Styrene-Free Liquid Resins for Composite Reformulation

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Abstract Three different classes of thermosetting styrene-free resins were investigated to assess their suitability to constitute the matrix phase in the reformulation of composites reinforced with mechanically recycled glass fibers. Resin reactivity and mechanical properties after curing were compared to commercial styrene-based, unsaturated polyester resins. The polymeric resin, acting as a binder, could be properly selected depending on the desired reactivity, processability, and mechanical behavior. Some prototypal examples of reformulated composites with different types and contents of recycled glass fibers were produced and mechanically tested. The combination of the epoxy resin with up to 60 wt% of mechanically recycled glass fibers resulted in an increase of elastic modulus up to 7.5 GPa.

Keywords Polymer-matrix composite · Recycling · Glass fiber · Mechanical properties · Wind turbine blade

1 Introduction and Context of Reference

The exponential growth of the human population and the linear economy models currently adopted worldwide represent key drivers for the continuously increasing demand for new manufacturing products and for their current consumption rate, which unsustainably impact on natural resources while generating growing levels of discarded materials and components. Indeed, a great number of end-of-life (EoL) products are being disposed of, leading to several environmental problems [1]. A representative example of EoL products are wind turbine blades, whose annual production volumes are expected to increase significantly in the coming decades, reaching 200,000 tons of wind blade wastes in 2034 [2]. Wind turbine blades are

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mainly composed of glass fiber reinforced polymers (GFRPs) and the application of a circular economy approach to EoL GFRPs management is one of the challenges of the modern wind turbine manufacturing industry [3, 4]. Responsible treatments of EoL composite products that may include reusing, recycling, or remanufacturing are desirable and beneficial both environmentally and economically because waste is minimized, while valuable components and materials are recovered [5, 6].

Several recycling technologies have been proposed and developed concerning fiber reinforced composite materials [7]. Among them, the mechanical treatment still represents the most suitable process to reduce the size of GFRP composite parts, since glass fibers (GFs) tend to be damaged during thermo-chemical processes [6, 7].

The combination of mechanically recycled GFRPs with a polymer matrix will give shape to a composite material whose reinforcement is a waste. The matrix selection in composite materials is also quite important because it has a large influence on the final properties of the composite being constructed. Particularly for recycled GFRPs, the presence of contamination in wastes as well as some degradation components may affect the behavior of composites reinforced with recycled GFRPs. The main roles of a matrix in both the pristine and recycled composites are:

- to hold and protect reinforcing materials from environmental and physical damage;
- to distribute and transfer the load to the reinforcements;
- to define external characteristics, such as the final shape of composites;
- to prevent the buckling of the fibers;
- to ensure the chemical and thermal compatibility with the reinforcement;
- to avoid rapid propagation of composite cracks [8, 9].

Depending on their final applications, polymeric composites can employ matrices that are thermoplastic or thermosetting. Both of them present advantages and disadvantages. Polymer matrices used for structural applications are almost exclusively based on thermosetting systems, thanks to the superior thermal stability, chemical resistance, low creep and relaxation properties and better ability to impregnate the fiber reinforcements of thermosetting in comparison with thermoplastic matrices [10].

2 State of the Art for Composite Reformulation from Mechanical Recycling

2.1 Brief Description of the Scientific and Industrial State-Of-The-Art

Unsaturated Polyesters. One of the most popular class of resins, as well as one of the most versatile group of synthetic polymers in composites manufacturing, is represented by unsaturated polyester (UP) resins. They can be found in a very wide range of engineering applications. Moreover, they are characterized by a highly favorable performance/cost ratio. Important product areas for UPs are marine, automotive, electric and electronic, building, constructions, sport and leisure, domestic and sanitary appliances, furniture as well as military applications [9]. The processing of a UP resin into a composite product can be done using several technologies: hand lay-up and spray lay-up, lamination, casting, compression molding, pultrusion, resin transfer molding (RTM), vacuum infusion and filament winding.

The advantages of UPs are their very good structural properties together with affordable costs. Other advantages include easy handling, processing, fabrication and a good balance of mechanical, electrical and chemical properties. Some special formulations offer high corrosion resistance and fire retardancy.

Vinyl Esters Resins. Vinyl esters are ester resins with unsaturated C=C terminal groups. The terminal unsaturation makes them very reactive. Moreover, the low number of esters group in the main chain of the polymer gives good chemical resistance to this class of resins. In terms of properties and cost, they present characteristics in between those of UP resins and epoxy resins, maintaining the processability and versatility of polyesters, while having mechanical performances closer to the epoxies. This range of properties fits the requirements of corrosion resistance products and for this reason, they are largely employed in this field. Other main markets include pultruded construction and electrical components, automotive structural applications, polymer concrete vessels for mining and chemical operations, high-performance marine applications and sporting goods.

Epoxy Resins. An epoxy resin is a formulation comprising an epoxy-functional oligomer combined with other molecules like polyamines and anhydrides able to cure into a rigid network. As for polyesters, epoxy resins exhibit tremendous versatility because they can be designed to meet a wide range of specific performance requirements. In addition, all epoxy systems involved in composite manufacturing are characterized by the presence of aromatic rings giving mechanical rigidity and thermal stability to the final solidified crosslinked polymer [11].

The main advantages of epoxy resins are:

- the relatively high polarity that confers excellent adhesion to a wide variety of fibers;

- dimensional accuracy of fabricated structures due to low cure shrinkage;
- absence of bubbles and voids due to the addition curing reaction without volatile byproducts;
- very stable and resistant crosslinked structure.

The epoxy composite market was valued at USD 21.6 billion in 2015 and is projected to reach USD 33.1 billion by 2021 driven by the increasing wind energy installations and the increasing use of epoxy composites in structural applications. Moreover, in the aerospace and defense industry, the need for lightweight materials to produce fuel-efficient vehicles due to the increasing environmental concerns, especially in Europe, is constantly increasing together with the growing demand from the pipe and tank and oil and gas industries. In addition, the use of epoxy composite is also increasing in the sporting goods industry for the manufacturing of products, such as tennis rackets, bicycles, fishing rods, and golf shafts [12].

Polyurethane Resins. Polyurethanes (PUs) are generally obtained by the reaction between polyisocyanates and polyols. Tuning the molecular weight, composition and functionality of the two components, a wide range of products can be obtained, like adhesives, coatings, elastomers and foams. Polymeric 4,4′-methylene diphenyl diisocyanate (MDI) is the polyisocyanate of choice for composite manufacturing due to its low viscosity and thereby good processability even at high filler loading, while polyethers and polyols are typically used as hardeners. As cast materials, PUs have gained importance as solvent-free systems, in combination with other components including desiccants, fillers, plasticizers, pigments, flame retardant additives, and catalysts.

The hardened PU materials range from hard and tough to soft and elastic. A general advantage when compared to other matrices is represented by the large toughness and elasticity. Making a comparison with other thermosetting resins, it is possible to state that PUs can be crosslinked as fast as polyesters but yield mechanical and thermal performances comparable to epoxies [13], but with a lower thermal stability.

For decades, crosslinked PUs have occupied a strong position as electrical insulation materials providing notable protection of electrical equipment from aggressive media such as water, chemicals, and dust [14]. Nowadays, the excellent mechanical properties of PU composites open the way to redesign existing profiles, in some cases allowing a redesign of the reinforcement package.

2.2 Limitations, Open Issues and Needs

In the field of UP resins, the incorporation of low molecular weight monomers as reactive diluents, most commonly styrene, enables to tune the final properties of the cured material, especially reducing the viscosity and improving processability. The dilution of UPs and vinyl ester resins in reactive monomers like styrene, results in the formation of a thermosetting resin with good heat resistance, excellent mechanical properties (particularly high tensile elongation) and chemical resistance [4].

However, styrene has several health and safety issues, because of its flammability, volatility and hazardous character. Its replacement is therefore needed for a better environmental sustainability of fiber reinforced polymer composites.

3 Development of Sustainable Styrene-Free Resins for Composite Reformulation

To select an adequate matrix material for remanufacturing, in terms of processability and mechanical properties, three styrene-free, thermosetting binders were investigated and characterized: an acrylic system; an epoxy resin; and a polyurethane resin. Subsequently, the epoxy resin was selected for further formulation studies and filled with different concentrations of mechanically recycled GFRPs. The corresponding composites were tested through thermogravimetric analysis (TGA) and tensile tests to measure the real content of the reinforcement phase contained in each sample and their mechanical properties. Some limitations regarding the ultimate tensile properties and the adhesion between the matrix and the recycled fibers as evidenced by scanning electron microscopy (SEM) images were found, and still need to be fully optimized. Nevertheless, the possibility of using recycled GFRPs as reinforcement phase to obtain new polymer-based composite materials with high values of elastic modulus was demonstrated.

4 Description of Materials and Methods

4.1 Liquid Resin Preparation

Acrylic Resin. The base acrylic resin was mainly composed of a bifunctional acrylate oligomer, an ethoxylated bisphenol A diacrylate (Fig. 1), named SR349 (Sartomer, Arkema).

As the viscosity of SR349 is too high, a methacrylic reactive solvent was added for dilution. The selection of the reactive diluent for SR349 was based on literature data [15]. Considering products, which could be at least partially obtained from renewable sources, four potential candidates, were identified and their chemical structures are shown in Fig. 2:

- isobornyl methacrylate (IBOMA);
- methyl methacrylate (MMA);
- lauryl methacrylate (LMA);
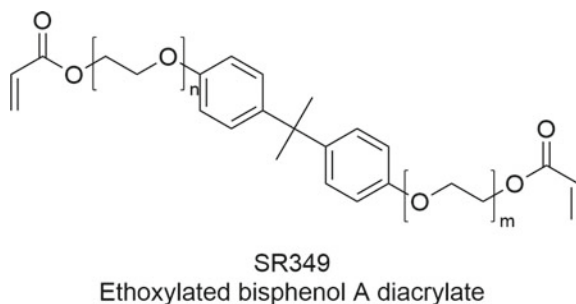- 1,4-butanediol dimethacrylate (BDDMA).

SR349
Ethoxylated bisphenol A diacrylate

Fig. 1 Chemical structure of the bifunctional acrylate oligomer, named SR349

IBOMA   Methyl Methacrylate

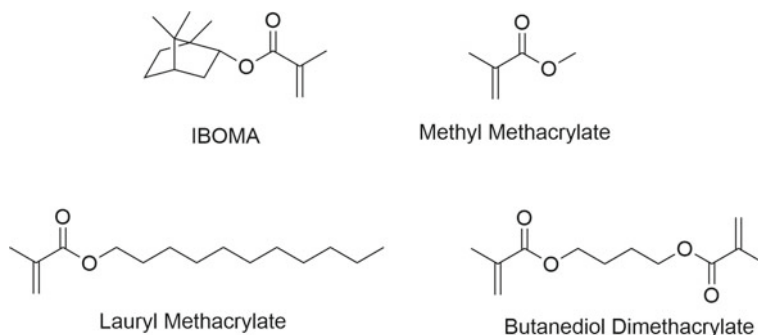Lauryl Methacrylate   Butanediol Dimethacrylate

Fig. 2 Chemical structures of some bio-based reactive diluents

After the rheological characterization shown in Sect. 5.2, BDDMA was selected as target reactive diluent and the acrylic resin formulation was developed according to the weight percentages reported in Table 1.

For the preparation of the acrylic resin, the following procedure was followed. SR349 and the reactive diluent were mixed in a beaker. An initiator/catalyst system was then added, according to the following order: (1) dicumyl peroxide; (2) cobalt(II) naphthenate; (3) 2-butanone peroxide. Once the initiator/catalyst system was mixed, the mixture turned from an uncolored state to a purple color and then to a dark green color. The mixing process generated gasses, resulting in the formation of a layer of

Table 1 Acrylic resin formulation

| Component	Weight fraction (%)
SR349	78.44
BDDMA	19.61
Dicumyl peroxide	0.29
Cobalt(II) naphthenate	0.19
2-Butanone peroxide	1.47

bubbles on top of the liquid resin. For this reason, a degassing process was performed, putting the resin under vacuum at 50 °C. Afterward, the resin was poured into a mold for the crosslinking. The thermal curing treatment, required for the crosslinking of the acrylic resin, consisted of:

- 2 h at room temperature;
- 3 h at 80 °C;
- 2 h at 140 °C.

Epoxy Resin. The epoxy resin is a bisphenol-A (epichlorohydrin) resin, containing an epoxy-terminated oligomer based on bisphenol-A (Fig. 3) and 1,4-bis(2,3-epoxypropoxy)butane (Fig. 4, Araldite®BY158, Huntsman Corporation). To tune the reactivity of the system, Araldite®BY158 was combined with either Aradur®2992 or Aradur®21 or both hardener mixtures, supplied by Huntsman. Aradur®2992 is a mixture of trimethylhexane-1,6-diamine (Fig. 5) and toluene-4-sulphonic acid, while Aradur®21 is a pure trimethylhexane-1,6-diamine curing agent.

Three different formulations (Table 2) were supplied by Huntsman and were used for the epoxy resin, depending on the desired gel time of the system (Table 3).
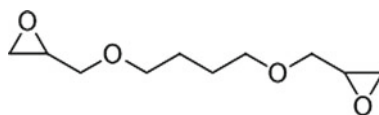
Depending on which formulation was chosen, the selected components were properly mixed in a beaker with a spatula. During mixing, a transition from clear to opaque
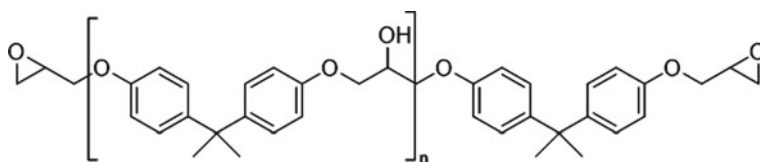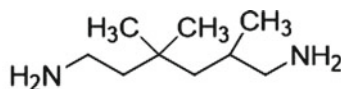

Bisphenol A diglycidyl ether

Fig. 3 Chemical structure of the epoxy-terminated oligomer-based bisphenol-A

Fig. 4 Chemical structure of 1,4-butanediol diglycidyl ether, which is a reactive diluent

1,4-Butanediol diglycidyl ether

Fig. 5 Chemical structure of trimethylhexane-1,6-diamine curing agent

Trimethylhexane-1,6-diamine

Table 2 Weight fractions and name for three different epoxy resin formulations

Component	Weight fraction (%)		
Araldite BY158	74.63	77.52	78.12
Aradur 2992	25.37	5.43	/
Aradur 21	/	17.05	21.88
Formulation name	EPO10	EPO	EPO80

Table 3 Epoxy resin formulations with their specific viscosity and gel time

| Formulation name	EPO10	EPO	EPO80
Viscosity at 25 °C (mPa s)	150	100	90
Gel time (min)	10	30	80

of the system was observed. When the resin became clear again, the mixing was interrupted and the resin was employed for further steps. The thermal curing treatment, required by the epoxy resin to cure in a solid material, was conducted as follows:

- 24 h at room temperature;
- 1 h at 100 °C.

As shown in Tables 2 and 3, three different formulations of the epoxy resin were considered. For this reason, the most catalyzed one was characterized by 10 min of gel time, the intermediate one by 30 min of gel time and the one without catalysts by 80 min of gel time. They were respectively named 'EPO10', 'EPO' and 'EPO80'.

Polyurethane Resin. The PU formulation consisted of an isocyanate and a polyol. Different polyols were tested to determine the optimal formulation, in terms of reactants miscibility, matrix rigidity, and the presence of voids in the cured material. For all the formulations, a molar ratio between hydroxyl groups and isocyanates of 1.05 was selected. The tested reactants were:

- Poly[(phenyl isocyanate)-co-formaldehyde] (PMDI) with average Mn ~ 400 (Fig. 6, Sigma Aldrich);
- Tripropylene glycol (purity ≥97%, Fig. 7, Sigma Aldrich);
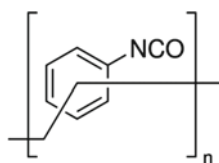
Fig. 6 Chemical structure of poly[(phenyl isocyanate)-co-formaldehyde] monomer
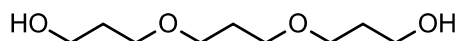
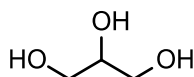**Fig. 7** Chemical structure of tripropylene glycol
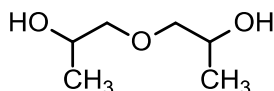
Fig. 8 Chemical structure of glycerol

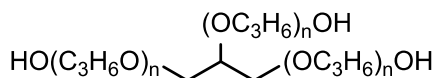**Fig. 9** Chemical structure of dipropylene glycol

Fig. 10 Chemical structure of glycerol propoxylate

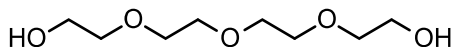**Fig. 11** Chemical structure of tetraethylene glycol

- Glycerol (purity ≥99.5%, Fig. 8, Sigma Aldrich);
- Dipropylene glycol (purity ≥99%, Fig. 9, Sigma Aldrich);
- Glycerol propoxylate with average Mn ~ 266, Fig. 10, Sigma Aldrich);
- Tetraethylene glycol (purity ≥99%, Fig. 11, Sigma Aldrich);
- UOP-L powder, 3A zeolite type molecular sieves for high-quality PU system, Obermeier GmbH & Co. KG Company.

After the measurement of glass transition temperature Tg shown in Sect. 5.2, the final formulation for the PU resin was selected and prepared according to the weight percentages reported in Table 4.

Processing of polyisocyanates, such as PMDI, requires the total absence of water, because the isocyanate groups can react with water in competition with the polyol, resulting in an incomplete and inefficient curing of the resin. To avoid this, tripropylene glycol was dehydrated under vacuum at 90 °C for 16 h under magnetic stirring in a flask. To deactivate the remaining water in the polyol, a zeolite-type molecular sieve (UOP-L powder, ten parts by weight with respect to the polyol) was added to the stirring polyol. Before the addition of tripropylene glycol, the zeolites needed to

Table 4 PU resin formulation	Component	Weight fraction (%)
	PMDI	52.89
	Tripropylene Glycol	42.83
	Zeolite powder	4.28

Table 5 Styrene-based conventional UP resin formulation

Component	Weight fraction (%)
SIRESTER FS 0910/M	98.33
Cobalt(II) naphthenate	1.47
2-butanone peroxide	0.20

be activated with a heat treatment at 350 °C for 4 h under vacuum. The mixture of tripropylene glycol and zeolites was stirred for 1 h under vacuum at 90 °C. Afterward, the proper quantity of PMDI was mixed with the glycol and the mixture was stirred for 15 min under vacuum at room temperature. The thermal curing treatment required by the PU resin to cure into a solid material was performed according to the following cycle:

- 1 h at 50 °C (during molding);
- 5 h at 80 °C.

Commercial styrene-based orthophthalic polyester resin. The UP resin, commercially named SIRESTER FS 0910/M (Sir Industriale, S.p.A.) was composed of a polyester binder, styrene (around $40 \div 50$ wt%), and octabenzone ($\leq 0.25\%$). The conventional styrene-based UP resin was provided in a ready-to-be-used liquid phase. However, the crosslinking required the addition of a catalytic system, composed of cobalt(II) naphthenate and 2-butanone peroxide. The formulation used for the conventional styrene-based UP resin is shown in Table 5.

4.2   Casting and Molding

Acrylic and epoxy liquid resins were cast into a rectangular aluminum mold. The resins undergoing this process were fluid enough to wet the whole mold surface and to generate a smooth surface. PU resins required a faster molding and a curing method to avoid contact between the mixture and the humidity of the air. For this reason, a hydraulic press was chosen to perform the compression molding of PU samples for 1 h at 50 °C. To assure that the cured material could be pulled-off after crosslinking without being damaged, a PTFE treated mold was designed and used.

4.3   Curing Cycle

Thermosetting polymers can achieve gelation with room temperature curing. However, a post-curing process is normally required to complete crosslinking. Different post-curing treatments were designed for the different resins and they are shown in Table 6.

Table 6 Curing cycles designed for the developed resins

Resin	Curing process
Acrylic	(i) 2 h at room temperature (ii) 3 h at 80 °C (iii) 2 h at 140 °C
Epoxy	(i) 24 h at room temperature (ii) 1 h at 100 °C
Polyurethane	(i) 1 h at 50 °C (during molding) (ii) 5 h at 80 °C
Styrene–based UP	(i) 24 h at room temperature (ii) 3 h at 80 °C

4.4 Composite Reformulation

The reformulation process of mechanically recycled composites with a fresh polymer matrix was mainly studied using the epoxy resin, due to the better mechanical performances showed by this type of resin (as described in Sect. 5.5).

Before the formulation with the resin, the shredded recyclate was dried at 50 °C in an oven for 2 h to remove entrapped humidity and improve the composite behavior [16]. Afterward, the liquid resin was poured into the beaker containing the recyclate and manually mixed with a spatula. Compression molding technology was selected to cure the very viscous mixture. Compression molding also enabled the realization of composite samples with a smooth surface and controlled thickness. A mold composed of stainless steel and poly(methyl methacrylate) plate was chosen to allow an easy detachment of the epoxy-based composites from the mold. Compression molding was carried out at room temperature for 24 h, to make the sample cure with the desired shape. Then, an off-mold post-curing treatment at 100 °C for 1 h was performed.

4.5 Characterization Methods

TGA was performed for mechanically recycled shredded composites based on glass fiber and UP, to measure the exact content of GFs in the recyclate flakes. All the tests were performed with a Q 500 instrument (TA Instruments®), setting a heating ramp from 25 to 800 °C at 20 °C/min in air atmosphere, to degrade the resin present in the recycled material and measure the glassy inorganic residue in the sample chamber.

Differential scanning calorimetry (DSC) analyses were performed using a DSC 823e (Mettler-Toledo®) instrument. To identify the glass transition temperature (Tg) of the crosslinked material, the tests consisted of the following three runs with a rate of 20 °C/min:

- first heating run from 25 to 250 °C to check the absence of any unreacted groups;
- cooling run from 250 to 0 °C; and
- second heating run from 0 to 250 °C to identify the Tg.

To determine the total crosslinking enthalpy of the resin, starting from a liquid sample of resin, a single heating DSC ramp from 0 °C to 250 °C was employed with a rate of 10 °C/min.

Rheological properties of liquid resins were measured by means of a rotational rheometer (Melvern instruments Ltd.) with a parallel-plate geometry, with a diameter equal to 20 mm and a gap of 0.5 mm between the plates.

The gel content method was used to evaluate the extent of crosslinking by measuring the effective gel percentage present in the crosslinked resin. The solid crosslinked sample was immersed into an adequate solvent, to allow the dissolution of any residual unreacted components. Acetone or tetrahydrofuran (THF) were selected as solvent, according to the solubility of the liquid resins. 70 mL of solvents were used for each gram of sample. The immersion lasted 24 h when using acetone and 7 h with THF.

At the end of the immersion, the residual, not solubilized, sample was introduced into a beaker. The solution was carefully filtered to collect every residual insolubilized particle in the filter itself, while the solution was poured into the flask. The filter was then introduced into the beaker, while the whole amount of solvent in the flask was evaporated. Afterward, both the flask and the beaker (with the filter inside) were inserted into a vacuum oven at 50 °C and left there for approximately 48 h, until their weights were constant. The final weights were used to calculate the final mass of the solubilized residue (m_{SOL}). Gel percentage (Gel%) was then evaluated with the Eq. (1), which defines the percentage of insolubilized material:

$$Gel\% = 100 \times \left(m_{sample} - m_{SOL} \right) / m_{sample} \tag{1}$$

where m_{sample} is the initial mass of the sample.

The tack-free time determination is a test that allows the estimation of the time required by a liquid resin to reach a correspondingly robust state for safe handling. This means that, from that moment, the partially-cured resin may be removed from the mold. The test involved the casting of a thin layer of the liquid polymeric resin in a round mold of PP, featuring a diameter of 1 cm. The layer, then, was periodically subjected to a scratch and the time required by the resin to recover was measured. The test was repeated until it was not possible to scratch the surface of the layer anymore.

Mechanically recycled fibers from composite materials are not completely liberated but are partially embedded in the cured matrix that was binding them in the 1st life application product. Therefore, it is important to measure the adhesion between the polymer resin constituting the former matrix and the "new" resins, employed in this work as matrices for remanufactured products. For this purpose, a PosiTest Pull-Off Adhesion Tester (DeFelsko) was used to measure the perpendicular force required to pull a material layer of specified area away from its substrate using hydraulic pressure connected to a metallic dolly. The highest value of tensile pull-off force that the layer can bear before detaching was measured and it represented the strength of adhesion to the substrate. In this specific case, a substrate made of the styrene-based polyester commercial resin was prepared. Then, a thin layer of the

chosen "styrene-free" reformulation resin was applied on the dolly surface. After that, the dolly was attached to the substrate and the pull-off test was performed. The test was performed for each of the three resins developed in this work.

For the tensile tests, a Zwick/Roell GmbH & Co. dynamometer (10 kN Allround Tisch), equipped with a 10 kN load cell was employed. The dimensions and the operative parameters were selected from the international standard related to testing conditions for isotropic and orthotropic fiber-reinforced plastic composites (ISO 527-4). In this case, rectangular shape specimens without end tabs were used. The dimensions indicated in the international standard ISO 527-4 were mostly scaled with a factor of 0.4.

5 Results and Validation

5.1 Characterization of the Recycled Reinforcement Materials

Two types of shredded flakes, obtained from EoL GF reinforced composites, were used. The first type consisted of coarse white flakes with a maximum dimension of around 4 mm, deriving from the EoL GF reinforced UP, produced for construction applications, shredded and supplied by Rivierasca S.p.A. The second type of recyclates was obtained by grinding EoL wind turbine blades, provided by Siemens Gamesa Renewable Energy S.A and shredded by STIIMA—CNR (Istituto di Sistemi e Tecnologie Industriali per il Manifatturiero Avanzato—Consiglio Nazionale delle Ricerche). EoL wind blades were made of an epoxy resin reinforced with a GF woven cloth.

Mechanically recycled glass fibers from composites for construction applications. Mechanically recyclates consisting of EoL GF reinforced polyester composites showed an average content of GFs of 30.5 ± 2.3 wt%, determined by TGA. These composites were originally composed of styrene-based orthophthalic polyester resin and 5 cm long fibers with a diameter of 13 μm. After the mechanical treatment, recycled composites consisted of matrix particles and GFs still partially embedded in the original matrix, as shown by representative SEM images of the recyclates (Fig. 12a). The average length of GFs turned out to be around 500 μm, after the elaboration of SEM images by ImageJ software.

Mechanically recycled glass fibers from composites for wind turbine blades. TGA tests were performed on different batches of the same recyclate and an average GF content of $71.5 \pm 3.0\%$ was measured. In order to estimate the average diameter of the fibers, SEM images were used and elaborated on through ImageJ software. The average diameter turned to be 20.5 ± 4.5 μm (Fig. 12b). The average length of fibers was determined by the elaboration of optical microscope images and photos taken by a common camera. Considering the median value of the distribution as an
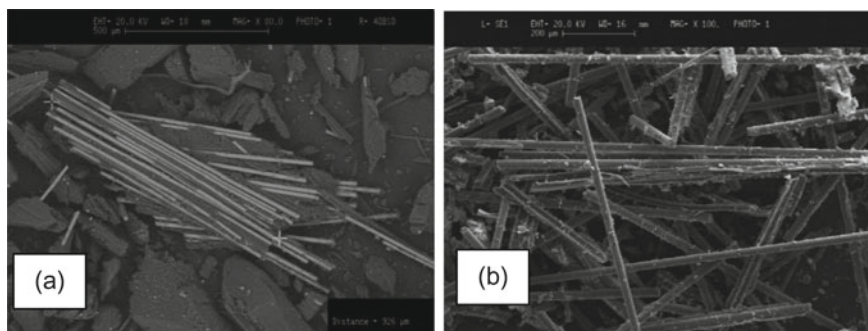
Fig. 12 Bundle of GFs present in the mechanically composite recyclates obtained by grinding **a** GF reinforced polyesters for building applications and **b** GF reinforced epoxy resins for wind turbine blades

average value, the fibers showed an average length of 157.7 μm. As an average, the degree of liberation of glass fibers from the cured matrix seemed much better than in the previous case.

5.2 Formulation and Crosslinking of Styrene-Free Liquid Resins

Acrylic Resin. To select the reactive diluent suitable for the acrylic resin, four candidates were identified (MMA, IBOMA, LMA, and BDDMA) and characterized considering the following properties: volatility; miscibility; viscosity cut; handling safety.

As shown in the literature, MMA showed a level of volatility comparable to styrene and higher than the that exhibited by the other systems [15]. IBOMA and LMA showed poor miscibility with SR349 and low viscosity cut. These considerations led to the selection of BDDMA as target reactive diluent. To determine the suitable amount of reactive diluent, different weight fractions of BDDMA and SR349 were analyzed through rheological analyses to assess the viscosity of the system. The rheological analysis shows a very weak shear-thinning behavior for the resin diluted with BDDMA (Fig. 13). Considering the commercial UP resin viscosity as a reference value (0.39 ± 0.04 Pas), an optimal percentage of BDDMA was found to be around 20 wt% (viscosity 0.30 ± 0.01 Pa·s). A further increase of BDDMA percentage was considered unnecessary.

The Tg of the crosslinked acrylic resin obtained with 80 wt% of SR349 and 20 wt% of BDDMA was evaluated via DSC. The Tg value is shown in Table 7, together with the gel content percentage for the solid resin, evaluated gravimetrically after solvent immersion and extraction.

Fig. 13 Viscosity curve of SR349 + BDDMA resin with different weight concentrations of reactive diluent (BDDMA, also called with the commercial name SR214)
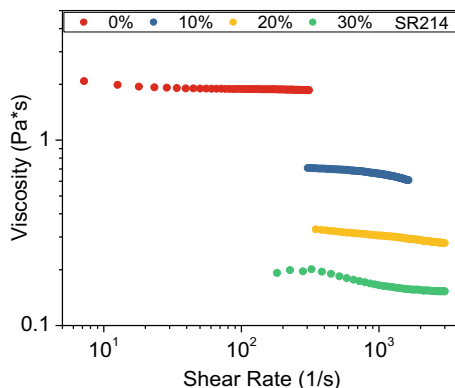

Table 7 Glass transition temperature (Tg) and gel content of the acrylic solid resin, obtained with 80 wt% of SR349 and 20 wt% of BDDMA

Properties	
Tg	123 ± 1 °C
Gel content	98 ± 1%

Epoxy Resin. DSC analyses were performed for all three epoxy systems and the results were found to be comparable. The Tg obtained by DSC and gel content evaluation tests for the solid epoxy resin (EPO) are shown in Table 8.

Polyurethane Resin. DSC analyses were performed to evaluate the Tg obtained by combining the polymer bearing isocyanate side groups with different diols. The results are listed in Table 9.

The formulation including the glycerol resulted too brittle, showing a Tg of 153 °C. Those involving dipropylene glycol and tetraethylene glycol were characterized by limited miscibility that produced biphasic materials (two Tg values were observed), not suitable for binders. On the other hand, formulation #3, with glycerol propoxylate, resulted too soft. Finally, formulation #5, obtained with MDI and tripropylene glycol, led to a cured resin with a Tg of 92 °C. Furthermore, this resin showed good miscibility and properly low viscosity, during processing. In light of the above, the formulation involving MDI and tripropylene glycol was selected as the PU system in further steps. The properties for the solid PU resin obtained with tripropylene glycol are provided in Table 10.

Table 8 Glass transition temperature (Tg) and gel content of the epoxy solid resin named EPO

Properties	
Tg	72 ± 1 °C
Gel content	98 ± 1%

Table 9 Glass transition temperature (Tg) of the polyurethane solid resin crosslinked with different glycols or polyols

Number	Isocyanate (Part A)	Polyol (Part B)	Molecular sieve (Part C)	Parts by Weight (A:B:C)	Tg (°C)
1	MDI	Glycerol	/	100:26:00	153
2	MDI	Dipropylene glycol	/	100.56:00	63.5; 143
3	MDI	Glycerol propoxylate	Zeolite A type	100:74:7.4	<80
4	MDI	Tetraethylene glycol	Zeolite A type	100:81.6:8.2	49; 104
5	MDI	Tripropylene glycol	Zeolite A type	100:81:8.1	92.5 ± 2.5

Table 10 Glass transition temperature (Tg) and gel content of the polyurethane solid resin obtained with tripropylene glycol

Properties	
Tg	93 ± 3 °C
Gel content	96 ± 1%

Table 11 Glass transition temperature (Tg) and gel content of solid commercial styrene-based unsaturated polyester resin

Properties	
Tg	121 ± 2 °C
Gel content	99 ± 1%

Commercial styrene-based orthophthalic polyester resin. The viscosity of the liquid commercial styrene-based UP resin was found to be 0.39 ± 0.04 Pa s. This value was used as a reference value for the other resins. The results obtained with DSC tests and gel content evaluation tests for the solid resin are provided in Table 11.

5.3 Reactivity of the Resins

A key property is the reactivity because it is crucial for the understanding of the time available for the molding process. For this reason, an evaluation of the de-molding time and an analysis with DSC measurements were conducted. The de-molding time determination method is a test that allows the estimation of the time required for a liquid resin to reach a correspondingly robust state for safe handling. This means

Table 12 De-molding time results of the different resins

Resin	Phase transition (min)*	De-molding time (min)
Styrene-based polyester	10	15
EPO10	15	20
EPO	90	240
EPO80	270	600
Acrylic	180	360
Polyurethane	30	180

*Liquid to a viscous phase transition

that the semi-cured resin may be removed from the mold for times longer than the de-molding time.

The test involved the casting of a thin layer of the liquid polymeric resin in a round mold of PP, featuring a diameter of 1 cm. The layer, then, was periodically subjected to a scratch and the time required by the resin to recover the scratch was measured. The test was repeated until it was not possible to scratch the surface of the layer anymore. The results of the de-molding time tests of the resins are shown in Table 12.

DSC analysis was instead used to determine the total crosslinking enthalpy of the resin. To this end, starting from a liquid sample, a single heating ramp was performed from 0 to 250 °C with a rate of 10 °C/min. The styrene-based polyester resin was considered as a benchmark, because it is currently used in a large number of applications, especially for composite manufacturing. The reactivity of resins for composite reformulation should be moderately high to guarantee good processability together with fast curing, to achieve larger productivity. The results of the reactivity of the resins obtained by DSC analysis are in good agreement with the gel time indications (Tables 11 and 12). According to the DSC curve, the styrene-based resin started to react at room temperature and a de-molding time of 15 min was measured in this case. A total exchanged enthalpy of 225.3 J/g was also measured for the styrene-based resin (Table 13). DSC curves for the epoxy systems are shown in Fig. 14. EPO10 showed a shorter curing time with a de-molding time of 20 min and values of onset and end temperatures comparable to those of reference resin. On the other hand, EPO and EPO80 respectively exhibited a de-molding time of 4 and 10 h and higher values of onset and end temperatures. All the epoxy binders started to react above room temperature and were characterized by almost the same large heat flux. Table 13 also shows that the onset temperature is a good indicator of the reactivity of the resins. Indeed, the resins with faster curing (lower gel and de-molding time) were characterized by lower onset temperature. By increasing the onset temperature, the reaction was slower (lower gel and de-molding time). Thus, the epoxy formulation could be tuned to achieve fast curing or, otherwise, a slow curing system. Moreover, EPO10 can be considered the system more similar to the benchmark in terms of reactivity.

Table 13 Peak temperature (T_{peak}), onset temperature (T_{onset}), end temperature (T_{end}), and peak area underneath the peaks measured by DSC for the liquid resins under investigation

Resin	T_{Peak} (°C)	T_{onset} (°C)	T_{end} (°C)	Peak area (J/g)
Styrene-based polyester	84	40	132	225
EPO10	91	55	146	424
EPO	101	66	178	458
EPO80	112	79	178	458
Acrylic	76	68	100	226
Polyurethane	108	58	192	153

Fig. 14 DSC curves of all three liquid epoxy formulations
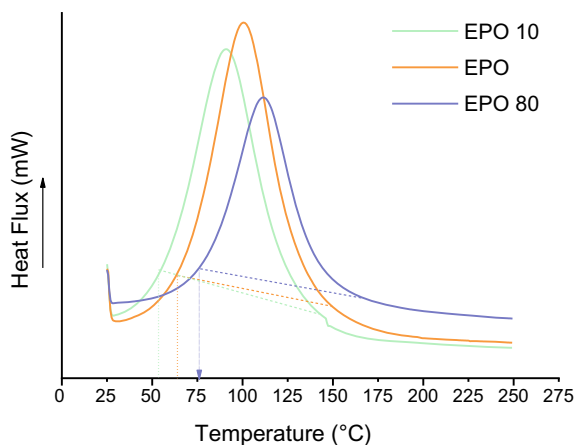
Regarding the acrylic resin, the measured amount of heat flux was comparable to the one of the commercial styrene-based polyester resin, but the onset temperature was found to be 68.4 °C. A much larger de-molding time of 6 h was also detected and this suggests that this resin has a slow crosslinking kinetics.

Characteristics similar to the previous one were observed for the PU system. A de-molding time of 3 h was observed and the onset temperature was higher than room temperature ($T_{onset} = 57.6$ °C). A heat flux of 153.39 J/g, which is lower than that observed on all three resins, was measured.

5.4 Adhesion Tests

Mechanically recycled GFs usually consist of GFs still partially embedded in the original matrix material (see Fig. 12). This could be a problem for the adhesion strength between the fresh matrix and the recycled reinforcement. A poor adhesion strength could result in unsatisfying mechanical performances of the final re-manufactured

Table 14 Pull-off tests results

Resin	Adhesion strength (MPa)	Failure type
Acrylic	5.6 ± 0.3	Cohesive
Epoxy	2.0 ± 0.6	Adhesive
Polyurethane	4.2 ± 0.4	Cohesive

product since the physical and mechanical properties of GFRP depend essentially on how tightly the resin adheres to GFs. This is related to how efficiently the mechanical stresses can be transferred from the matrix to the reinforcing fiber. It was important, therefore, to reliably estimate the adhesion of the different resins to the recycled material through the pull-off test. A styrene-based polyester substrate was prepared and the candidate resins were the adhesives between the dolly and the substrate. The pull-off test results are shown in Table 14.

The best adhesion was achieved by the acrylic resin with a value of adhesion strength of 5.6 ± 0.3 MPa, while the epoxy and the PU showed lower results, respectively characterized by an adhesion strength of 2.0 ± 0.6 and 4.2 ± 0.4 MPa. If the failure occurred along with the interface between the adhesive and the substrate, the specific value of load required to peel off the dolly from the substrate was set as the level of the adhesion strength. On the contrary, if the failure occurred in the substrate bulk, the level of cohesive strength in the substrate was measured. When the substrate failed and thus the cohesive strength was established, the adhesive strength could not be determined, but it was considered to be greater than the cohesive strength value. This was the case with acrylic and PU resins.

5.5 Tensile Tests

Mechanical properties of the crosslinked resins under investigation were determined by tensile tests. As a reference system for commercial applications, tensile tests were also performed on the commercial styrene-based polyester resin. Young's modulus (E), tensile strength (σ_b), and deformation at break (ε_b) are reported in Fig. 15.

Considering the high value of Tg (123 °C) and the gel content (98%), the acrylic resin was expected to be a very rigid material with a high degree of crosslinking. Tensile tests confirmed these expectations (Fig. 15). When compared to the reference styrene-based resin, the acrylic one showed a lower Young's modulus (about 1 GPa lower) together with a slight increase of elongation at break. On the contrary, concerning the tensile strength (including the standard deviation), the average value of the acrylic proved to be almost the same as the reference one. This means that the acrylic resin was a less stiff material, capable of larger deformation at break when compared to the styrene-based resin.

The epoxy resin under investigation was characterized by a Tg of 73 °C and a gel content of 98%. Due to the lower Tg and the presence of a few residual reactive
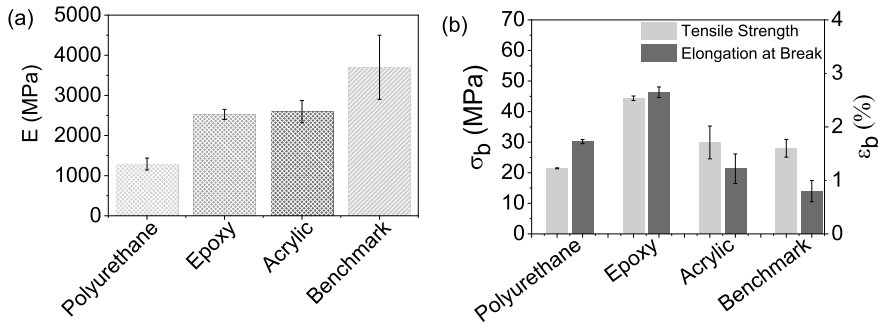
Fig. 15 Young's modulus (E), tensile strength (σ_b), and deformation at break (ε_b) for the three styrene-free resins under investigation, compared with the styrene-based reference resin

groups, a rigid material with good elongation capacity was expected. Indeed, the resin showed almost the same average Young's modulus as the acrylic resin, and an average value of elongation at break doubled (Fig. 15). Furthermore, a very high tensile strength was measured (Fig. 15b). Also, the epoxy resin showed a lower elastic modulus and a higher average tensile strength and elongation at break than the reference.

A PU resin was selected to find an alternative type of binder with slightly different characteristics. More specifically, it should provide a more ductile and tougher matrix, able to bear higher deformations. According to the data obtained, the desired objectives were only partially achieved. Indeed, the PU resin showed a low Young's modulus and tensile strength (respectively 1.7 GPa and 21.5 MPa), in agreement with the desired mechanical behavior (Fig. 15). However, the determined average elongation at break was too low. This could be due to the presence of some defects in the tested specimens. Those defects likely originated from humidity trapped in the tripropylene glycol reagent, during the manufacturing process. Defects gave rise to stress intensification and led to the premature fracture of the sample.

A comparison between the mechanical properties of the crosslinked resins developed was performed and the one showing the best performances was selected for the following tests. The average Young's modulus comparison is provided in Fig. 15a, whereas tensile strength and deformation at break of the different systems are compared in Fig. 15b. The PU resin was characterized by lower mechanical properties. The epoxy and acrylic resins also exhibited an elastic modulus lower than the styrene-based polyester resin, but ultimate properties at break were found comparable for the acrylic resin and even higher for the epoxy resin, in comparison with to the standard styrene-based system. The acrylic and epoxy systems were analogous in terms of stiffness, considering the very similar average Young's modulus. However, the epoxy material showed a larger capability to sustain more intensive loads and deformations. Thus, the epoxy resin seemed the most appropriate candidate for the combination with the recycled fibers. Furthermore, most of the GFRP products from

the wind energy sector employ an epoxy matrix. Hence, a large stream of mechanically recycled fibers, still partially embedded in an epoxy resin, is expected to affect the composite market. For this reason, the composite remanufacturing, involving a new epoxy binder, should result in an improved adhesion between matrix and fibers, ultimately yielding better mechanical properties.

6 Feasibility Evaluation of Reprocessed Composites Using Mechanical Recyclates

6.1 Polymer Composites with Mechanically Recycled Glass Fibers from the Construction Sector

The reformulation of mechanically recycled composites with a polymer matrix was mainly performed with the epoxy resin, due to the higher mechanical performances showed in the previous section. Three formulations, which were different in terms of weight concentration of recycled coarse flakes added to the liquid resin, were mechanically tested. More specifically, they were characterized by 30, 35, and 40 wt% of reinforcement material and named 'EPO30', 'EPO35' and 'EPO40', respectively. The results of tensile tests are reported in Table 15.

It is clear that the remanufacturing process resulted in an improvement of modulus and therefore of stiffness (Table 15). However, no significant changes were found by increasing the percentage of recyclate from 30% to 40 wt%. This can be due to the small variation in GF content, going from 9 wt% to 12 wt% in the case of fibers weight fraction of 30% and 40%, respectively.

On the other hand, the remanufacturing process led to a large reduction of tensile strength and elongation at break, which may be due to the poor interfacial adhesion and to the presence of defects, originated during the manufacturing operations.

Table 15 Young's modulus (E), tensile strength (σ_b), and deformation at break (ε_b) for the three differently epoxy systems reinforced with different amounts of mechanically recycled composites from the construction sector

	E (GPa)	σ_b (MPa)	ε_b (%)
EPO	2.53 ± 0.13	44.70 ± 0.74	2.65 ± 0.09
EPO30	3.16 ± 0.38	26.02 ± 4.18	0.91 ± 0.13
EPO35	3.41 ± 0.40	28.29 ± 5.07	0.92 ± 0.16
EPO40	3.45 ± 0.31	30.82 ± 5.29	0.96 ± 0.13

6.2 Polymer Composites with Mechanically Recycled Glass Fibers from the Wind Energy Sector

The remanufactured composites were obtained firstly by mixing the epoxy resin with the recyclates, then by applying vacuum to enhance the wettability of the new resin with the recyclates. Finally, compression molding was used to obtain the final object. In this case, the use of the epoxy resin as a matrix should improve the adhesion between the new resin and the GFs, because the original resin used for the wind blade was also an epoxy system.

Different percentages of recycled materials were mixed with the epoxy resin and good results for recyclate feed concentration up to 60% were achieved, as the final object did not show any evident defect. As shown in Fig. 16, the samples loaded with the 60% of recyclates showed a high elastic modulus of 7.4 GPa, comparable to that measured for standard GF composites for building applications. For percentages higher than 60 wt%, the final specimens showed voids and defects and no increase in Young's modulus, compared to samples reinforced with 60 wt% of recyclates. The presence of defects in the specimens also explained the values of tensile strength and elongation at break for samples reinforced with 65% and 70 wt% of recyclates that are lower than those loaded with 60 wt%

The decrease of values measured for ultimate mechanical properties by increasing the percentage of recyclates added in the epoxy resin can also be due to small contaminations present on the surface of GFs and acting as defect, as shown in Fig. 17d. SEM images of a single mechanical recycled GF were acquired to understand if these pieces are residues of the old matrix or parts of the new one attached to the fiber surface. These small pieces were assigned to residues of the old matrix because they were found only in the recycled materials. In Fig. 17b and c, examples of frictional sliding and fiber pull-out are represented. Frictional sliding constitutes one of the most significant sources of fracture for most composites with fibers. Indeed, this
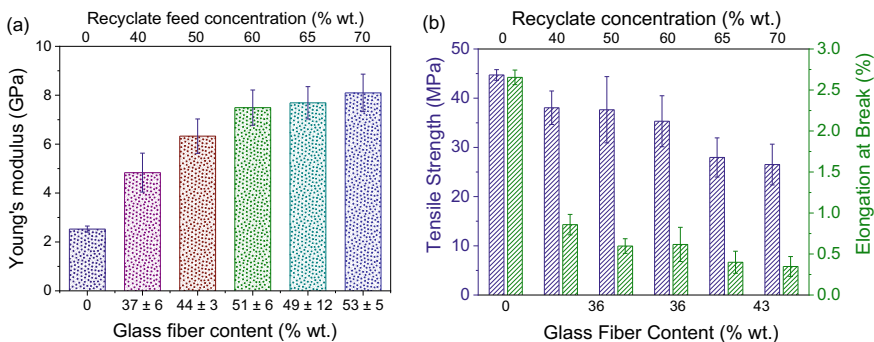

Fig. 16 **a** Young's modulus (E), **b** tensile strength (σ_b), and deformation at break (ε_b) for the epoxy systems reinforced with different amounts of mechanically recycled composites from the wind energy sector
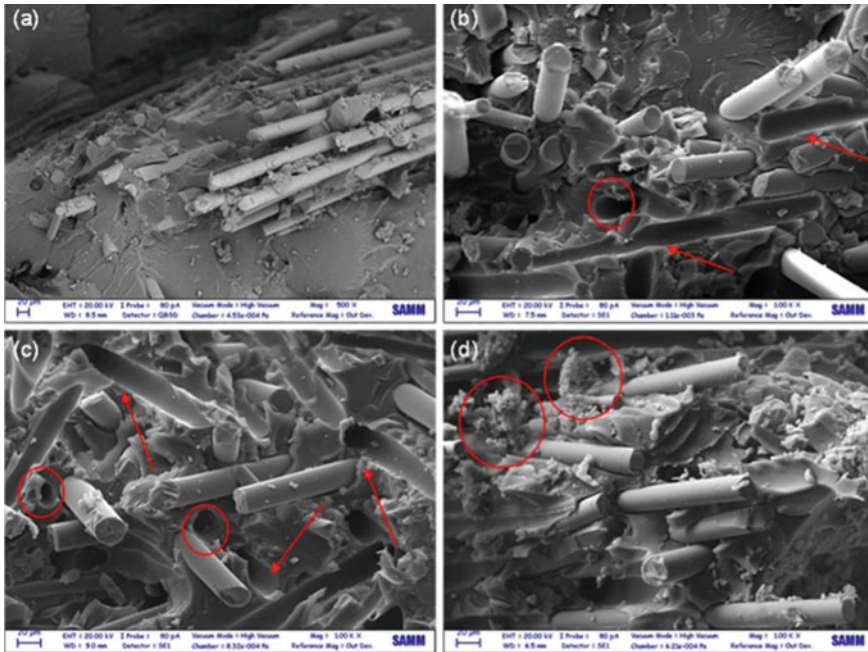
Fig. 17 SEM images with a magnification of $1000\times$ of epoxy systems reinforced with **a** 40%, **b** 50%, **c** 60%, and **d** 70 wt% of mechanically recycled composites from the wind energy sector

process can absorb large quantities of energy depending on the superficial roughness, contact pressure, and sliding distance, which result in the pull-out of fibers from their socket in the resin. The voids, observable in many regions and indicated by the arrows, represented signs of the previously described phenomena. Moreover, also the voids present in the matrix surrounded by red circles represent regions subjected to the fiber pull-out [17].

7 Conclusions and Future Research Perspectives

Three different thermosetting resins were developed and tested to assess their suitability to constitute the matrix phase in a composite material. Their reactivity and mechanical properties were compared to those of resins currently used in commercial applications. Moreover, the polymeric resin, acting as reinforcement binder, could be properly selected depending on the desired reactivity, processability, and mechanical behavior. The epoxy resin seemed the most appropriate candidate for incorporation of mechanically recycled fibers. On the other hand, a poor level of adhesion was found between two of the resins under investigation and the unsaturated polyester

resin, which was used as a matrix in composites for building applications and probably will present as a residue in the corresponding mechanically recycled GFs. This could represent a limitation because it could lead to a poor level of adhesion and defects in final remanufactured composites.

The feasibility of the composite remanufacturing process has been evaluated so far combining the epoxy resin with mechanically recycled GFs obtained from EoL GFRP for construction applications. Promising results, showing an improvement of elastic modulus and therefore of stiffness in comparison with neat resin, were obtained. However, no significant changes were observed by increasing the recyclate percentage from 30 to 40%, due to the low corresponding variation (only 3 wt%) of the GF content in the tested range of recyclate percentage. Moreover, an increase of 25–35% in the elastic modulus of remanufactured composites was only observed, because the maximum recyclate percentage used so far corresponds to 12% of GF weight fraction in the composites. A reduction of mechanical properties at break was observed for remanufactured composites when compared to the neat resin, probably due to some defects and flaws present in the remanufactured samples.

A viable opportunity can be provided by the use of a different type of recyclate with a much larger content of GFs. This opportunity was given by the recyclate coming from the wind energy sector. Recyclate materials obtained from the mechanical recycling of wind turbine blades showed a GF weight fraction of nearly 70 wt% This type of recycled reinforcement phase allows the addition of GF contents comparable or even larger than the ones measured in commercial products for construction applications. A tensile modulus of 7.5 GPa was measured for samples reinforced with the 60 wt% of mechanically recycled GFs. However, during mechanical tests, a decrease of the tensile strength and elongation at break was registered by increasing the amount of recycled GFs. SEM analysis of the fractured specimens of the recycled GF epoxy composites was exploited to gain some insight into some phenomena related to the matrix-fiber adhesion, such as frictional sliding and fiber pull-out.

This study suggests that composites recovered from the wind energy sector can be recycled for the remanufacturing of products for application fields requiring lower mechanical performances (i.e., building and sanitary sectors) in a cross-sectorial approach. Therefore, the obtained results provide a clear evidence of the possibility to reuse mechanically recycled GFs as reinforcement in styrene-free composites materials.

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