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Recycling of Carbon Fiber Laminates by Thermo-mechanical Disassembly and Hybrid Panel Compression Molding

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Abstract: *An innovative recycling process for thermoset composite laminates is proposed by thermo-mechanical disassembly and further compression molding of hybrid thermoformable composite plates. Due to the thermo-mechanical process, single cured plies are extracted from the waste laminate. Subsequently re-lamination is performed by interposing thermoplastic films between the reclaimed composite plies. Final consolidation is carried out by compression molding. In order to show the feasibility of the novel recycling technology, carbon fiber reinforced composite plates by autoclave molding were thermo-mechanically disassembled in a manual roll bending machine after heating in oven. Reclaimed cured plies were laminated by alternating thermoplastic interlayers made of low density polyethylene. The hybrid laminate was consolidated at the temperature of 220°C and the holding pressure of 38.5 bar. Results from bending tests on virgin and recycled plates showed the very good agglomeration of the hybrid samples and the optimal preservation of performances of initial cured plies of the virgin material into the recycled plate.*

Keywords*: carbon fiber laminate, composite recycling, hybrid composites, compression molding*

1. Introduction

In the last decades the use of polymeric matrix composites (PMC) has recorded an impressive growth since their thermo-mechanical properties make them particularly suitable for numerous applications. The reinforcement can be of various natures, but glass and carbon fibers are the most common. Glass fiber reinforced plastics (GFRPs) are preferred for low- and medium-load application because of their low cost. Carbon fiber reinforced plastics (CFRPs) are much more expensive but they are light-weight materials and are able to carry high loads thus replacing metals in structures. CFRPs are increasingly used in high-value fields in which the weight reduction of the overall structure is a design target such as aeronautics, aerospace, automotive and sports industries. Unfortunately end-of-life of GFRPs and CFRPs is still an issue, and landfills or incineration are the typical solutions.

In the past decades, wasted PMCs was not sufficient to represent a social and environmental issue because of their low diffusion but nowadays the amount of dismissed materials is growing constantly. According to Lefeuvre et al. [1] the amount of wasted CFRP in 2050 will be equal to almost half a million of tons, and the main part of this quantity will be located in North America (162,000 t) and Europe (145,000 t). Thermoplastic PMCs have a possible recycling strategy thanks to their ability of being reshaped at high temperature. Thermosetting PMCs, as most of GFRPs and CFRPs, cannot re-enter primary processing steps because of their cross-linked structure which is formed during manufacturing of the virgin part.

Composite recycling technologies are grouped in three main categories: mechanical recycling, thermal recycling and chemical recycling. Mechanical recycling is the first basic step and consists in reducing the part size by cutting and grinding. Grains rich of fibers and grains rich of resin are produced by mechanical recycling and can be separated on the basis of their density or dimension. Fiber rich grains are used as fillers in new composites, mainly thermoplastic. Mechanical recycling affects the integrity of the fibers and shortens their length. Thermal recycling deals with the composite matrix de-poly-merization or evacuation by the material long residence at high temperature. Long and clean fibers can

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be theoretically obtained thanks to an appropriate control of the processing parameters but thermal aging affects fiber strength, and part cutting or pelletizing is necessary to optimize the use of reactors. Pyrolysis is the most known thermal recycling process carried out in absence of oxygen. Since the process is highly energy consuming, its industrial sustainability is under question also for high-value materials such as CFRP. Chemical recycling involves the matrix recycling technique; the matrix is evacuated at high temperature and in de-polymerization by the combined action of solvents, temperature and pressure. A catalyst may be used to fasten the de-polymerization reaction. Solvolysis is the most popular chemical recycling method but is not suitable for all the organic matrices. Recovered fibers have mechanical properties comparable with those of the virgin ones.

All the recycling strategies of composite materials are still under development for GFRPs and CFRPs. Dealing with thermal recycling, in 2020, Gopalraj et al. [2] used a cone calorimeter to recover both carbon and glass fibers. The recycling processes took place at atmospheric pressure and 550°C. Carbon fibers were extracted after 20-25 min of processing with a recovery rate about 95-98 wt% whereas glass fibers reached a recovery rate of 80-82 wt% after the same time. Moreover, Gopalraj et al. [2] re-processed recovered fibers by mixing with epoxy resin and compression molding at volume fractions of 40 and 60 wt%. Despite of the final good mechanical performances, the advantage of this kind of solutions is questionable because of the high cost and quality of epoxy liquid systems. According to Hao et al. [3] carbon fibers from a cured epoxy prepreg can be recovered via microwave pyrolysis. Their tests were carried out at 450, 550, and 650°C. Pyrolysis occurred at all these temperatures but the char residue on the fibers surface as well as the overall amount of char is reduced as the temperature increases. On the other hand, lowering the processing temperature leads to higher strength. They discuss a reduction in the strength that was less than the 20% but it seems not negligible by considering the high energy input required.

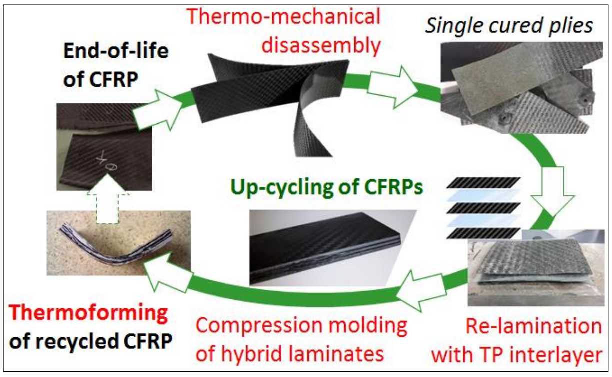

Figure 1. Circular approach of TS-CFRP up-cycling

For chemical recycling, in 2019, Zhu et al. [4] showed that the catalyst effect in chemical recycling can be favored by electrochemical promotion. The recycling process was carried out at room temperature and atmospheric pressure. Reclaimed carbon fibers had residual tensile strength about 90% of the virgin fibers but 121% residual interfacial shear strength. A chemical recycling was implemented also by Lee et al. [5] in 2020 to recover carbon fibers from an epoxy composite. They used benzyltrimethyl-ammonium bromide (BTAB) and sodium dodecyl sulphate (SDS) to favor the interfacial separation between the resin and the fibers. This method allowed processing time of 1 h, fibers with smooth surface, clean and with no defects. Recovered carbon fibers had tensile strength about 96.9% of virgin fibers. The main issue seems to be related to the chemical substances and waste. More recently, in 2021, Xing et al. [6] have induced composite swelling via acetic acid at high temperature. Composite delaminates into single layers at 160-220°C after 1h. These layers can be cut into various shapes and re-processed. The measured flexural strength was in between 47% and 89% of virgin samples. In the end, Deng et al. [7], in 2021, have proposed the solvothermal degradation of CFR boron phenolic resin composites in a teflon-lined autoclave at 225°C and 280°C for 1–4 h. The selected solvents were 1-propanol, water and acetone whereas KOH was used as an additive to fasten the resin degradation. The degradation ratio 98.3% at maximum as a small amount of resin residue was left on the reclaimed fiber surface. Recycled composites with reclaimed fibers and boron phenolic resin showed a flexural strength higher than the virgin due to a better interface between fibers and matrix.

This study deals with an innovative thermo-mechanical recycling process during which the temperature is used only for laminate disassembly. The circular approach of this new recycling technology is shown in Figure 1, and is better identified by the term "up-cycling". Up-cycling means that a higher added value is given to recycled parts because of such properties provided to the waste material thanks to its previous life. Starting from thermoset (TS) CFRP composites is possible to manufacture thermo-formable sheets and plates by compression molding. Waste TS laminates are thermo-mechanically disassembled so that single cured plies are extracted. These plies are joined by using thermoplastic (TP) interlayers in the shape of films during compression molding. Thanks to the TP nature of the joining films, plates can be thermoformed to produce other composite structures.

2. Materials and methods

Industrial CFRP plates have been used to show the feasibility of the recycling strategy. Autoclave molded 3-ply laminates have been recovered with nominal size of 240 x 80 x 2 mm^3. The laminate was made of woven fabrics. In order to test virgin material properties, 3 samples with 80 x 20 mm^2 were extracted from one laminate for bending tests.

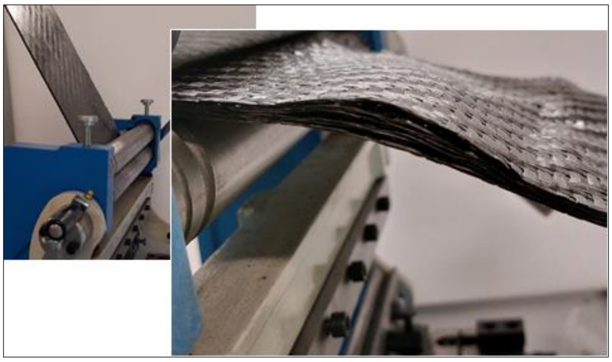

Figure 2. Thermo-mechanical disassembly of a composite laminate

For thermo-mechanical disassembly, plates to recycle were heated in an oven (by Nabertherm) at 250°C for 15 min. After heating, a manual roll-bending machine (by BS Macchine) was used to apply required strain as shown in Figure 2. For the disassembly procedure, the laminate is positioned between bending rolls and their gap is tailored to have the maximum deflection without fiber breaking. The hot-bending step is repeated until the composite is fully delaminated. In absence of heated rolls, if the laminate cools down due to multiple passes, it is necessary to add another heating step in oven. The gap between the rolls, the number of passes, and the number of heating steps depend on the structure and size of the plate to recycle, and are optimized to maximize the plate deformation in absence of fiber damages.

TS disassembled plies were used to manufacture new TS-TP hybrid composites. Reclaimed plies were laminated by interposing low-density polyethylene (LDPE) films which were extracted from a roll with 60 µm thickness. Both TS reclaimed plies and LDPE films were cut with the size of 130x80 mm^2. During lamination, 2 TS-plies were alternated with 10 LDPE films according to Figure 3. The final re-assembled laminate was compression molded for consolidation as shown in Figure 4. A laboratory procedure was used with pre-compressed molds in the oven. The mold was aluminum made with a square cavity having a size of 140x140 mm^2. The pressure was applied in cold conditions by a spring with a load of 40 kN thus providing a maximum initial pressure of 38.5 bar. The oven temperature was 220°C and the molding time about 30 min to compensate the initial room temperature of the mold. After molding, burrs were trimmed to obtain the nominal size of 130x80 mm^2. The average thickness of the molded hybrid laminates was 1.7±0.2 mm with a value of 826 µm per ply, instead of the 670 µm per ply of the virgin laminate (+24%). Mechanical performances of virgin and recycled samples were measured by 3-point bending (MTS Insight 5) with a span of 60 mm at the rate of 1 mm/min up to sample failure.

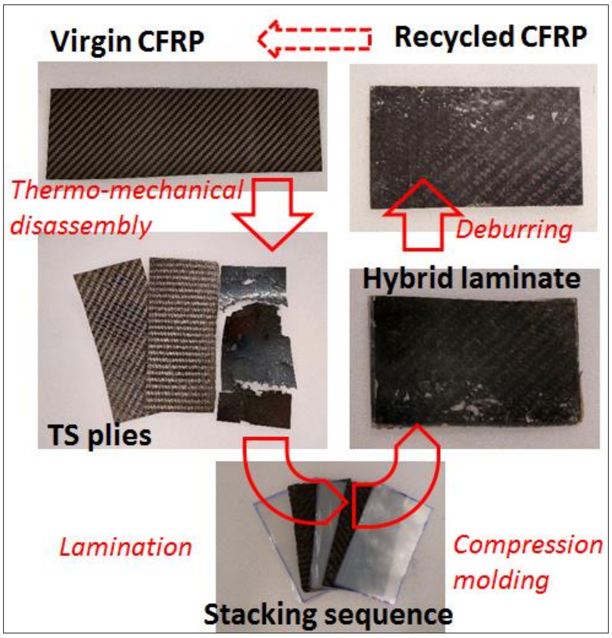

Figure 3. Manufacturing procedure of hybrid composite laminates

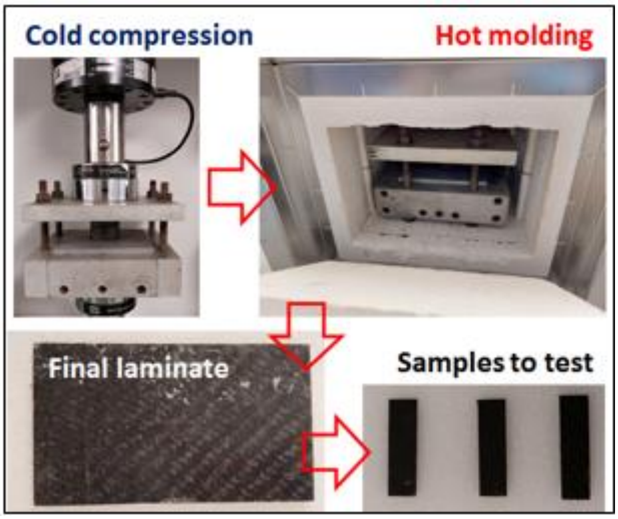

Figure 4. Compression molding step and sample extraction

3. Results and discussions

In the molded hybrid laminate, a good adhesion between LDPE and TS plies was observed. A smooth surface on the top ply was also found thanks to this affinity. The re-manufactured composite, generally speaking, shows a good compaction among the layers, and cavities are absent through the thickness. Both edge bleeding and surface bleeding occur during molding with positive effects on laminate consolidation. Moreover, hybrid laminates have a plain surface without warping or distortion.

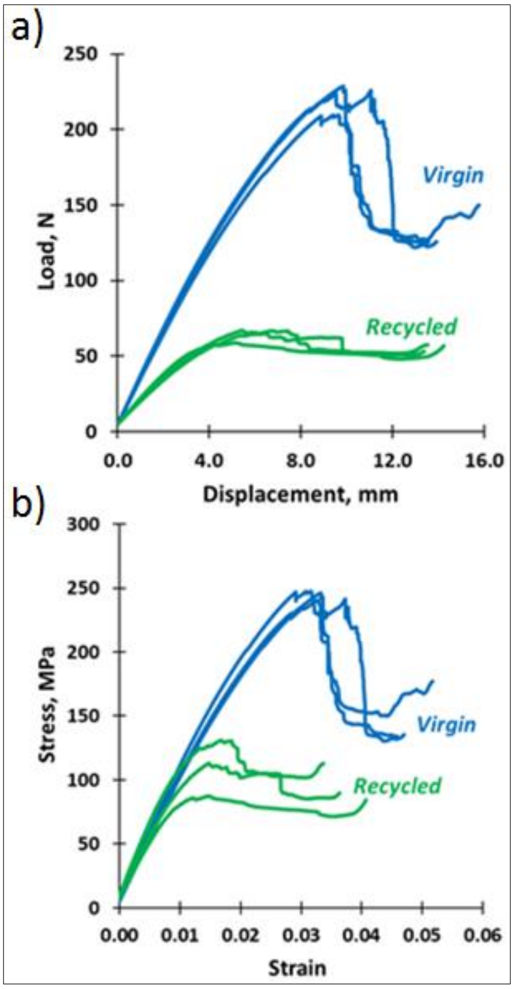

Figure 5. Bending tests on virgin and recycled samples in terms of load-displacement (a) and stress-strain (b)

Results from bending tests are shown in Figure 5 in terms of load-displacement (a) and stress-strain (b) curves. Virgin and recycled laminates present different stiffness but comparable elastic modulus because of the different number of plies but similar ply thickness. In the case of hybrid laminates, curve dispersion increases after normalization. This occurrence is related to the high thickness of the LDPE top and bottom layer.

From a quantitative point of view, in the first loading step, the bending strength of the 3-ply virgin laminate is 245±3 MPa, much higher than the 2-ply recycled composite (110±22 MPa). This large difference is not related to the different number of plies but the soft behavior of the LDPE interlayer. In fact, the shape of the bending curve is very different and a plateau-like trend is present after the maximum stress.

At the state of the art, manufacturing of TP CFRP laminates is made by compression molding of TP prepregs into plates. These plates can be subsequently thermoformed in the desired shape. Hot-stamping and injection over-molding are alternatives. However, it is very difficult making impregnation of long CF tissues with TP matrices because of their high viscosity at elevated temperatures. Fiber distortion occurs during resin bleeding. For this reason, unidirectional (UD) tapes are generally available on the market with TP matrix. Woven fabric prepregs are very rare and expensive as they are produced by matrix spray. Final prepregs often do not provide expected performances. Not all the fabrics can be used as fiber impregnation partially occurs during laminate consolidation. An alternative is making compression molding of dry fabrics laminated with thermoplastic films, but overall performances are not comparable with those made by using prepregs. As a result, nowadays there is a big necessity of finding new industrial solutions to produce thermo-formable CFRP plates above all with woven CF fabrics. The proposed manufacturing strategy solves contemporarily two problems, the first is recycling of spent CFRPs, and the second is providing thermo-formable CFRP laminates to the market.

The recycling procedure aims to consolidate hybrid composite laminates with TS structural plies and TP interlayers. Single cured plies are not produced from virgin raw materials but they are extracted by already consolidated multi-ply laminates. Moreover the interlayer sheet with high viscosity resin is made of a TP polymer which provides additional properties such as thermo-formability, damping, and resilience. The perfect agglomeration is guaranteed by a proper selection of the TP film as a function of the composite resin matrix. A physical mechanism works also in the case of poor compatibility because of asperities on the recycled ply surfaces which are mechanically embedded in the TP interlayer.

This is the case of the proposed experimentation where LDPE is used to join composite plies with epoxy matrix. LDPE and epoxies do not show very high chemical affinity, but the final agglomeration of the hybrid panel is very good. From a conceptual point of view, the final hybrid laminate is perfectly engineered as a TS old matrix is present close to the fibers where perfect impregnation is necessary whereas a TP binder is present between plies.

The core of the re-processing technology is the thermo-mechanical disassembly. Fibers tend to break if high bending loads are applied at room temperature because of the matrix rigidity. Instead, if the laminate is heated at a temperature over the glass transition temperature of the resin matrix, a bending load produces delamination and allows ply separation. After laminate decomposition, the single ply is rigid but very flexible. For this reason, by incorporating in the final hybrid structure, it can be shaped by further application of loads and temperature. Experimental tests show that the thermo-mechanical disassembly works already by using existing machines such as roll bending machines.

By recycling the TS composite, a TS-TP hybrid composite is made that can be re-shaped by thermo-forming or compression molding again. In fact, if delamination occurs because of the rigid behavior of the TS plies, those cracks are immediately closed by the molten TP interlayer and do not appear in the final shaped part. Thanks to the hybrid nature of the recycled laminate, shaped products may be repaired after failure by means of a thermo-mechanical re-consolidation process. Measured properties of recycled laminates are very attractive for many structural applications where these additional functional behaviors would be much appreciated.

4. Conclusions

In this work an innovative recycling technology for TS composites is proposed. The method is based on the thermo-mechanical disassembly of waste laminates, and subsequently re-assembly with TP interlayers. In this way, it is possible to recover both the fibers and the matrix thus reducing the overall amount of dismissed materials. As a TP binder is present in the hybrid laminate, the final recycled part is recyclable as well. Indeed the mechanism of disassembly is still working if the part is heated above the softening temperature of the thermoplastic interlayer. Therefore the plies can be separated and re-assembled several times. In alternative, recycled composites can be crushed, and pellets can be compression molded also without any other use of materials as the residual thermoplastic resin would work as a binder.

Thermosetting matrices of waste CFRP composites polymerize during the production process. A compact 3D network is generated that cannot flow under heating and makes impossible re-processing by using primary production processes. Nowadays, the two main strategies for TS composite recycling consist in composite grinding or pyrolysis, as energy recovery is not very convenient. Grinding is the old solution for all the difficult-to-recycle materials but the market has shown the very poor interest in reprocessing this kind of powders. Only black organic parts can be manufactured, and hybrid recycled fillers provide poor final performances to molded parts in comparison with virgin fillers. For this reason, pyrolysis has been strongly studied as a way to improve the quality of fillers. By pyrolysis, fibers can be recovered by the matrix evacuation but their strength can significantly reduce. Moreover, pyrolysis requires energy which is only partially recovered by burning resulting gas and liquids. Gas and liquids are full of contaminants that can be released in the environment if an expensive capture system is not used. Pyrolysis systems very often need material pelletizing and always result in recovering short fibers from original continuous fibers. In the end, commercial materials made of recovered fibers show very poor performances. Due to pyrolysis, also coupling agents are removed from the fibers with negative effects on final products. In the end, soft mats are typically produced but they tend to absorb an excess of resin during manufacturing, leading to an inferior than expected performance of final products. In this scenario, the proposed recycling technology is the only one that may allow maximizing the useful life of the material by reducing the amount of waste as well as the consumption of raw materials and the energy associated to their processing. Measured mechanical properties of recycled composites confirm their suitability for many structural uses. Carbon aesthetic appearance and additional functionalities such as reparability and damping may push the interest of the market toward these up-cycled materials.

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References

1. LEFEUVRE, A., GARNIER, S., JACQUEMIN, L., PILLAIN, B., SONNEMANN, G., Anticipating in-use stocks of carbon fiber reinforced polymers and related waste flows generated by the commercial aeronautical sector until 2050, *Resources, Conservation and Recycling*, 125, 2017, 264-272.
2. GOPALRAJ, S.K., KÄRKI, T., A study to investigate the mechanical properties of recycled carbon fibre/glass fibre-reinforced epoxy composites using a novel thermal recycling process, *Processes*, 8 (8), 2020, 954.
3. HAO, S., HE, L., LIU, J., LIU, Y., RUDD, C., LIU, X., Recovery of carbon fibre from waste prepreg via microwave pyrolysis, *Polymers*, 13 (8), 2021, 1231.
4. ZHU, J.-H., CHEN, P.-Y., SU, M.-N., PEI, C., XING, F., Recycling of carbon fibre reinforced plastics by electrically driven heterogeneous catalytic degradation of epoxy resin, *Green Chemistry*, 21 (7), 2019, 1635-1647.
5. LEE, M., KIM, D.H., PARK, J.-J., YOU, N.-H., GOH, M., Fast chemical recycling of carbon fiber reinforced plastic at ambient pressure using an aqueous solvent accelerated by a surfactant, *Waste Management*, 118, 2020, 190-196.
6. XING, M., LI, Z., ZHENG, G., DU, Y., CHEN, C., WANG, Y., Recycling of carbon fiber-reinforced epoxy resin composite via a novel acetic acid swelling technology, *Composites Part B: Engineering*, 224, 2021, 109230.
7. DENG, Z., YUE, J., HUANG, Z., Solvothermal degradation and reuse of carbon fiber reinforced boron phenolic resin composites, *Composites Part B: Engineering*, 221, 2021, 109011.

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