Recycling of thermoset fiberglass by direct molding of ground powders

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Abstract. Fiberglass production in western Europe exceeds one million tons per year, and data of the European Commission inform that at their end-of-life, 25% of waste fiberglass is sent to landfill. Being a thermosetting material, it polymerizes during its production, when a molecular network is generated into the matrix. This network is responsible for its optimal properties, but it prevents the material flow under heating and thus reprocessing. A new recycling process for fiberglass waste has been proposed by the authors without any use of virgin materials or additives. This technology consists of a *direct molding* (i.e., compression molding) of pulverized fiberglass. The material agglomeration depends on the combination of several mechanisms, from residual reactivity, to powder re-activation and incipient degradation during molding. Residual fiberglass powder has been recovered from a factory that specializes in technical laminates, where a grinding process is used to provide the expected tolerance to the products. The recovered powder has been direct molded to manufacture small samples for mechanical testing. Such powder shows thermal activation in the DSC (differential scanning calorimetry) at low temperature (about 80°C). This study shows the feasibility of recycling waste fiberglass without using any virgin material; these new findings are related to the use of industrial powders, their testing under 4-point bending and the obtaining a good, molded surface.

Introduction

In recent decades, fiberglass has become widely used in many applications, from technical to commercial, domestic, but also sports and construction. Specifically, fiberglass is, as widely known, a composite material formed by the combination of a polymer matrix and glass fibers in different shapes. Generally, the use of glass fibers is due to several properties such as lightness, durability, anti-corrosiveness, and relative cost-effectiveness. All this has led to its use in both traditional and high-tech industries. Fiberglass can consist of a thermoplastic matrix (e.g., polypropylene) or a thermosetting matrix (e.g., epoxy or polyester). Typically, thermoset matrix such as polyester is used in many applications due to the ease of process in obtaining large and complex parts such as boats, wind blades or tanks. On the other hand, the use of thermoplastic matrix is rarer; except for injection-molded parts with discrete glass fibers. Nowadays, the global fiberglass industry has undergone steady growth due to versatility and low cost of this material. In addition, such growth is expected to continue given the increasing demand for alternative and green energy sources, like wind energy.

The above-mentioned properties of fiberglass have contributed to the development of more advanced and efficient systems and products in various sectors. This is likely to lead to a further expansion of market demand for fiberglass products in coming years. Factually, in 2022 the global composites market size was estimated at USD 93.69 billion and is expected to grow at a compound annual growth rate (CAGR) of 7.2% from 2023 to 2030 [1].

From this point of view, these quantities of produced and utilized fiberglass represent a big issue for the environment. Given the countless and disparate applications of this material, fiberglass recycling is an important issue to address. Throughout the years many technological solutions have been proposed for fiberglass waste management. Generally, in mechanical composite recycling processes there are always disassembly and/or pulverization steps. As pulverization can also be a way to reduce the volumes to be sent to landfills research on this process step date back to 1994 with Ferguson [2], however, a real recycling process, should also involve the re-processing of the final powders. Unfortunately, there are only a few industrial solutions for the recycling of pulverized powders, and they have two main applications: the use of powders for the filling of composites or for energy recovery [3,4].

The scientific literature for fiberglass recycling has been more active in the past. In 1997, Yoon et al. and Rastelly et al. proposed chemical methods to recycle unsaturated polyester (UP), used as a fiberglass matrix. The first uses propylene glycol to recycle UP, to extract reagents that can be cured by adding maleic anhydride; the downsides of this method are the use of large amounts of virgin UP (up to 90%) and chemical reagents [5]. The second proposed similar chemical recycling process to obtain glycolic raw materials to synthesize again UP resin by reaction with dibasic acid or a diisocyanate compound [6]. However, the idea of chemically reprocessing UP waste was shelved, and the research then focused mainly on combustion and pyrolysis of this waste. The recovery of fibers from waste thermoset composites via fluidized bed process has been proposed by Kennerley et al. [7]. However, the fibers thus recovered had a strength reduced to about half that of virgin fiber.

Thermal processes for fiberglass recycling were also investigated in literature. These processes involve the use of heat to break the scrap composites down; the differentiation between them revolves around the amounts of energy and recovered material. Pyrolysis has been studied with fine results by Cunliffe et al. [8] and Kaminsky et al. [9], however, the cost of the equipment used, as well as the overall energy loss during the process, make pyrolysis products unattractive for industrial applications. This is also due to additional processes required to increase the efficiency of pyrolysis products, such as cleaning the glass fibers or burning the pyrolytic oil. Lopez et al. studied the thermolysis of fiberglass to recover valuable products and energy, particularly 68 wt% solid residue, 24 wt% of the liquid (oil) and 8.0 wt% of gas fractions. The remaining solid phase can be converted in a wollastonite and plagioclase-based glass–ceramic materials. The method, although interesting, involves complex and energy-intensive costs and processes.

Currently, the state of the art is basically unvaried, and fiberglass is typically sent to landfill at a cost that depends on the country. The fact that fiberglass recycling research has fallen out of grace for years is confirmed by Pickering in his review of recycling technologies for thermoset composites [10]. More recent studies have not changed the situation, for despite the variety of methods and studies on the subject, no one has yet found commercial success or industrial diffusion. For example, Kamimura et al. (2011) investigated de-polymerization of UP and waste fiberglass by using ionic liquids and microwave to accelerate the reaction rate [11]. Unfortunately, the process is set-up to recover only glass fibers and no mention is given to the re-use of the organic part. At the same time, all the most recent studies are based on the pulverization and reuse of powders as fillers for composites [12-14]. As a result, it seems that this method remains the easiest way to recycle. However, fiberglass consumption rates are much higher than those of powder reuse as a filler.

A new recycling process for fiberglass waste has been proposed by the current authors without any use of virgin materials or additives [15]. This technology consists of a *direct molding* (i.e. compression molding) of pulverized fiberglass. The material agglomeration depends on the combination of several mechanisms, from residual reactivity, to powder re-activation and incipient degradation during molding [16]. In fact, pulverizing can be a way to give new reactivity to the final powder. Specifically, on the outer surface of the powder particles broken bonds can act as polymerizing sites. In addition, if there is a residual reactivity of the material, this can increase the reactivity of the powder itself. This study represents a step forward compared to the previous ones, as an industrial fiberglass powder is molded by direct molding without the addition of binders or virgin material. The results were very promising in terms of process easiness and proven feasibility, starting from industrially grounded powders.

Experimental

Fiberglass powder evaluation

A powder of waste fiberglass has been recovered from a factory of technical laminates, where a grinding process is used to reseize the products. Specifically, the powder was collected during the grinding of insulation panels of refrigerated trucks. These fiberglass laminates have a polyester matrix. At first, powder size distribution was measured by means of a stereo microscope (Leica S9i). A burning test was carried out in an oven at 600 °C for 2 h to measure the real glass content of grinded powders. Moreover, to evaluate glass transition temperature of polyester resin, differential scanning calorimetry (by Perkin Elmer DSC6) was performed on a sample of fiberglass powder. A double scan was carried out from room temperature to 150 °C, at 10 °C/min and the second scan was used to extract the glass transition temperature.

Fiberglass recycling

Recycled fiberglass samples were produced by compression molding of the industrial grinded powders without any addition of virgin material or linking agent (direct molding), according to the process scheme shown in Fig.1.

Rectangular samples (90x15 mm^2) were molded by using an aluminum alloy mold which consisted of several parts (Fig. 2a): a shaped upper punch ①, with a blind hole for the placement of a compression spring ②, an intermediate plate with four removable walls ③ fixed by screws, matching with the shaped punch and a bottom flat mold ④. After the spring is placed on the top of the mold with a positioning pin, the mold was positioned between two steel plates ⑤ with long screws ⑥ inserted into the walls for mold clamping. The removable bottom plate was chosen for simplifying sample extraction after molding. Moreover, the spring (269.2 N/mm, 32 mm of diameter) was inserted to guarantee the compression pressure of the mold during heating, because of the high contraction of the particulate under pressure during molding.

At first 6 g of fiberglass powder was inserted into the mold, then the mold was compressed by means of an electromechanical press (MTS Insight 5) up to 3.45 kN (for a related pressure of 2.55 MPa) at a loading rate of 1 mm/min and with a load holding time of 800 s (Fig. 2b).

Sample consolidation was carried out in a muffle furnace (Nabertherm, Controller B 170) at different temperatures 150 °C, 200 °C and 250 °C and for a molding time of 60 min. After molding, the mold was left in the muffle to cool down to room temperature before sample extraction.

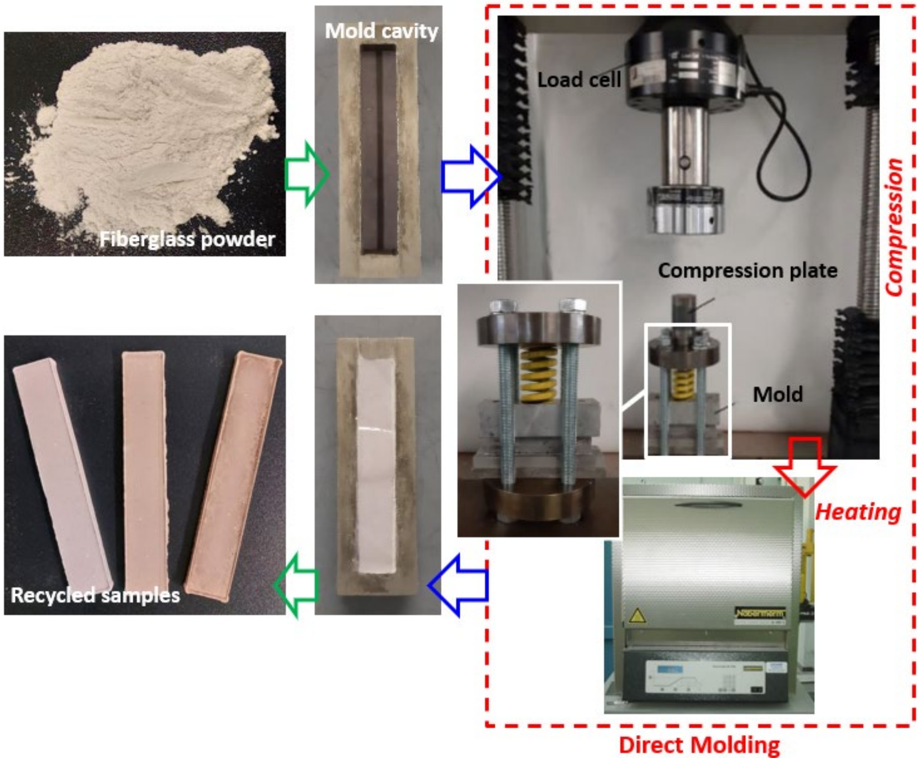


Figure 1: Process set-up scheme

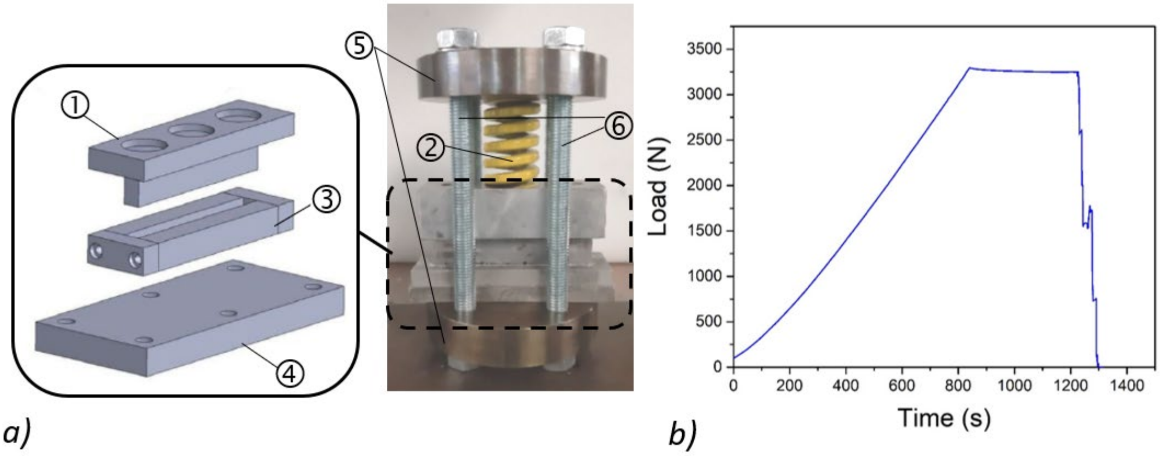


Figure 2: a) Aluminum mold details and b) loading vs time program of the compression step of the mold.

In direct molding, high temperatures are necessary to promote particle mobility and agglomeration, and high pressures to ensure better contact between particles. Different consolidation temperatures were evaluated to assess the most suitable molding conditions avoiding material degradation. Moreover, using a spring to compress, the maximum pressure is limited by its maximum packing force.

Physical and Mechanical testing

Density of the recycled fiberglass samples was extracted by measuring sizes and weights. Four-point bending tests were used for testing mechanical properties of the molded samples The tests were performed following the ASTM D6272-02 (2008) by means of the MTS Insight 5 electro-mechanical testing machine. The applied load was displacement controlled (at 1 mm/min) and the span length among supports was 60 mm and the central span (pure bending) length was 20 mm.

The test set-up is shown in Fig.3. The deflection and the applied load were recorded and the flexural strength, the maximum deformation and the flexural modulus have been calculated according to ASTM D 6272-02.

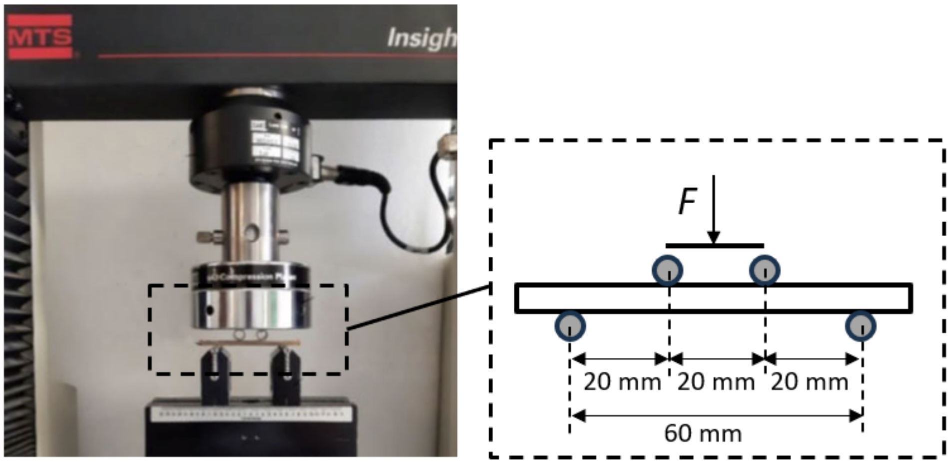


Figure 3: 4-point bending step configuration.

Result and analysis

Images of samples from grinded fiberglass powder are reported in Fig.4 and they show how the powders are made of a mixture of resin particles and chopped fibers (of about 200-300 µm of length). Moreover, the real glass content of recycled powders was evaluated by burning tests. The initial mass of fiberglass powder was 0.5 g while the residual after the test was 0.09 g. Accordingly, the glass content was about 18.7%.

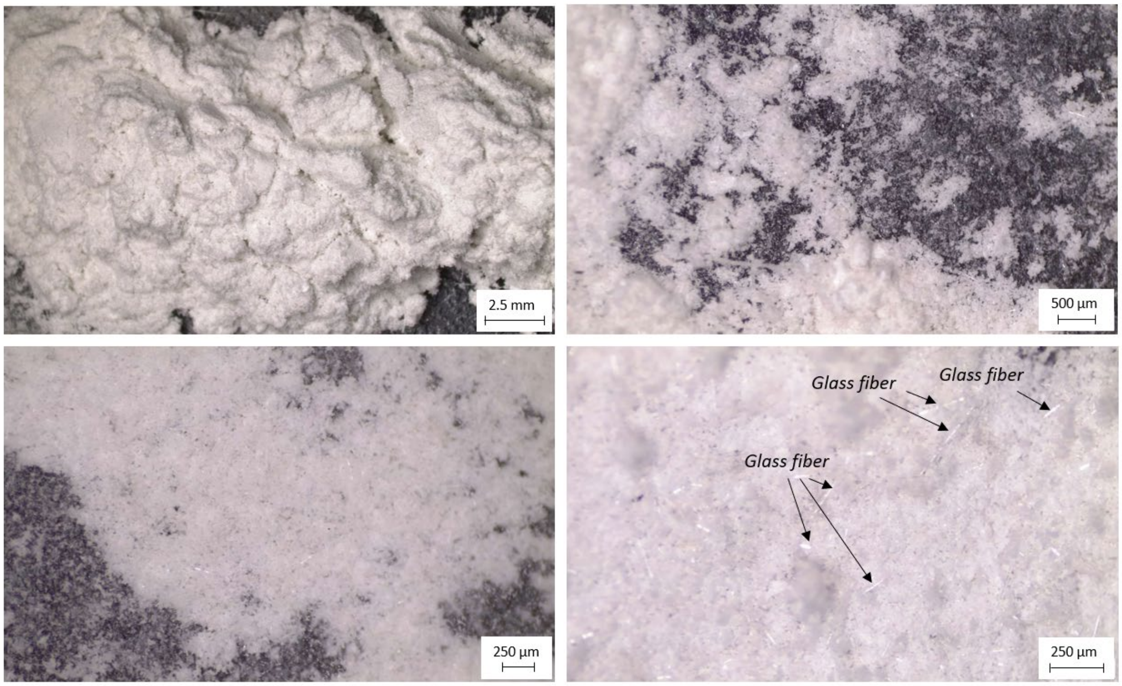


Figure 4: Fiberglass powder stereoscope images.

A DSC scan was performed on a sample of initial fiberglass powder. A peak is visible in the first scan, around 80 °C (Fig. 5), showing a residual activity of the polyester resin matrix for that temperature. This datum was considered to define the minimum value for the molding temperature of recycled fiberglass.

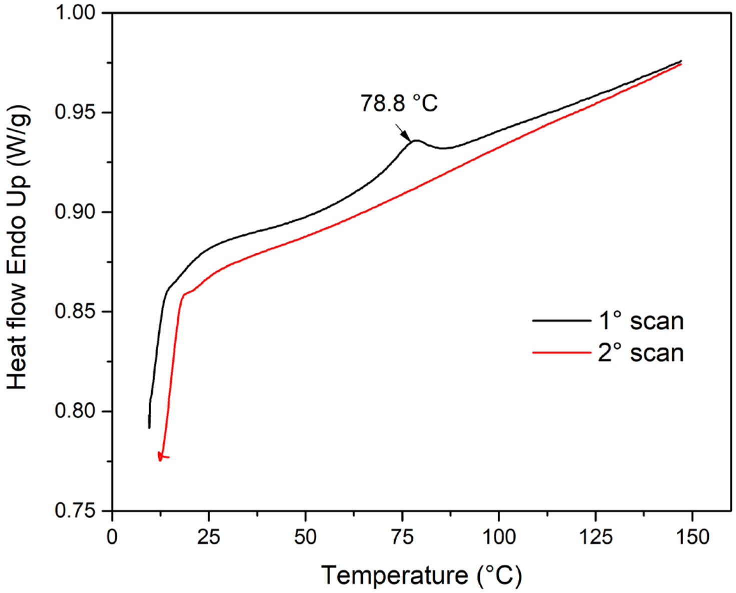
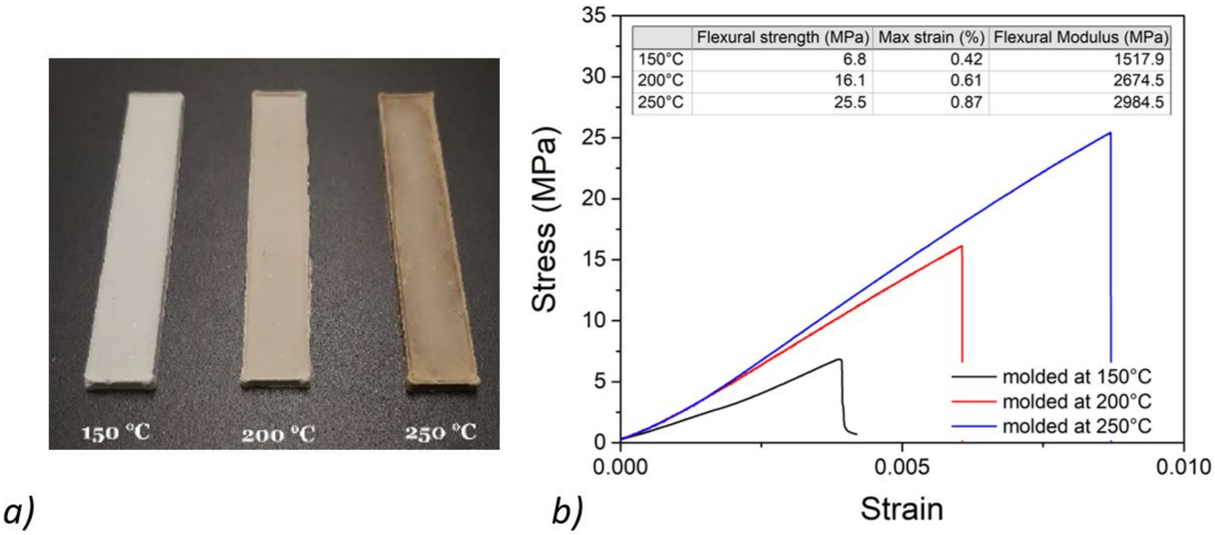


Figure 5: Fiberglass powder DSC curves.

After molding, recycled samples showed a dark yellow surface which was related to surface oxidation (Fig. 6a). However, the surface appearance of all samples is good. There are no particles being released from the surface, which is continuous, smooth and consistent. To evaluate the efficiency of the recycling stage, density and flexural properties were evaluated on the rectangular recycled fiberglass samples. Average sample dimensions and density values after direct molding process are about: 3.5± 0.29 mm in thickness, 16.1±0.26 mm in width and 1.14±0.055 g/cm^3 in density. Analyzing the measured data, it was noted that for the same mass of powder inserted into the mold, the average thickness decrease as the process temperature increases (at 250 °C is about 3.2 ±0.08 mm). This trend can be attributed to the increasing viscosity of the polymer as the temperature increases. This allows a better compaction of the powders, therefore a slight increase in the density of the samples (up to 1.19 g/cm^3 at 250 °C). This implies that during the heating step in the muffle, a higher setting temperature allowed to obtain a greater agglomeration of particles. The flexural tests depicted in Figure 6b then showed that the higher process temperature has given a greater consolidation to the recycled fiberglass powder, therefore showing major flexural resistance (Fig. 6b).



	Flexural strength (MPa)	Max strain (%)	Flexural Modulus (MPa)
150°C	6.8	0.42	1517.9
200°C	16.1	0.61	2674.5
250°C	25.5	0.87	2984.5

Figure 6: Molded samples at different temperatures, b) bending curves and calculated values of flexural strength, maximum strain and flexural modulus.

In general, the directly molded samples are quite brittle, but increasing the processing temperature during molding allowed to reach a flexure strength over 25 MPa together with an elastic modulus over 2.9 GPa. These properties can be appealing for various purposes; for example, the result may potentially replace plasterboard. In fact, plasterboard is made by a film of paper and a central part of gypsum. Plasterboard is largely diffused for false ceilings and separation walls; it has low performances and an environmental impact due to the combination of paper and gypsum which are difficult to be separated.

A closer look at the results show how fiberglass particles could be easily used in direct molding. Starting with the same powder with uniform sizes and with identical residual reactivity, only the process parameters are those that contribute to the final cohesion of the material. In direct molding, main process parameters are molding pressure, temperature, and time. Molding pressure should allow contact between particles, so a higher pressure would result in a major connection and higher final performances. On the other hand, restrictions are given by process systems and molds and are also due to the limits of resin compressibility (too high pressure could results in poor improvements). In this study, the pressure was maintained at 2.55 MPa by a compressed spring and it was similar for the different molded samples. The time was fixed for all the samples. Only the temperature of the oven during molding was varied. In fact, the molding temperature has limits given by the material degradation. A limited degradation is necessary to create new links amongst particles, if it excesses it could result in polymer cracking inside the particles. Likewise, very high temperatures could result in VOCs (Volatile Organic Compounds) and burning [8]. According to all these considerations, different temperatures have been evaluated and the maximum temperature was established at 250 °C to exalt resin mobility.

A comparison with virgin fiberglass samples was not carried out as only the recovered powder was supplied and not the virgin panels of fiberglass. However, in previous studies it has been evaluated as the final properties of the recycled samples are not equivalent to virgin fiberglass, but other industrial applications seem to be possible as replacement for plasterboard panels [15]. At least at a laboratory level, the authors assessed the feasibility of multiple recycling operations [16].

Summary

A direct molding technology for recycling fiberglass powders has been proposed. Further analyses are crucial to deepen several aspects and understand if this solution is cost-effective. However recycled fiberglass has shown good mechanical properties which are dependent on the processing temperature.

The main goal of this study is the demonstration of feasibility of recycling waste fiberglass without adding any virgin material and using industrially wasted fiberglass powder. Moreover, new findings of the present study, indicate good final mechanical properties as outcome of a 4-point bending test and have shown a good molded surface. The final samples surfaces' appearance is an important achievement as it would allow the application of the material without the need to cover it with dedicated coatings. The authors further suggest a study on the utilization of particle functionalization, as several substances could be used to change the particle surface (e.g., ionic liquids or propylene glycol).

The current work, alongside with previous studies from the authors, aim to spark up the interest on the usage of new technical solutions for composite recycling, especially in the context of sustainable manufacturing processes and waste reduction. The current lack of any state-of-art processes to reprocess fiberglass waste without the usage of any additives or virgin materials, underline the importance of the present study. Other common technical solutions, like pyrolysis or burning, could still be used in further recycling steps when already recycled fiberglass would be deteriorated to a point where its residual properties would be unacceptable.

Acknowledgement

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