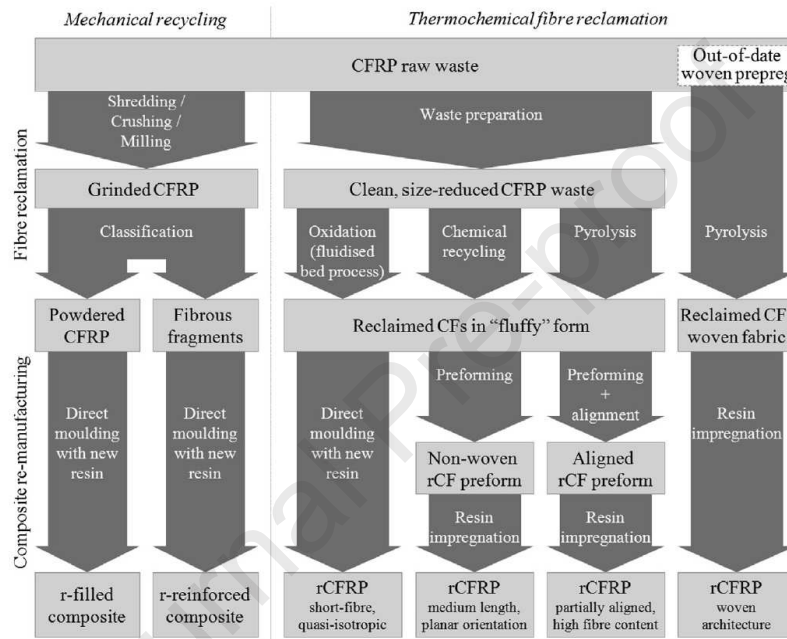


Figure 5. Overview of polymer composites recycling processes (referred to CFRPs) [27].

2.1 Mechanical recycling

From a general point of view, in mechanical recycling FRPs are shredded, crushed or milled, and the resulting materials are then classified in powdered products (with an elevated content of resin) and fibrous components (rich in fibers) [33,34]. The recovered materials can be then used as filler or reinforcement through re-impregnation with new resin, or they can be added in asphalts and cements [35]. The resulting particulate grades are mainly utilized as filler, while the fibrous components with higher aspect ratio are utilized as reinforcement [33]. For instance, it was demonstrated that recycled composite particles can replace up to 88 wt% of the calcium carbonate in SMC, without substantial modifications of the resulting tensile and flexural properties [36]. When the use of recycled composites in SMC and in bulk moulding compound (BMC) is considered, some technological problems related to the increase of viscosity of the uncured resin and to the delay of the crosslinking reaction, due to the thermal

conductivity decrease, must be taken into account [37,38]. In another case, finely ground (size lower than 20 μm) composite waste was recycled in its own production stream in order to replace CaCO_3 filler, obtaining substantial improvements of the stress at break and of the damping properties [39,40]. Another possibility is to use recycled composites as filler and/or reinforcement in thermoplastic matrices (like PP), obtaining a substantial improvement of the stress at break, associated to a reduction of the Charpy impact strength [41,42]. Many examples of the effect of grinded and sieved composite recyclates on the mechanical behaviour of different polymer matrices can be found in the book of Goodship [7]. Alternatively, mechanically recycled composites can be broken and incorporated in concrete, obtaining some improvements in compressive and flexural properties, accompanied by a substantial increase of ductility [43].

2.2 Thermo-chemical recycling

Thermo-chemical recycling consists in the recovery of the reinforcing fibers through thermal or chemical methods, and the matrix (generally with thermosetting nature) is decomposed. The fibers obtained after these reclamation processes generally possess mechanical properties comparable to the virgin ones, even if in some cases some surface defects and a deterioration of the strength has been noticed [44]. Through pyrolysis it is also possible to decompose the uncured resin in out of date woven CF prepregs and to recover the fibers. In this way, recycled carbon fiber (rCFs) can be then re-impregnated, retaining thus the original woven morphology of the prepreg (see Figure 5).

Pyrolysis is one of the most diffused recycling technology for FRPs, and it is based on the thermal degradation of the polymer matrix under an inert atmosphere (e.g. nitrogen). In this process the organic part of the composite is decomposed into lower molecular weight components, that could be recovered and re-utilized in some cases [45]. Therefore, in the pyrolytic recycling process not only filler particles and fibers can be obtained, but also organic components and liquid fuels can be recovered. Pyrolysis is generally performed in a temperature range between 300 °C and 500 °C, and also some specific catalysts can be adopted to lower the processing temperature [7]. There are different kinds of pyrolyzers (fixed bed reactors, rotary kilns, screw pyrolyzers, fluidized bed reactors), and a complete description of their peculiarities was provided in a paper of J. Scheirs [46]. For instance, in a recent paper of Evans et al. thermosetting laminates with a polyester matrix were recycled through a pyrolytic process performed at 600 °C, and the resulting degradation products were investigated by GC/MS (gas chromatography/mass spectroscopy) [47]. In FRPs with epoxy

matrix the pyrolytic process performed at 300-400 °C led to the cleavage of the ether bonds between aromatic and aliphatic carbons, releasing bisphenol A. Increasing the processing temperature above 600 °C phenol, methyl-, ethyl- and isopropenylphenol pyrolysis products were obtained, without any solid residue [7]. For as concerns the production of fuels and gasoline from the pyrolytic recycling of composites, Torres et al. treated an unsaturated polyester/GF SMC, obtaining C₅-C₂₀ organic liquid compounds [48]. Giorgini and Yun pyrolyzed CFRPs and GFRPs, obtaining some pyrolytic gas (H₂, CH₄, CO and CO₂, etc.) and oil (benzene, toluene and ethylbenzene, etc.) [49,50]. However, in most cases the re-utilization of these fuels is not economically viable, and sometimes it could be better to exploit the resin calorific power to render the pyrolytic recycling self-sustained. It is important to underline that nowadays pyrolysis is one of the recycling techniques with full size commercial scale application [51].

Among thermal recycling processes for composites, oxidation is particularly interesting, as it consists in the thermal decomposition of the polymer matrix at 450-550 °C under an oxygen rich flow. One of the most diffused oxidative processes is the fluidized bed process (FBP), developed at the University of Nottingham, represented in Figure 6 [52]. In this technology composite scraps with mean size of about 25 mm are put on a metallic mesh covered by a silica bed. The scraps are then subjected to a hot air stream that decomposes the matrix, and both the oxidized compounds and the reinforcing fibers are transported by the air stream, while the other components (like metallic ones) sink in the bed. Through a cyclone separator it is possible to recover the fibers, and then the remaining compounds are fully oxidized in an afterburner. In some cases, the calorific power generated by the decomposition of the matrix can be recovered and utilized to feed the process.

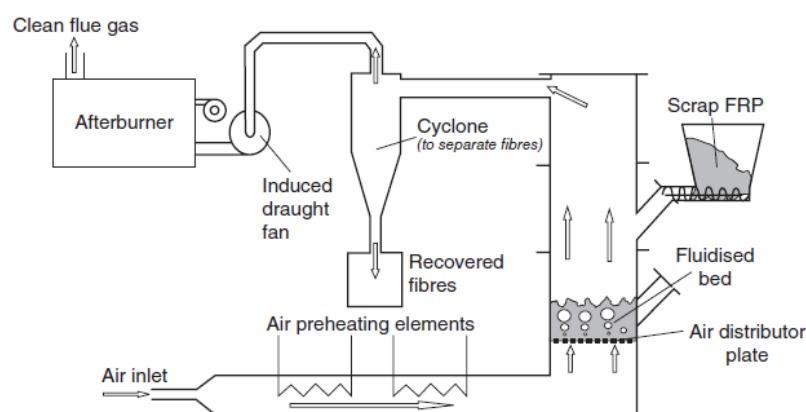


Figure 6. General scheme of the fluidized bed recycling process [52].

It was demonstrated that through FBP technique it is possible to obtain both CFs and GFs with good quality and in fluffy form (density of about 50 kg/m³). The recovered fibers retain the pristine elastic modulus, while the tensile strength is decreased, especially at elevated processing temperatures, because of the oxidation of the fibers and of the surface damage caused by the agitation in the FBP reactor [38,53].

Microwave recycling is a particular kind of pyrolytic process in which the matrix of the laminates is decomposed through microwave radiation. In the case of CFRPs, the microwave energy is internally absorbed by the CFs, increasing thus the decomposition rate and reducing the processing time [54]. It is a novel, clean and environmentally friendly method, that could be easily controlled and allows an efficient recovery of the fibers. For instance, Lester et al. applied microwave pyrolysis to decompose CFRPs at a power of 3 kW for 8 s, obtaining CFs with good mechanical performances and clean surfaces [55]. Moreover, Firebird Advanced Materials Inc. developed for the first time a small scale continuous microwave recycling plant for CFRPs [56].

In chemical recycling of composites, FRPs scraps are treated at low-medium temperature (below 350 °C) in reactive media constituted by catalytic solutions, alcohols and supercritical fluids. In this way, it is possible to collect the fibers in fluffy form, while the matrix is decomposed in oligomers that can be re-utilized as chemical feedstock for different applications [27]. Among chemical recycling techniques applied to thermosetting FRPs, hydrolysis, glycolysis, solvolysis and acid digestion are the most important ones [36]. In a paper of Winter et al., a direct comparison of different chemical routes for recycling SMCs has been performed [57]. Even if potentially interesting, chemical recycling is probably the least mature technology for the processing of thermosetting waste composites. In particular, hydrolytic recycling of thermoset FRPs seems to be limited by the need of separating different matrix polymers within the composite waste and of grinding the material to a very fine particle size [58]. Glycolysis was recently utilized to degrade polyester resin with glycol, obtaining precursors that could be potentially involved in a novel synthesis of unsaturated polyester or polyurethane [59]. Solvolysis treatment through ethylamine, ethanol and potassium hydroxide resulted effective in the solubilization of the matrix and in the recovery of visually clean fibres, while a solution of dimethyl sulphoxide (DMSO) and toluene in equal parts was applied to extract aramid fibers epoxy by solvent swelling [60]. The extensive utilization of the acid digestion chemical recycling is limited by the use of hazardous

chemicals and conditions, and the resulting decomposition products are often constituted by complex hydrocarbon/acid mixtures [61].

To date, several chemical recycling methods have been proposed, but even the most advanced techniques would still destroy the size, the braided order and the surface of CFs in different degree [62,63], and only random short fluffy fibres and woven fabric pieces can be reclaimed. Such recovered CFs can never be reincorporated in the same high-tech applications where they are recovered from. In a recent paper of Yuan et al. [64], a new synthesis was proposed to prepare recyclable CF-reinforced poly(hexahydrotriazine) resin composites. In that work, multiple recycling experiments demonstrated that the prepared laminates showed performance comparable to those of their commercial counterparts, and that it was possible to obtain multiple intact recoveries of CFs and near-total recycling of both the constituents, through gentle depolymerization in certain dilute acid solutions.

Supercritical fluids chemical recycling methods are based on the use of substances above their critical temperature and pressure. In fact, supercritical fluids, like water and alcohol, characterized by high solubility and diffusivity, are able to decompose polymer matrix of waste composites, obtaining gas, liquid and solid products [65]. For instance, both near-critical and supercritical water was utilized to recover CFs from waste CFRPs. The resulting fibers possessed a stress at break near ($> 90\%$) to the virgin ones, and a removal efficiency of 95% was obtained with the addition of a KOH catalyst [66]. In many cases supercritical alcohol was utilized to recycle CFRPs. Nottingham University used supercritical propanol with KOH or CsOH catalysts to recycle CFRPs, obtaining a decomposition rate of the epoxy matrix up to 98% and retaining the original tensile strength of the fibers [67-69].

2.3 Re-impregnation of recycled composites

Regardless to the recycling technique, the second stage of composite recycling technology is based in the re-impregnation of the recovered fibers. The main limitation to the re-use of recycled fibers stays in their discontinuous, unsized and fluffy morphology [27]. It is thus very difficult to utilize these reinforcements for the development of structural composites. When recycled fibers are applied in direct moulding technique, they can be added to different polymer matrices through injection moulding (for thermoplastics) and bulk moulding compound compression (for thermosettings). The elevated pressure involved in these processes often leads to a substantial reduction of the fiber length, limiting thus the stiffness, the strength and the electrical conductivity (for CFs) of the resulting composites [27]. Another way to utilize recycled fibers is based on their conversion in nonwoven 2D or 3D preforms,

that can be them impregnated through resin infusion or resin transfer molding (RTM). The discontinuous morphology and the random orientation of the reinforcements limit the mechanical properties of the resulting materials, that often reach a plateau at $V_f = 0.3$ [70,71]. In some cases, it is possible to align discontinuous rCFs through different techniques (like centrifugal alignment rig), obtaining rCFRPs having an elastic modulus comparable to that of aerospace-graded Al and woven CFRPs [72]. In Table 3 possible ways of reusing and apply recovered products obtained by different recycling methods are summarized.

Table 3. Reuse and application of recovered products obtained by different recycling methods (adapted from [54]).

recycling method	reuse and application
mechanical	<ul style="list-style-type: none"> • composites reinforced by recycled fiber • concrete reinforced by crushed CFRP pieces
thermal	
pyrolysis	<ul style="list-style-type: none"> • composites reinforced by short recycled fiber • organic liquid fuels • pyrolytic gas or oil
fluidized bed	<ul style="list-style-type: none"> • bulk moulding compound (BMC) • electromagnetic shielding materials • high-modulus composites
microwave pyrolysis	<ul style="list-style-type: none"> • composites reinforced by short recycled fibers
chemical	
supercritical fluid	<ul style="list-style-type: none"> • composites reinforced by short recycled fibers
solvolysis	<ul style="list-style-type: none"> • fuel gas

The greatest part of the recycled composites (especially rCFRPs) are applied in non-structural components, like interior of aircrafts in aeronautics industry [73]. Recycled FRPs can be also widely utilized to develop automotive components, replacing thus more traditional materials, in the construction industry, sports and household goods, and also in some components for wind turbines. An interesting non-structural application of rCFs is represented by the possibility to produce electromagnetic interference shielding veils, possessing attenuation levels up to 40 dB [74], and heating elements for the food industry [75]. Recently, rCFs have been also inserted in high performance ceramic disk brakes [27].

3. Recycling of composite materials for wind blades

The structure of WTs is mainly composed by metals (steel, aluminium, copper), reinforcing fibers (GFs, CFs) and epoxy resin. Unlike glass and carbon fibers, metals are characterized by

elevated recycling rates, because of their homogenous composition and their economic value. In Figure 7 an overview of the material volumes related to WT's, together with their end-of-life disposal routes, is reported [76].

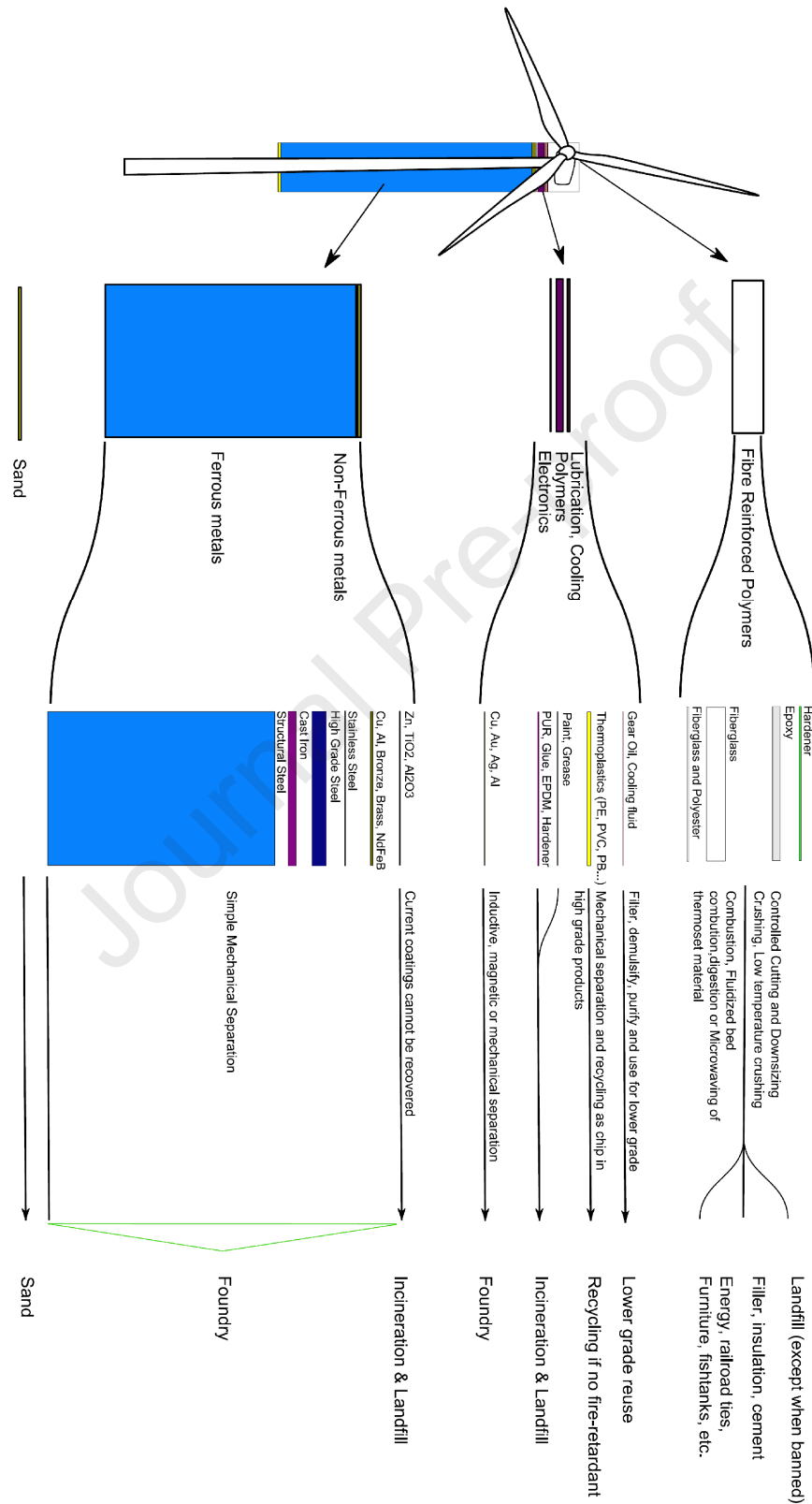


Figure 7. Recycling and end of life disposal routes of the most important WT's parts [76].

As reported in Chapter 1, the most widely utilized material for manufacturing wind blades in plants with nominal power 1-3 MW is the epoxy/GF composites (V_f around 50%), as epoxy resin possesses good chemical resistance and mechanical performances, while GFs are diffused on the market and are relatively cheap [77]. Regardless to the manufacturing technique, the overall waste for producing each blade is generally around 10%, and also the consumables utilised for the infusion process (i.e. peel ply, breeding fabric, vacuum bags and vacuum tape) must be taken into account. For a 5.4 t blade, this means that there are about 540 kg of manufacturing waste and 120 kg of consumables that must be disposed of. Therefore, for a WT with a nominal power of 1.65 MW, it means that there are about 18.6 t of composite materials used in the blades. Considering the growth rate of the utilization of the wind energy, it can be estimated that the overall amount of waste composites deriving from WTs in the next 20 years will be higher than 10^6 t. According to other predictions, it was estimated that by 2034 about 225000 t of rotor blades will be annually recycled in the world [76]. It is therefore clear that the end of life of composite materials should be carefully analyzed [7]. According to the analysis reported in the book of Goodship [7], landfilling is no longer an economically feasible option for the high volumes involved, while incineration with some energy recovery can represent a near- to medium-term solution. Instead, the recovery of composite for wind blades and their recycling through different techniques could be probably the best options for the future. However, the literature scarcity on WTs life cycle assessment (LCA) studies and also the limited industrial trials clearly show that much research efforts will be required to deal with composites waste problem. The most important economic consideration that must be done when the problem of composites recycling is analyzed is whether there is a market for the recyclates [78]. In fact, companies involved in composite waste management have to face big problems related to economies of scale and transportation costs, that can be solved only with a reliable feedstock at their disposal. In the following paragraphs, several literature examples of recycling of composite structures recovered from wind blades are provided.

3.1 Mechanical recycling

Mechanical recycling of waste composites is probably the simplest method, and this solution has been already scaled-up to a commercial level [37]. Mechanically shredded composites (SC) are constituted by a mixture of individual fibres, longer fibre bundles partly impregnated with resin and clusters of materials. It is therefore clear that SC quality is a key aspect for the

recycling of composite parts, and that the most valuable fractions are those with an elevated long fiber concentration. The utilization of SC in new thermosetting matrices is mainly related to the possibility of limiting the amount of fibres in existing composites and reducing the cost of the product, without changing the manufacturing technique [79]. As already said, the main limit of this technique is represented by the impossibility to obtain continuous fibers. Moreover, in some cases the intrinsic mechanical properties of the recycled fibers are considerably reduced.

A literature review of Beauson et al. was focused on the recycling of shredded composite materials recovered from WT's, utilizing rGFs for the production of new composites [80]. In that work an interesting approach, based on the reinforcement weight content, was adopted. It was highlighted that an increase of the SC concentration led to a general drop of the mechanical properties of the composites, if compared to a reference material made with only virgin fibers (see Figure 8). It was therefore concluded that a composite prepared with SC could not show better performances with respect to the corresponding composite without any reinforcement, because the reinforcing fibers were often damaged or they were not properly mixed within the new composites. Moreover, it was probably necessary to adjust and optimize the process parameters.

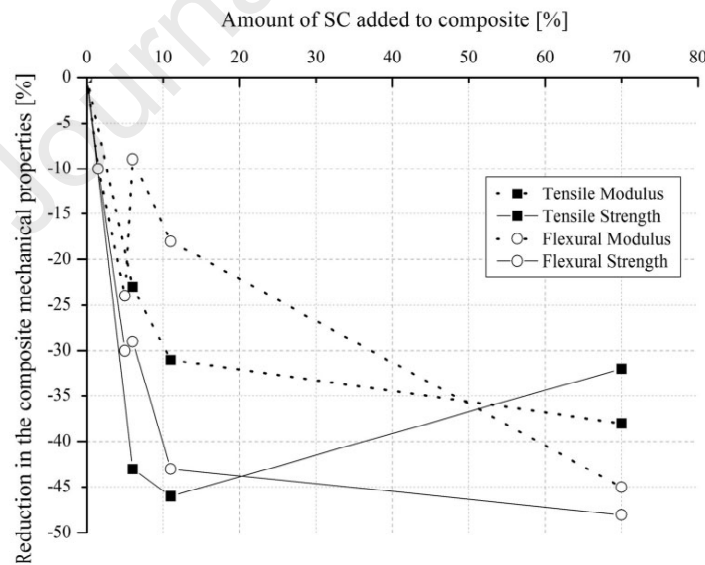


Figure 8. Reduction in the mechanical properties related to the amount of SC in the composite [80].

Another paper of Beauson et al. provided a comprehensive investigation of the mechanical properties of polyester resin composites reinforced with SCs, recovered from a wind turbine blade 26 m long, in which a polyester resin was utilized as matrix [81]. Recovered composite

blade was shredded through a rotating cylinder hammer and the resulting materials were manually sieved to separate fine and coarse fractions. Through a special vacuum resin infusion technique composites with SC contents ranging from 10 up to 30 wt% were prepared. It was shown that the stiffness of the new composites increased with the SC amount, ranging from 4.2 to 5.8 GPa, and it was systematically higher with respect to that of the neat polyester sample (3.4 GPa). On the other hand, all the composites were characterized by a lower tensile strength (15-29 MPa) than that of the unfilled plate (49 MPa), and also the failure strain was negatively affected by SC introduction. Representative scanning electron microscope (SEM) micrographs of the fracture surfaces of the failed tensile specimens (see Figure 9) evidenced large debonding cracks between glass fiber bundles and polyester matrix, negatively contributing to the failure properties of the composites. Moreover, an evident fiber pull-out, typical of a limited fibre/matrix interfacial adhesion, could be detected. It was therefore concluded that the observed decrease of the failure properties in recycled composites was due to the non optimal bonding between SC and the new polyester matrix, and that physical or chemical treatments would be probably required to activate the surface of the old polyester matrix for a better bonding with the new resin.

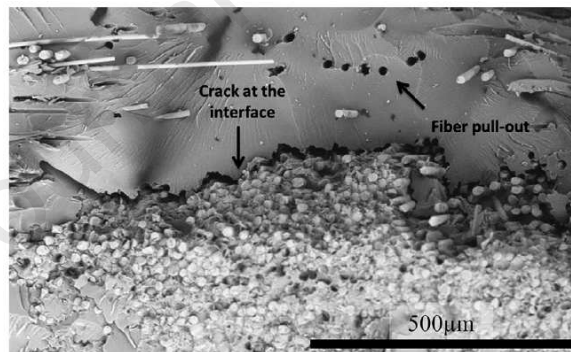


Figure 9. SEM image of the fracture surface of SC composites [81].

It is also possible to use mechanically recycled fibers in additive manufacturing technologies, like fused deposition modeling (FDM). In a recent paper of Rahimizadeh et al. short glass fibers from scrap wind turbine blades were recovered and mixed with a polylactic acid (PLA) matrix through a double extrusion process, to prepare novel composite filaments for FDM [82]. In this work, a double sieving operation was adopted to separate the fibers having a length higher than 0.4 mm, in order to avoid 3D printer nozzle clogging and jamming. Composite filaments with fiber concentrations up to 25 wt% were utilized to produce 3D printed tensile specimens. As reported in Figure 10(a-c), samples with a recyclate content of 25 wt% showed an increase of the specific stiffness of the 74% with respect to neat PLA,

associated to a reduction of the specific tensile strength and of the failure strain of 42% and 65%, respectively. Moreover, it was also found that PLA samples reinforced with recycled GFs had a specific modulus and tensile strength respectively 18% and 19% higher than those of samples reinforced with virgin GFs. This result was explained considering that the surface of recycled glass fibers (rGFs) was partially covered with epoxy particles, that had a favourable interaction and thus improved interfacial bonding with the PLA matrix.

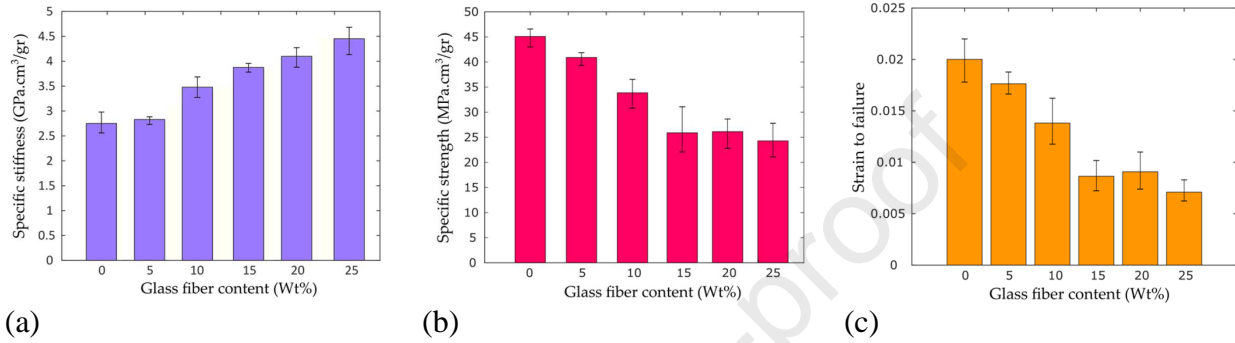


Figure 10. Tensile properties of rGFs reinforced PLA specimens with different recycled fiber contents. (a) Specific stiffness, (b) specific strength and (c) failure strain [82].

Another possibility for mechanically recycled composites is to use them as a filler in concrete. For instance, Schmidl and Hinrichs recycled rotor blades with GF reinforced thermosetting composites by mechanical recycling, and the resulting materials were then used in cement production [83].

3.2 Thermal recycling

As reported in Chapter 2, thermal recycling technology mainly includes pyrolysis, fluidized bed recycling process and microwave pyrolysis. As the load transfer capability in polymer composites is strongly dependent both on the intrinsic mechanical properties of the reinforcing fibers and on the interfacial shear strength, the latter aspect should be taken into account also in recycled FRPs. In a recent work of Rahimizadeh, et al., both thermal and mechanical recycling methods were considered to reclaim glass fibers from end-of-life wind turbine blades [84]. WT blades were cut in small pieces and then grinded through a hammer mill, the resulting materials were then sieved with a screen classifier of 19 mm. The thermal recycling process was performed in a pyrolysis furnace at 550 °C for 45 min under a nitrogen atmosphere, followed by an oxidation at the same temperature for 10 min, in order to remove residual ashes on the fiber surface. Single fibers extracted from both mechanically and

thermally recycled fiber bundles were then utilized for single fiber tensile and pull-out tests, by using a PLA matrix applied for Fused Deposition Modeling (FDM). SEM micrographs of the recycled and virgin fibers are shown in Figure 11(a-c). It is evident that mechanically recycled fibers were characterized by a higher surface roughness, because of the presence of epoxy residues deriving from the grinding process, while pyrolyzed and virgin glass fibers presented a smoother profile. As it could be expected, virgin fibers presented the highest stress at break, i.e. 20% higher than mechanically recycled GFs and 60% higher than pyrolyzed ones. Interestingly, elastic modulus of pyrolyzed fibers was 17% higher than that of the grinded ones. For as concerns the interfacial bonding strength, mechanically recycled fibers showed the highest apparent interfacial shear strength (IFSS), i.e. 13 MPa, that was respectively 14% and 26% higher than that of pyrolyzed and virgin glass fibers. This result was explained considering that epoxy residues in grinded GF could increase the surface roughness and favoured interlocking mechanisms and chemical interactions with PLA molecules through hydrogen bonds. For the same reason, pyrolyzed fibers showed higher IFSS values with respect to the virgin ones. In these conditions, the beneficial contribution of the silanization on virgin fibers had a minor effect.

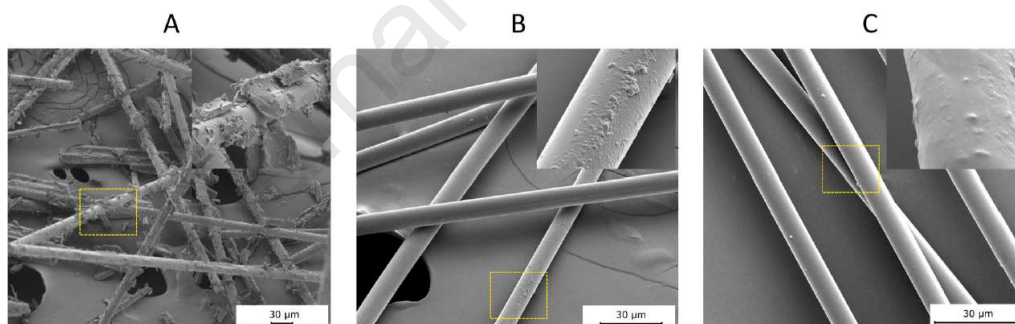


Figure 11. SEM images of the surface morphology of different GFs: (a) ground fibers, (b) pyrolyzed fibers and (c) virgin fibers [84].

In a paper of Akesson et al. the effectiveness of recycling GFRPs recovered from a used WT through microwave pyrolysis was investigated [85]. Composite scraps having a dimension between 7 and 30 mm were collected and pyrolyzed in a temperature interval 300-600 °C under a nitrogen atmosphere through microwaves generated by three magnetrons having a nominal power of 1 kW. Non-woven fibre mats were then prepared by manually blending the recycled fibres with a bicomponent fibre, and used as reinforcement of an unsaturated polyester resin. In this way, composites with both thermally recycled and virgin fibers were prepared by hand lay-up at different relative proportions (i.e. 0, 50, 75 and 100 wt% of virgin

fibres). Fibers pyrolyzed at 440 °C lost about 25% of their original tenacity, passing from 0.48 to 0.35 N/Tex. The results of the flexural tests on the prepared composites are summarized in Table 4. Both the stiffness and the strength were progressively decreased by adding recycled fibers, demonstrating that the reinforcing effect of the mats obtained from recycled fibers was rather poor. For instance, in VF75 sample the flexural strength passed from 189 to 157 MPa, while the flexural modulus was decreased from 16 MPa up to 12 MPa. In order to explain these results, it was hypothesized that the degradation of the GF sizing determined a lowering of the fiber/matrix interfacial adhesion. Moreover, also the quality of the recycled fibre mats was not optimal, as courser fibre aggregates, acting as potential stress concentrators, were present.

Table 4. Flexural properties of composites prepared by using virgin and recycled non-woven fabrics in different amounts (adapted from [85]).

composite	flexural modulus (MPa)	flexural strength (MPa)	elongation at break (%)
VF100	16.2 ± 3.0	188.8 ± 39.2	3.0 ± 1.2
VF75	12.4 ± 0.9	156.7 ± 25.0	4.1 ± 0.1
VF50	8.6 ± 1.6	103.9 ± 27.3	4.6 ± 0.1
VF0	6.4 ± 0.4	61.1 ± 9.0	4.9 ± 0.1

3.3 Chemical recycling

Chemical recycling technology is based on the chemical decomposition of the matrix to recover both the reinforcing fibers and some degradation products, that could be utilized to prepare fresh polymeric materials or other valuable chemicals. Even if at the beginning chemical recycling methods were mainly focused in the recovery of only the fibrous reinforcements, recently, many studies have demonstrated that decomposing thermosetting resins in mild conditions it is possible to recover also low molecular weight oligomers for high value added applications [86]. Even if at a general level the recycling effect is better, these methods applied to thermoset composites are technically difficult and quite expensive. Nowadays, the most interesting chemical recycling methods are the solvolysis and the use of supercritical fluids.

As reported in Chapter 2, through solvolysis it is possible to depolymerize the resin by using a proper solvent and temperature. Through this method it is possible to obtain an efficient recovery of both the fibers and the resin, but the solvents generally utilized are toxic and

expensive. Among the most important European projects financed by the EU on the recycling of FRPs, the EURECOMP project was specifically devoted to the recycling of thermosetting composites through solvolysis [87], in order to recover the fibres as a valuable reinforcement in new composites, and to obtain from the matrix precious precursors for the chemical industry. The most important conclusions of these projects are reported in the papers of Oliveux et al. [88,89] and Kao et al. [90]. On the other hand, super/subcritical fluid recycling technology is a promising clean and environmental friendly process, that allows the recovery of fibers with clean surface and good mechanical properties. However, the temperature and pressure conditions are often rather heavy, and expensive equipment is often required. Because of these reasons, the recovery of thermosetting resin composites by supercritical fluid technology is still in the laboratory stage [54].

Considering that chemical recycling technologies are at the beginning of their development stage, it is not easy to find in literature specific works devoted to the chemical recycling of thermosetting composites recovered from wind blades. The Danish innovation consortium GENVIND, active between 2012 and 2016, tried to give an overview on the different recycling methods for wind turbines and to propose secondary applications [87]. In this project, both the solvolysis below supercritical conditions (through nitric acid, ammonia or glycol at temperature below 100 °C and/or pressure lower than 1 bar) and the supercritical fluid recycling (through water or ethanol) were considered. It was concluded that many of these recycling methods are highly specialized, and this aspect puts a serious limit to where it is being offered and how widespread it can be. Moreover, the feasibility of these processes is limited also because they are generally time and energy demanding. This is the main reason why the greatest part of the chemical recycling processes are still at a lab-scale or pilot-scale level, and their full-scale efficacy has not yet verified.

4. Innovative solutions for composite blades with improved recyclability

On the basis of the information reported in the previous chapters, it emerges that both GF and CF reinforced thermoset composites are difficult to be effectively recycled, and in some cases they have high recycling cost. Therefore, researchers have conducted many studies on novel recyclable composite materials, to be applied also in the wind industry. At present, FRPs with improved recyclability mainly include modified thermosetting composites, thermoplastic composites and natural fiber composites [54].

4.1 Modified thermosetting composites

Considering that thermosetting polymers are generally infusible and insoluble, many efforts have been recently devoted to introduce active covalent bonds in epoxy systems [91-93]. Under external stimuli such as light, heat and irradiation, the breaking and recombination of covalent bonds can be obtained. In other words, covalent adaptable networks (CANs) can be utilized for mending or self-healing, for the activation of shape change or stress reduction mechanisms, and for recycling/reprocessing thermosetting polymers. In the latter case, an epoxy matrix could be reshaped and reprocessed like a thermoplastic. At a general level, CANs can be divided in two categories, depending if the dynamic macromolecular structure can be obtained through bond exchange or through equilibrium shifts leading to reversible depolymerization.

In CANs systems belonging to the first category, exchangeable bonds are subjected to cleavage and reformation, and thus the total number of bonds (i.e. the crosslinked structure and the original stiffness of the matrix) is retained [92]. CANs based on addition-fragmentation chain transfer (AFT) capable moieties, like allyl sulfides or trithiocarbonates, have been recently developed. The thiyl radical-mediated addition-fragmentation of an allyl sulphide could be an example of CANs based on AFT reactions (see Figure 12). In these systems, the generation of radical species and thus the bond exchange reactions can be realized through the exposure to light, thanks to the action of a radical-based photoinitiator. For instance, photoinduced repeatable self-healing of covalently crosslinked structures through re-organization of photoresponsive trithiocarbonate (TTC) units was reported by Amamoto et al. [91].

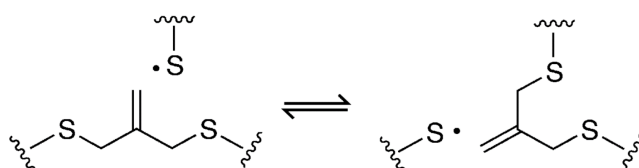


Figure 12. An example of the thiyl radical-mediated addition-fragmentation of an allyl sulphide. In this reaction, reactants and products are identical and the reaction outcome is simply an exchange of bond connectivity [92].

In a recent paper of Montarnal et al., temperature sensitive CAN structures based on transesterification (TE) reactions in epoxy systems have been recently developed (see Figure 13) [93]. The advantages of this approach are related to the activation of a fully reversible

plastic flow simply applying a thermal stimulus, without the need of radical generators. TE reaction rates are three orders of magnitude faster at 100 °C than at ambient temperature, and progressively increase with the temperature. Therefore, at elevated temperature the material behaves like a thermoplastic above its softening point, while at ambient conditions its mechanical properties are very near to those of an irreversible thermosetting polymer.

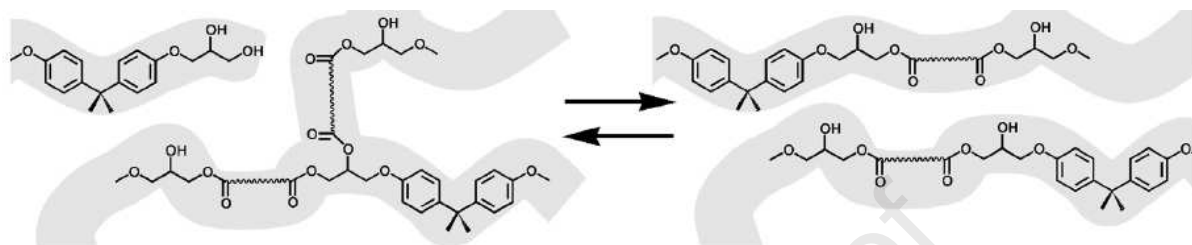


Figure 13. An example of transesterification exchange reaction in hydroxy-ester networks, in which the total number of bonds is retained [93].

In a paper of Taynton et al. [94] the preparation of fully recyclable CFRPs from woven CF sheets and malleable polyimine networks was described. A closed loop recycling of these composites was achieved through dissolution of the polyimine binder via dynamic covalent bond exchange with an excess of a monomer, leading to the recovery of full-length fiber, as well as complete recovery of the matrix. This approach was based on the use of covalently cross-linked yet malleable polyimines, which undergo dynamic covalent bond exchange reactions in response to chemical or physical stimuli.

The second category of CAN systems is based on thermoreversible bond structures in which, thanks to the presence of Diels-Alder adducts, polymerization-depolymerization reactions occur [95]. For instance, the equilibrium Diels-Alder adduct reaction between a furan-based diene and a maleimide-based dieneophile determines the formation of crosslinked structures at low temperature and the depolymerization upon heating (see Figure 14). In these conditions, the reprocessing and/or the crack healing of the polymer matrix can be performed at elevated temperatures.

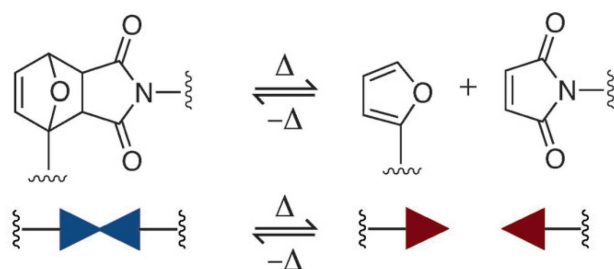


Figure 14. Representation of a reversible polymerization/depolymerization process in polymer networks based on Diels-Alder reactions between furan and maleimide [95].

Therefore, the approach based on thermoresponsive CANs could be a promising alternative of the recycling of FRPs, but the number of active covalent bonds is rather limited, and also the remoulding conditions are particularly demanding. Moreover, composite materials are often utilized for high-temperature applications, in which the dimensional stability is a fundamental requirement. In this case, the possibility to use different stimuli such as light of an appropriate wavelength or suitable solvents could be possible solutions. However, much efforts should be performed in the future to further develop these systems and to expand their use in full-scale industrial applications.

A new generation of hardeners for epoxy resins, called Recyclamines[®], have been recently proposed by Connora Technologies, with the aim to develop recyclable thermosets which can be easily converted into reprocessable thermoplastics. Therefore, epoxy hardeners derived from polyamine structures, in which amino end groups can be tethered together by a central cleavable group, were prepared. In order to induce crosslinks cleavage in the epoxy network and obtain a thermoplastic molecular structure, a combination of elevated temperature (70-100 °C) and pH (acidic conditions) are required. In these conditions, starting from equimolar mixtures of bisphenols and epichlorohydrin, true thermoplastics can be produced [96]. Depending upon the bisphenol utilized for the synthesis, a wide variety of amorphous, moldable matrices, called poly(-hydroxyethers) or phenoxy resins, can be produced, having glass transition temperatures (T_g) from 80 to 175 °C. In this research field, La Rosa et al. investigated the possibility to recycle CFRPs with a green epoxy resin mixed with a degradable polyamine ether [97]. The prepared composites were solubilized in an acetic solution at 80 °C for 1.5 h, and the fibers were then separated through filtration. Upon solution neutralization with NaOH it was possible to recover both a thermoplastic polymer and clean CFs. The environmental advantage of this approach was confirmed by LCA results. An interesting possibility to produce recyclable matrices for composite materials derives from recyclable thermoset hyperbranched resins. Yu et al. developed a low viscosity, degradable

epoxy-ended hyperbranched polyester (DEHP), obtained by a reaction between epichlorohydrin and a carboxyl-ended hyperbranched polyester [98]. It was shown that DEHP was able to reinforce and toughen the diglycidyl ether of bisphenol-A (DGEBA) and also the cured DEHP/DGEBA composites. Moreover, the introduction of DEHP promoted degradation of the cured DEHP/DGEBA composites. In particular, by introducing 12 wt% DEHP the prepared composites were completely degraded in only 2 h at about 90 °C, highlighting thus the good degradation and recycling properties of the DEHP [99].

In a recent paper Xu et al. presented the synthesis of thermoset hyperbranched polymers (HER-HT_n) containing a reversible heterocyclic structure (hexahydro-s-triazine), that could be degraded under mild conditions [100]. The cured materials showed remarkable thermo-mechanical properties and rapid degradability in environmentally friendly phosphoric acid solutions. Moreover, the cured HER-HT_n could be completely digested at 90 °C in only 2 h, to recover 2-aminobenzyl alcohol at a rate of 85%. The recovered product could be then used to synthesize the initial hexahydro-s-triazine monomer, confirming thus the reversibility of the hexahydro-s-triazine structure and the recyclability of the HER-HT_n.

Garcia et al. showed a simple one-pot, low-temperature polycondensation reaction between paraformaldehyde and 4,4'-oxydianiline, in order to obtain hemiaminal dynamic covalent networks (HDCNs), which could further cyclize at elevated temperatures, producing poly(hexahydrotriazine)s (PHTs) [101]. Both materials were strong thermosetting polymers, and the PHTs showed high stiffness, excellent solvent and environmental stress cracking resistance. Interestingly, both HDCNs and PHTs could be digested at pH < 2, to reclaim the bisaniline monomers.

4.2 Thermoplastic composites

Nowadays thermoplastic composites find large application in aerospace and automotive sectors, but they started to be considered in the wind industry only after 2005. The interest towards thermoplastic matrices derives from the need to dismantle the first batch of service blades and from the consequent abandonment of a large number of blade materials, that could be hardly recycled [102]. Moreover, thermoplastic composites could be interesting because they are endowed with shorter and cheaper manufacturing cycle times [103]. Recently, several papers on the potential of thermoplastic composites for WT blades have been published [104-110,102,111]. As already reported in Chapter 2, composite materials are generally characterized by elevated embodied energy values, and thus recovery of their

constituents can lead to considerable economic and environmental advantages [112]. Moreover, the possibility of reclaiming both the matrix and full-length fibers at the end of life through dissolution of the thermoplastic phase at low temperatures could be an interesting option to re-introduce recovered materials into the supply chain [113]. For instance, Brown et al. analysed the structural performances of a vertical axis thermoplastic composite WT blade constituted by a sandwich structure with commingled woven GF/PP thermoplastic composite skins and a polyethylene terephthalate (PET) foam core [104]. Garate et al. investigated the possibility to produce WT blades based on a PP matrix with 65% E-glass fibers [107]. In the paper of Nat et al., 30% CF/polyether ether ketone (PEEK) thermoplastic composite was utilized as plying material for WT blades [102].

The production of traditional thermosetting composite WT blades is generally performed through vacuum infusion processes but, due to their elevated viscosity at the molten/softened state, thermoplastic polymers are not suitable to be processed in this way. In order to overcome this limitation, novel low viscosity thermoplastic solutions, processable with liquid moulding technologies and possessing good thermo-mechanical properties, have been recently developed [114,115,111,116]. In these systems, the liquid monomer of a thermoplastic matrix is infiltrated together with an activator in the woven fabric of the reinforcement. Polymerization reaction can then take place within the fiber bed, obtaining thus a thermoplastic FRP.

Different thermoplastic composites with low viscosity polyamide based systems have been recently developed. An anionic polylactam 12 (APLC12), precursor of polyamide 12 (PA12), has been proposed by EMS Chemie AG. Tailoring the initiator and the reaction temperature, it is possible to perform PA12 polymerization from few seconds to several minutes, and also composites with elevated fiber concentration can be impregnated [116]. Moreover, the prepared material showed a very limited shrinkage during polymerization and were characterized with a void concentration below 1%. Rijswijk et al. synthesized an anionic polyamide 6 (APA6) starting from a carbamoylcaprolactam activator (see reaction scheme in Figure 15) [111]. Moreover, the surface chemistry and morphology of the reinforcing fibers were modified to improve the interfacial adhesion with APA6 matrix [117,118]. In these papers, it was demonstrated that increasing the moulding temperature a stronger interfacial bonding could be obtained, but the crystallinity degree of the matrix was reduced, therefore a compromise between these two effects was necessary. It was also shown that a stronger interaction of the activators with the fibers did not necessary increase the mechanical performance of the material.

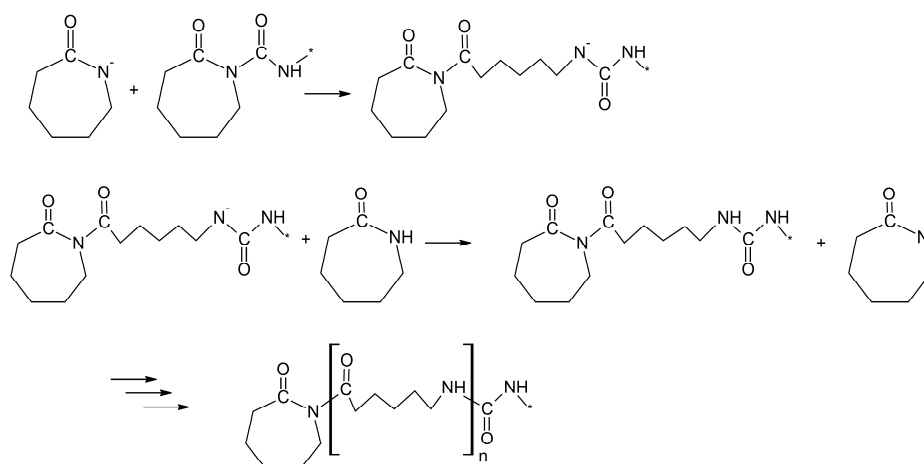


Figure 15. Anionic polymerization of caprolactam into polyamide 6 using a carbamoylcaprolactam activator [117].

Among innovative flowable thermoplastic resins for thermoplastic FRPs, also cyclic butylene terephthalate (CBT), precursor of poly(butylene terephthalate) (PBT), was considered [115]. In a paper of Ishak et al., cyclic butylene terephthalate (CBT) has been polymerized *in situ* at $T = 190\text{ }^{\circ}\text{C}$ both in the presence and absence of woven glass fabrics. The thermal properties of the *in situ* polymerized PBT were compared with those of a commercial injection moulded PBT. It was found that the crystallinity of the injection moulded PBT was significantly lower than that of the *in situ* synthesized one, that was thus more brittle. *In situ* polymerized composites reinforced with GFs at a concentration of 50 vol% were prepared by compression moulding at $190\text{ }^{\circ}\text{C}$, and SEM images highlighted a good interfacial fiber-matrix bonding (see Figure 16(a-b)). For this reason, this formulation was utilized to produce for the first time recyclable wind turbine blades with a length of 12.6 m.

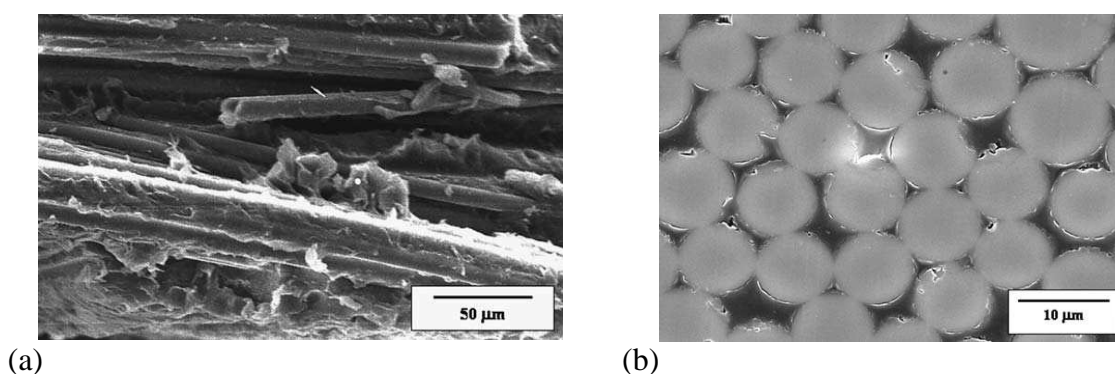


Figure 16. (a) SEM micrograph showing the good interfacial bonding between *in situ* polymerized PBT and GFs. (b) SEM micrograph of polished surface showing the fiber dispersion and quality of impregnation of *in situ* polymerized PBT/GF composites [115].

In a recent paper of Cousins et al. the possibility of recycling a spar cap of a WT blade prepared with a GF reinforced Elium[®] thermoplastic matrix was shown [114]. Elium[®] is a liquid thermoplastic resin belonging to the family of methacrylates, that could be applied in infusion processes. Thanks to the presence of a peroxide initiator, it can be polymerized at high temperature and converted in a solid thermoplastic polymer [119]. Interestingly, polymerized Elium[®] resin can be dissolved in chloroform and recovered in methanol, recovering thus in recycling operations both the matrix and full-length GFs. Also Murray et al. recently investigated the possibility to use Elium[®] thermoplastic resin in GF reinforced composites for wind blades, and performed a comparison with traditional GFRP/epoxy WT blades [109,110]. The results of this comparison showed that both the static performance and the fatigue behaviour of the two blades were similar, but thermoplastic composite blade showed increased damping, and thus reduced operational loads, with respect to traditional epoxy based systems.

4.3 Natural fiber composites

Nowadays GFs dominate the market of the fibers for composite materials, and in 2015 about the 95% of the composites were reinforced with this material [120]. Due to the increasing environmental concerns on the use of non-renewable resources, an increasing attention has been recently paid on the replacement of traditional reinforcing materials with natural biodegradable fibers [121]. Natural fibers such as flax, coir and bamboo are easily available and are characterized by low processing costs. Natural fiber reinforced composites (NFRCs) present some advantages over synthetic fiber reinforced laminates [122-124], like low density, limited cost and biodegradability [54]. Also natural fiber reinforced composites can be grinded at their end of life, re-impregnated and re-utilized in an open loop recycling perspective, but probably the most attractive option for these materials is their biodegradation. According to the Natural Fiber Composites Market forecasts, it is expected that global NFRCs market size will increase from \$4.46 billion in 2016 up to \$10.89 billion by 2024, thanks also to the need of lightweight and fuel-efficient vehicles [125]. Even if the interest in NFRCs has been up to now focused on automotive applications, they have been recently applied also in buildings, in thermal insulating materials and in furniture, and some possible future application sectors could be sports, clothes, packaging and aerospace components [125]. On the other hand, the most heavy limitations in the further expansion of NFRCs are represented by some intrinsic features of natural fibers, like their variable quality and limited mechanical

properties, their water absorption tendency and limited thermal stability. Moreover, they are incompatible with hydrophobic matrices and often tend to agglomerate. In literature, it is possible to find recent reviews about the last developments on NFRCs [125-127]. Both thermoplastic and thermosetting resins can be used as matrices for natural fibers. Because most natural fibers are not thermally stable above 200 °C, only polymer matrices that can be processed below this temperature can be utilized (i.e. PP, low density polyethylene (LDPE), high density polyethylene (HDPE) and PLA). Quite surprisingly, only few works dealing with degradation mechanisms of NFRCs under light or environmental exposure or under the attack of fungi and microbial agents can be found in literature. These factors should be crucial design parameters in NFRCs, as natural fibers can easily degrade in the biological, photochemical and aqueous environment. These tests were mainly performed only on thermoplastic composites with biodegradable matrices (like PLA), and many attempts have been recently made to improve the biodegradability of NFRCs through modification of the matrix and of the reinforcing fibers [127].

In a recent paper of Kalagi et al., it was analyzed the possibility to replace traditional composite materials reinforced with CFs and GFs for wind blades with natural fibers. In that work, application of NFRCs in wind turbine, their most important technical requirements, their properties and the manufacturing technologies of these materials were reviewed [128]. In a work of Mendez et al., green textile/woven composites that could be potentially utilized as an alternative to materials derived from non-renewable sources was considered [129]. Flax and hemp fabrics were chosen as fibers, while a commercially available marine resin, able to resist in moist environment, was utilized as matrix. After a comprehensive mechanical characterization of the composites, the possibility of using natural bast fibers for the development of small WT blades was analyzed.

According to the work of Shah et al., a noticeable lack of fatigue data of NFRCs limits their application in critical components, like rotor blades. Therefore, the fatigue behaviour of a 3.5 m wind blade constructed with a hemp/polyester composite was investigated. Fatigue diagrams developed in this paper confirmed that NFRC blades could satisfy the 20 year design life criteria, taking into account also a proper safety factor [130]. Considering that WTs applied in tropical region should operate at low wind speeds, lightweight NFRCs could represent an interesting option to increase their size (and thus the generated power) without causing inertial problems. Sundar et al., considered the possibility to reinforce an epoxy resin with flax fibres [131]. However, due to the limited fiber-matrix adhesion and the elevated voids content, these NFRCs were much weaker than GF reinforced ones, and they could be

thus applied only in non-structural components of WT blades. In the paper of Park et al. the structural design of a HAWT blade with a nominal power of 1 kW, prepared by using a flax/epoxy composite, was carried out [132]. A detailed analysis through a finite element method highlighted that this blade could be acceptable for structural safety and stability, blade tip deflection, weight and resonance possibility.

5. Conclusions and future perspectives

Considering the increasing number of end of life WT blades and the recent concerns on resource conservation and environmental protection, growing attention has been paid to the recycling of thermosetting FRPs for wind turbine blades. This review gives an overview of the main recycling technologies that could be nowadays utilized for these materials.

In this review, mechanical and thermo-chemical processes were presented. Mechanical recycling is economically feasible and probably represents the most mature technology, but inevitably leads to a general downgrading of the recycled products and thus to the production of secondary components for non-structural and lower value applications. Moreover, new markets for mechanically recycled composites needs to be detected, and virgin continuous reinforcing fibers (and new resin) for the production of new WT blades, replacing the dismantled ones, are required. In this sense, the environmental sustainability of this process is questionable. Pyrolytic processes (with or without microwave application) seem to represent an interesting option for the recycling of composite blades, and some examples of commercial application of this technology can be found on the market. Even in this case, the problems related to the discontinuous morphology of the recovered fibers and the need to find new market applications for the chemicals derived from the pyrolysis need to be carefully analyzed. At the present state chemical recycling, due to the use of hazardous chemicals/solvents and harsh processing conditions, does not represent a feasible solution for a full scale recovery of waste composites in the wind energy market. However chemical recycling through supercritical fluids, involving the use of environmentally friendly substances, could be an interesting option, if an adequate upscaling of this technology will be realized.

In summary, each recycling method has its own pros and cons, and there is no single method to recycle all composite materials. Therefore, tailor-made solutions must be developed, especially to solve the recovery problem of each type of material. Moreover, the effect of the different recycling routes on the microstructural and mechanical properties of the recycled

fibers should be carefully analyzed. Cheaper, environmentally friendly and more efficient recycling processes are required. Moreover, innovative remanufacturing technologies for high performance products are needed to expand the market for recycled materials. In other words, recycled products should be reused with high value to meet the requirements of a sustainable development.

Considering the issues related to the recycling of traditional thermosetting composites, more attention should be probably paid in the future to recyclable and environmentally friendly composite blade materials. The possibility to use modified thermosetting resins, that could be processed like a traditional epoxy resin and that could be recycled like thermoplastics, if heated or irradiated, represents an interesting option for the future. In this case, the heaviest problem is represented by the limited number of matrices that are actually available on the market and their cost. The possibility to use thermoplastic composites for wind blades, constituted by low viscosity precursors that could be applied through resin infusion, probably represents one of the most promising perspectives for the future wind blade technology. On the other hand, the development of composite blades with natural fibers embedded in biodegradable matrices could be interesting both for the reduction of the embedded energy related to the blade production and for the possibility to dispose of the components through biodegradation after the end of life. In this case, the problems related to the constancy of the thermo-mechanical properties of the reinforcements and to the water absorption of biodegradable matrices should be overcome.

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6. References

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AUTHOR DECLARATION

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We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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