23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

RECYCLING OF CARBON FIBER COMPOSITES: STATE OF ART AND INCOMING APPLICATIONS

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Abstract. *The use of Carbon Fiber Reinforced Plastics (CFRPs) from many industries (sports, automotive, shipbuilding and especially aerospace) is increasing every year. Low weight and good mechanical properties - strength and stiffness - are the main reasons to their application in structures. However, the amount of CFRP waste produced by aerospace is increasing as well. Some techniques have been researched in order to manage this waste – mechanical, chemical and thermal(pyrolysis and fluidized bed) recycling processes. Chemical and thermal processes brings better reclaimed fibers for noble reuse (structural, mainly). Studies have found that recycling can reduce the environmental impacts when compared with common dispose (landfill and incineration) and even reuse both: the reclaimed fibers and the matrix. Moreover, some recycling methods can even bring back reclaimed fibers with 90% of mechanical properties compared with their virgin precursors, and generate energy from decomposition of the polymeric matrix, making the recycling unit self-sustaining. This paper aims to study the actual state of art of recycling of CFRPs over the world – researches, economical application and environmental assessment.*

Keywords: *Recycling, state-of-art, CFRP waste.*

1. INTRODUCTION

The amount of CFRP employing in many areas is increasing every year, specially in aerospace industry, given its versatility and high performance driven by good mechanical properties, low weight and reasonable cost, when compared with metals. In the last decade, the world's demand for carbon fiber has grown from 16000 to 55000 ton/year (Onishi, 2012). Until 2020, it is expected to reach 140000 ton/year , at a growing rate over 13% (Roberts, 2011).

This exponential growing of CF (Carbon Fiber) composites manufacturing carries out an increasing amount of CF waste, when the products reaches their end-of-life's (EOL) cycles. During the past decade, researchers from all over the world have been working intensively in order to find new ways of disposing and reuse CFRP waste. Recycling technologies are being able to reclaim fibers with mechanical properties very similar to their virgin precursors. Moreover, rCFs (recycled Carbon Fibers) uses less manufacturing energy and has lower costs when compared to vCFs (virgin Carbon Fibers). Besides, the environmental impacts are reduced as well,as shown in figure1.

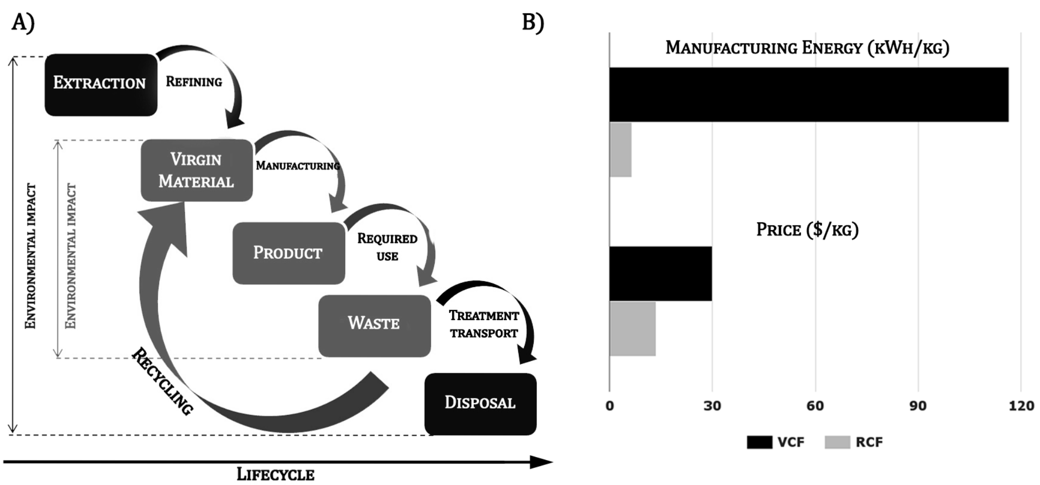

Figure 1. Comparison between vCF and rCF. (A) Lifecycle and environmental impacts. (B) Manufacturing energy and cost. Fonts: Adapted from Pimenta and Pinho. (2014) and Carberry (2008)

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Most part of CFRP today is landfilled or incinerated, a non-sustainable technique of disposal, that releases huge volumes of CO_2 and toxic gases like fluorides, chlorides and hydrocarbons in atmosphere, that comes from the burning process of the matrix of the composites. In therms of environment, mechanical properties and economic, recycling of CF is proving to be a promising technique employed in order to 1)reducing of environmental impacts 2)recovering of fibers with mechanical perfomance very close to the original CF and 3)high potential of reducing production and disposal costs. This trending is already happening, huge aircraft manufacturers as Boeing and Airbus are investing massively in materials recovering on EOL aircrafts - AFRA (Aircraft Fleet Recycling) and PAMELA (Process for Advanced Management of End of Life of Aircraft) are some examples.

2. RECYCLING OF CFRP: OVERVIEW AND DEMAND

According to Rush (2007), between 2007 and 2025 about 200 commercial passenger aircraft per year are expected to meet their EOL. The most recent commercial aircrafts provided by Boeing (787) and Airbus (A380) has about 35 tons of CF composites in their structures, approximately half of total aircraft weight.

A viable recycling process must guarantee reclaimed material with similar particularities when compared to their virgin precursors, plus, good mechanical properties (stiffness, strength, toughness) in order to allow the reuse nearest the original use, including structural application (Kouparitsas *et al.*, 2002).

To Piñero-Hernanz *et al.* (2008), however, there are three essential points in analysis of a recycling process's efficiency: matrix removal (done by MEV as shown in figure 2), the second is the quality and potential of application of rCF and the third is the maintance of mechanical properties in the rCF.

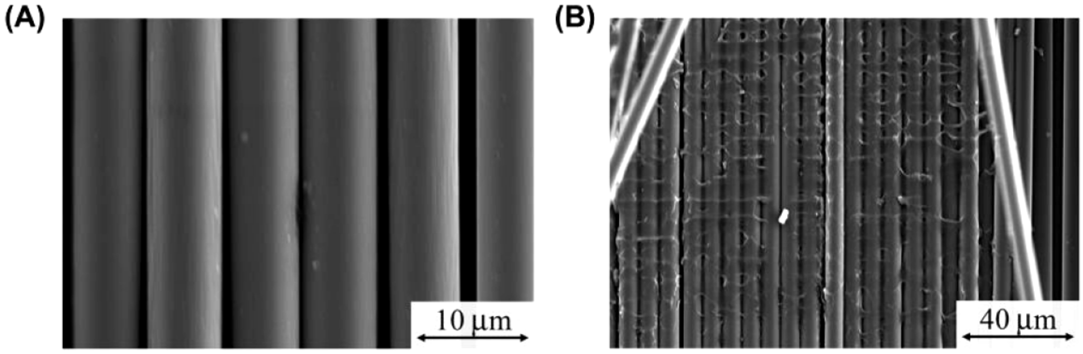


Figure 2. rCF obtained from pyrolysis seen under a scanning electron microscope. (A) Clean Fibers (B) Fibers with residual resin. Font: Pimenta and Pinho. (2014)

The amount of CFRP waste from aircraft industry includes EOL pre-impregnated fabrics, manufacturing cut-offs, testing materials, production tools and EOL components (Pimenta and Pinho, 2011).

The problematic in CF waste management is on the destination costs, once that recycling industries still aren't common. Destination costs include waste sorting, storage and transportation. Currently, most of CFRP waste is landfilled (Carberry, 2008). However, landfilling isn't appropriated for several reasons:

- Water, soil and air pollution and contamination, degrading of complex ecosystem and climax environments, damages to local fauna;
- Legislation: In Brazil, the National Policy for Waste Management (N^o, 2010) was only created in 2010 and does not define a specific resolution to manage correctly composite waste. CFRP waste is classified, by this law, as a Class II B waste (Non-dangerous and inert) .
- Costs: As shown in figure 1, costs and energy required to obtain CFRP from raw material are expensive.
- Economic: Legal landfilling cost is about 0.20 $/kg (Meyer *et al.*, 2007); recycling could reduce costs of common disposal and convert an expansive waste disposal into a profitable reusable material (Technotes, 2003).

There are many benefits that classifies Recycling as the best method to CF waste final management. Common methods (incineration and landfill) may release toxic chemical composts into air, soil and water. Using rCF instead of vCF in manufacturing of new composites, there are huge environmental benefits (Witik *et al.*, 2013), as shown in figure 3.

There is also a huge vantage in therms of productivity about closing the producing loop (as shown in figure 1 and optimize the material lifecycle. This concern is helping the development of large researches and also is leading companies and industries to invest in recycling technologies in order to apply them on a industrial and commercial scale (Pimenta, 2013).

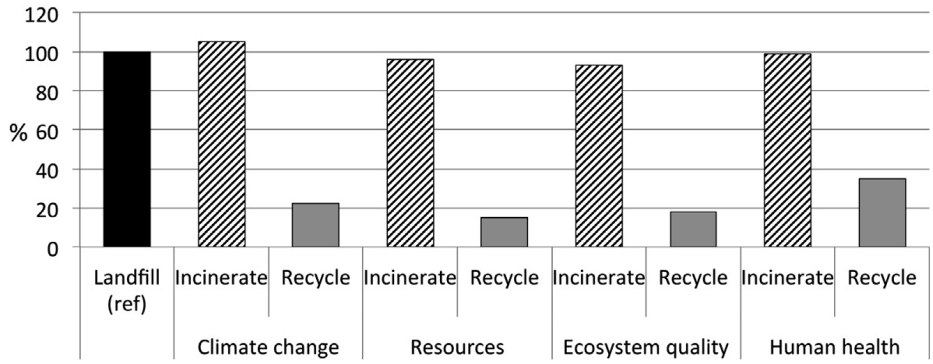


Figure 3. Comparison between recycling and common CF disposal in therms of impacts. font: Witik *et al.* (2013)

As an incentive from governments doesn't happens, major of technology and research at industrial scale is financiered by companies (Aircraft manufacturers, fiber and resin suppliers). Here, we're going to present the principal initiatives happening over the world:

- The PAMELA (Process for Advanced Management of EOL Aircraft) project aims to implement a platform for dismantling parts and assemblies and also valorisation of materials from EOL aircraft (PAMELA). The main contributors are European aircraft manufacturers, waste managers and CF recyclers.
- AFRA (Aircraft Fleet Recycling Association) main scope is incentive the sustainable management of EOL airframes and engines (AFRA, 2015). Contributors includes Aircraft manufacturers, material recyclers, technology developers and others.
- ECRC (European Composites Recycling Services Company) aims to create an European-wide waste management system for handling composite waste (ECRC, 2014). It is composed by resin suppliers, fiber suppliers and compounders.
- The JCMA (Japan Carbon Fiber Manufactureres Association) objectives are to establish the CF recycling system and to study the feasibility of starting a recycling business. It was merged with JCFA (Japan Chemical Fibers Association) in 2014 and has not started his activities yet. (JCMA, 2015).
- Carbon Fibre Recycling and Reuse (GO Carbon Fiber) its the world's first conference exclusively dedicated to CFRP recycling (GOC). It is formed by researchers, rCF producers and users, such as rCFRP researchers.

However, the recycling of composites is not a simple process. They have complex composition (fibers, matrix and fillers); some types of resins can not be remolded and they may be associated with other materials (such as sandwich structures). (Pickering, 2006a).

3. CFRP RECYCLING TECHNOLOGIES

The principal technologies to recycling of composites are included in three basic methods: mechanical recycling, thermal recycling and chemical recycling.

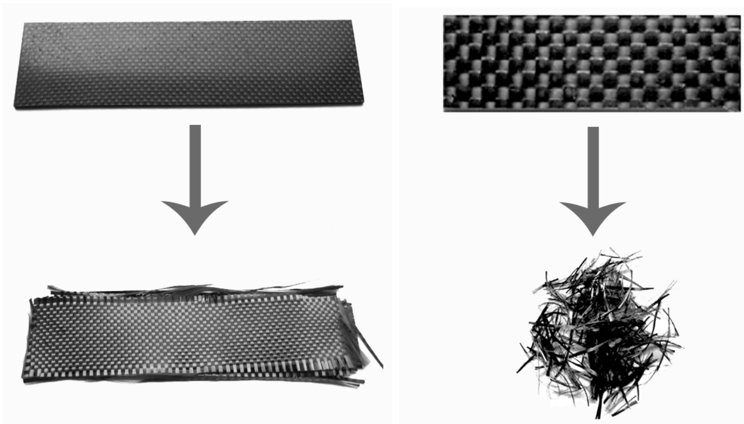
Each recycling process has its particularities in therms of: 1)Origin of raw material 2)Required use after recycling and 3) Cost and viability. The determination of mechanical properties of rCF is a good startpoint to design the composite of remanufacturing. rCF with satisfactory mechanical properties when compared with vCF allows it to be used in structural applications, given the shape of the reclaimed fibers also. Many process (chemical and mechanical) transforms reclaimed fibers into 'fluffy' and small pieces. Pyrolysis and chemical solvolysing via supercritical liquids brings back fibers with shapes closest to the original.Figure 4 shows examples of rCF obtained by chemical recycling and the different shapes of rCF related to them.

Figure 5 shows a compilation of studies and researchers efforts to evaluate how much the different recycling processes damages the fibers and, consequently, their mechanical properties.

The sections above will present the recycling techniques, their procedures and possible applications.

3.1 Mechanical recycling

Mechanical recycling breaks the CF composite into small pieces by mechanical processes such as milling, cutting, or shredding; generating two sub-products: powdered products (rich in resin) and fibrous products(rich in fibers) (Kouparitsas *et al.*, 2002).



(a) (b)

Figure 4. CF reclaimed by chemical recycling. (a) Using supercritical alcohol; (b) Using subcritical water

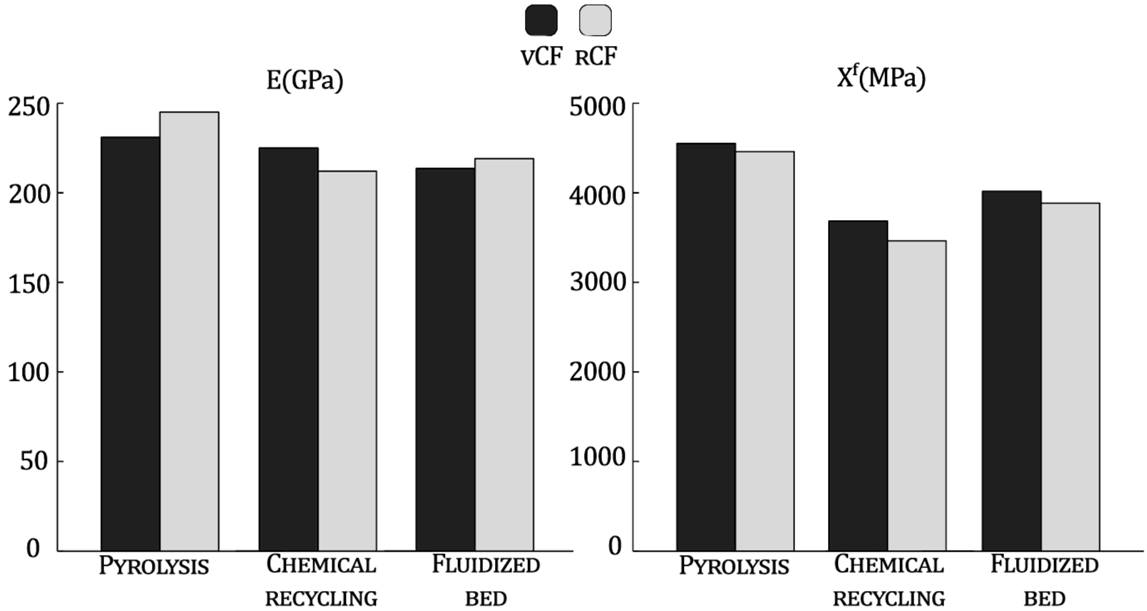


Figure 5. Stiffness and strength of vCF and rCF. Fonts: Pyrolysis - EMMERICH and KUPPINGER (2014), Pimenta (2013); Chemical recycling - OUMAN *et al.* (2014); Fluidized bed: JIANG *et al.* (2009)

Hence the mechanical crashing of CFRP reduces drastically the mechanical properties of rCFs, its applications are limited to non-structural uses, such as filling material on concrete alloys and reinforcement for new composites (OGI *et al.*, 2005).

There are many ways to reprocessing of polymers made of rCF, such as thermoforming, compression molding, extrusion and injection. The reprocessing needs to follow this steps: 1) extraction of polymeric waste, 2)milling, 3)washing, 4)drying and 5)reprocessing. There aren't many details about this steps, because of the process protection by intellectual property ends (da Silva Spinacé and De Paoli, 2005).

3.2 Chemical recycling

Many techniques of chemical recycling have been perfomed in the last year, looking for best rCF in terms of mechanical properties and maintenance of lamina's original shape. Subcritical and supercritical fluids have been showing as promising, plus, they have high power of polymer degradation (Okajima. *et al.*, 2012).

The use of reactive solvents (solvolysis)to breakdown chemical bonds even in termofix matrices is proven to be efficient to degrade the resin with less degradation of fibers (Liu *et al.*, 2012).

Liu *et al.* (2012) had test different concentrations of phenolic composts and KOH into subcritical water, obtaining rCF with tensile strength near to 2.62GPa for rCF after re-sizing, compared with vCF that reached 2.64GPa.

Piñero-Hernanz *et al.* (2008) evaluated different alcoholic solvents under supercritical and subcritical states, reclaiming fibers from 85% to 99% of tensile strength comparing with vCF.

3.3 Thermal recycling

Thermal processes extracts matrix from fibers using high temperatures, complying with different thermal properties of fibers and matrix in order to reach the ideal temperature to extract more resin and not damage fibers (Pickering, 2006b). Most common thermal process of CF recycling are pyrolysis and fluidized bed reactors.

3.3.1 Pyrolysis

Pyrolysis consists on degradation of organic molecules of the material, under a controlled and inert atmosphere with almost no occurance of oxygen and at high temperatures (from 400ºC to 700ºC) depending on operational conditions (Park *et al.*, 2013). The matrix and sizing are both burned out, and the final product are clean fibers. Pyrolysis can even allow the reuse of the matrix subproducts (gases and oil), taking advantage of its calorific power making this method as a potential self-sustainable process. However, existing studies suggest that this reuse is not economically viable yet (Alsop, 2009)(Pimenta and Pinho., 2014).

This process has been vastly studied on waste management, due to its relative low cost, high efficiency, generation of stable wastes, quick start and end, minimal emission of hazardous waste when associated to efficient gas system of treatment (like plasma technologies) and producing rCF with good mechanical performance (Chae *et al.*, 2006) (Pimenta, 2013).

It is currently the only recycling method with full-size commercial-scale: ELG Carbon Fibre, Ltd (United Kingdom); MIT-RCF (Reengineered Carbon Fiber, a Materials Innovation and Technologies company - United States); CFK Valley(Germany), Karborek S.p.A. (Italy), Recaltech (Brazil).

3.3.2 Fluidized bed process

The basic difference between fluidized bed (FB) and pyrolysis processes are: 1) the range of temperature in FB, it is approximately from 450º to 550ºC. 2) the atmosphere composition in FB is oxygen rich (Pickering, 2006b).

Scraps of CF reduced to pieces about 25mm large are fed into a bed of silica on a metallic mesh. Hot air flows into the bed and burns the resin, carrying out fiber filaments and oxidized matrix molecules, and heavy metals remains in the bed - this makes the FB suitable for contaminated scraps. Then, the flow runs trough a cyclone to separate fiber from matrix, that is burn in a burning-chamber in the end of process.

A synthesis of recycling technologies is shown in Table 1, that compares advantages and drawbacks of the previously presented methods.

4. COMPOSITES RE-MANUFACTURING

Following the recycling, fibers are ready to re-manufacturing. Consists on impregnate resin into reclaimed fibers. The methods of this process sometimes need to have some adaptations comparing with the original processes (for example, rCF obtained from prepregs scraps surely will be submitted to another manufacturing method compared to their precursors). The design and the definition of method used of rCFRP depends on: shape of reclaimed fibers, their quality and required reuse. There are four families of re-manufacturing processes, that will be shortly introduced.

The Direct Molding processes (such as injection molding and bulk molding compression) has been applied to re-manufacturing of composites. They are also available for virgin composites, but produces composites with modest stiffness and strength, because the high pressure used in these processes reduces fiber length (Pimenta and Pinho., 2014).

Impregnation of nonwoven preforms are the most difused method of rCFRP manufacturing, in which reclaimed fibers are transformed into nonwoven 2D or 3D products, followed by impregnation via Resin Transfer Molding (RTM), RIFT, etc. These rCF don't have a continuous form, the fibers aren't aligned and disposed randomly. Their permeability are low, which induces an addition of pressure on molding, that eventually causes breaking of fibers during manufacture. (Pimenta and Pinho., 2014), (Pimenta and Pinho, 2011).

Aligned fibers rCF fabrics, however, have potential to produce better composites in therms of mechanical performance and composite's fiber content. In this context, there are two other techniques of rCF composites re-manufacturing. Impregnation of aligned preforms is the first example. In fact, it can be applied to anyone of the two methods mentioned above. According to Pimenta and Pinho. (2014), composites made of aligned rCF infusion can reach aerospace-graded aluminum and some vCF woven in therms of mechanical properties.

All the three methods already mentioned are applied to recovered fibers that have their original shape and architecture damaged or destroyed by the recycling process chosen. However, knowing process (chemical and thermal) that keep the original shape of vCF to rCF produces interesting and powerful recycled wovens. Impregnation of woven recycled fabrics can be made by infusion, via RTM, RIFT or other process. It's products have the best mechanical properties when compared to that previously mentioned.

Table 1. Comparison between recycling technologies. Font: Pimenta and Pinho. (2014)

Process	Advantages	Drawbacks
Mechanical	• Simple process; • Recovery of both fibers and resin; • No use or production of hazardous	• Modest mechanical performance • Unstructured, coarse and variable fiber architecture • Limited remanufacturing possibilities
Chemical	• Very high retention of fiber properties; • potential for recovering valuable matrix products;	• Fiber adhesion to epoxy resins is commonly reduced • Low tolerance to contamination • Environmental impact if using hazardous solvents • Reduced scalability of most process
Pyrolysis	• High retention of fiber properties for optimized processes; • Energy recovery from the resin; • Good adhesion between rCFs and resin • Existing commercial implementations	• Possible deposition of residual matrix/char on fiber surface • Quality of fibers is sensitive to processing parameters; • need for off-gases treatment unit • Allows original shape maintenance
Fluidized bed	• Can be used in contaminated materials; • No residual products on fiber surface; • Well estabilished and documented process	• Large degradation on fiber strength; • Fiber length degradation • Unstructured rCF architeture • No material recovery from the matrix

5. RCF AND RCFRP APPLICATIONS

As mentioned, the recovery products will have their potential powered or reduced according to the recycling process chosen and the quality of re-manufacturing. Structural applications are the main target to explore the potential of this noble material. However, non-structural applications have good economy balance and requires simple operation. Some successful non-structural material produced includes sports goods, heating elements (food industry), ceramic disk brakes and electromagnetic interference shielding veils.

5.1 Structural applications

RCFRPs used in structural applications are the most promising reuse of rCF, in order to take advantage of the good mechanical properties offered by CF and produce composites with high aggregated-value. Aeronautical industry is getting ready to enjoy the benefits and possible building of rCFRP structural parts (AFRA and PAMELA are hugely invests in this field). Researches from all over the world are driving the reuse of CFRP waste to high levels, what indicates a promising investment. Aircraft interiors are a good start point. George (2009) manufactured seat armrest.

However, other industries like automotive can use rCFRP to build car parts, hence their have better properties when compared to usually virgin materials used. Warrior *et al.* (2009) reported crashworthy, wing mirror cover and car door panel. Nakagawa *et al.* (2009) succesfully produced rCF driver seats.

6. CONCLUSION

The background of CFRP recycling is promising, specially in aircraft industry. Companies are investing massively and researchers efforts aims to exploit all the advantages of rCF by optimizing recycling processes and applications. Laws are becoming more restrict and environmental assessment of CFRP recycling, allied to huge economic gains ensures the feasibility of rCF application.

Governments need to worry and concern about aircraft waste, establishing new policies based on a renewed point of view of materials - reuse, cycling and correctly managing resources brings economic benefits, better natural resources management and environmental responsability.

Private initiatives also need to happen, in order to create global groups of support and commerce of rCF, making it an usual and competitive material in many industry segments. Varieties of market for rCF buyers and users need to be established, in order to determinate a demand of rCF manufacturing and distribution.

Researching also needs to investigate the properties and possible applicability of this materials, joining efforts with companies to certificate their process and make sure this products are going to reach their best properties and marketing outlook.

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