PYROGASIFICATION OF COMPOSITE MATERIALS FROM AEROSPACE INDUSTRY FOR CARBON FIBER RECOVERY

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ABSTRACT

The use and production of carbon fibre reinforced composites (CFRPs) generate significant problems related to the disposal and consumption of non-renewable resources. Therefore, the possibility of processing CFRPs to recover carbon fibers (rCF) is a promising option for the circular economy of composites. There are currently several technologies for recycling CFRCs, classified into three main types, such as mechanical, chemical, and thermal recycling. Pyrolysis is a technically feasible and economical process and consumes only 5-10% of the energy required for virgin fiber production. For these reasons, it is the most developed process on an industrial scale in Europe.

The present work aims to develop a methodology to study and optimize the pyrogasification process for cured and uncured CRFP waste from the aerospace industry. The process consists of a first phase of pyrolysis in an inert atmosphere (N_2) and a second phase of controlled gasification in an oxidizing environment (O_2/N_2). Single-fiber mechanical tests, morphological analyses, and atomic mapping have made it possible to determine treatments that return recycled fibers with mechanical performance comparable to virgin ones.

1 Introduction

Carbon fiber-reinforced composite materials (CFRCs) combine high mechanical properties with low weight [1, 2] and are widely used in many industries to replace conventional high-performance materials. The global demand for CFRCs is continuously growing and increased from 128.500 in 2018 to 141.500 tons/year in 2019 and is expected to be approximately 197000 tons/year in 2023 [3-5]. The use and production of CFRCs generate significant problems related to the disposal and consumption of non-renewable resources. European legislation has imposed more stringent controls on CFRC waste management [6]. The waste consists mainly of off-cuts and end-of-life products currently disposed of in landfills or incinerated, eliminating the value of carbon fibers (CFs) [3-5, 7-8]. Furthermore, CFs production requires a significant amount of energy (183-286 MJ/kg), so the possibility of recovering composites for CFs reuse is a promising option for sustainability, circular economy, and the implementation of EU requirements [9-10]. There are several technologies for CFRCs recycling, classified into three main types, such as mechanical, chemical, and thermal recycling. Mechanical recycling involves CFRCs grinding to obtain shreds or powders used as fillers in low-value applications [2, 11, 12]. Chemical and thermal recycling, on the other hand, allows the partial recovery of fiber length. Fibers are completely separated from the matrix from which monomers or petrochemical feedstocks can be recovered [12]. Chemical recycling employs solvents, even at high temperatures and pressure. Thermal recycling uses high temperatures to decompose the matrix. Pyrolysis is a technically feasible and economic process and consumes only 5-10% of the energy required for virgin fiber production [1, 11, 13-15]. For these reasons, it is the most developed process on an industrial scale in Europe [13, 16].

The present work aims to develop a methodology to study and optimize the pyro-gasification process for aircraft CRFPs, according to the scheme in Figure 1. One specific industrial material type, both in prepreg and cured composite form, was selected to study the pyro-gasification process and recover

carbon fibers. The material samples were subjected to thermogravimetric analysis (TGA) to investigate the degradation kinetics of the polymer matrix and the weight loss as a function of time and temperature. These tests lead to the definition of optimal working temperature. Preliminary information on residence times, obtained from TGA analysis, was used to fine-tune the thermochemical process, implemented in a suitably equipped lab scale plant. The process consists of an initial pyrolysis step in an inert atmosphere (N_2) and a second gasification step in an oxidizing environment (O_2/N_2). Different treatments were carried out, varying the pyrolysis and gasification time. The sample weight loss was calculated after each process step and for each treatment. Samples considered satisfying by an initial overall analysis were subjected to morphological characterization by scanning electron microscope (SEM) to verify the absence of surface char and possible degradation and measure fiber diameters. The single fiber tensile tests were performed to determine the effect of pyrogasification treatments and compare the mechanical properties of recycled fibers with virgin ones. In particular, the values of Young's modulus, tensile load, and elongation at break were monitored, i.e., the essential properties for defining possible new applications of recycled CFs. Once determined the best treatments, the fibers were again analyzed with SEM to measure their diameters. Through EDX analysis, it was possible to compare the surface distribution of oxygen and carbon, so the quality of the recycled fibers compared to the initial virgin fibers. Too long gasification treatments or at too high temperatures could lead to greater surface oxidation resulting in loss of mechanical properties. As a result of the analyses, it was possible to determine the optimal processes for recycling carbon fibers from cured and uncured material, ensuring comparable performance with virgin fibers used in the aerospace industry.

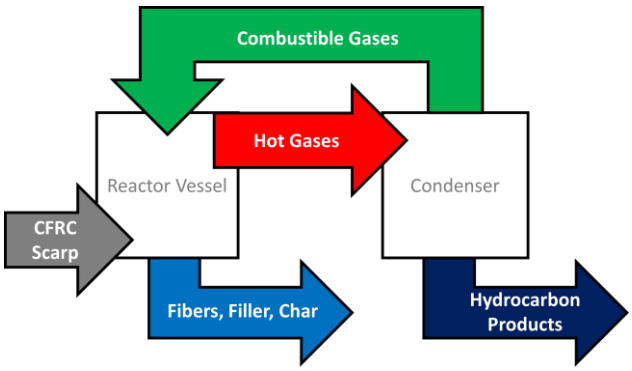


Figure 1: Pyro-gasification process scheme

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study are scraps of cured and uncured CFRP typically used in aircrafts provided by Leonardo SpA. The material is named CFRP-G for commercial confidentiality, and it is a composite consisting of an epoxy matrix and high-strength, intermediate-modulus carbon fibers. Cured scraps were collected during component trimming operations; uncured scraps are from expired material and cuttings. Virgin fibers used for comparison were obtained from prepregs that were washed several times in both CH_2Cl_2 and acetone in order to remove surface sizing.

2.1 Method

The goal of the work is to optimize the pyrogasification process for aerospace composite scraps. The process has two steps: during the first (pyrolysis), the samples are subjected to the process temperature in an inert atmosphere (N_2) to remove the polymer matrix; the second step (gasification) takes place in an oxidizing environment (air) and is used to decompose the char, formed during the pyrolysis.. In this way, matrix-free recycled carbon fibers (rCFs) are obtained. Preliminary characterization of CFRP -G was performed through the following tests:

- Thermogravimetric analysis (TGA) to evaluate optimal process temperature (Tp) and the

mass variation as a function of time
- Pyrogasification in the lab scale pilot plant and weight loss calculation
- Morphological analysis of the fibers with scanning electron microscope (SEM),
- Single fiber tensile test to determine the mechanical properties of the fibers
- Diameter measurements of fibers obtained from the best treatments
- Atomic mapping with Energy-dispersive X-ray spectroscopy (EDX) to determine the surface distribution of oxygen and carbon present on the fibers.

The mechanical properties and morphological characteristics of rCFs were compared with the respective virgin fibers. The optimized treatment will be the one that allows obtain rCFs with performance close to that of virgin fibers.

Samples were subjected to TGA analysis to study the material behaviour during pyrolysis and gasification steps. The test details are provided below:

- Step 1: ramp 40°C/min from 25°C to T_p in N_2 atmosphere
- Step 2: isotherm at T_p in N_2 atmosphere (pyrolysis), with a duration time (t_p) for uncured scraps and for cured scraps
- Step 3: isotherm at T_p in air (gasification) to achieve constant mass loss over time (plateau, t_g).

Almost three samples were tested for each type of waste.

The Tp temperature was chosen based on the literature review and previous experience of the research team. Preliminary information on residence times obtained from TGA analyses was used to fine-tune the lab scale process, which involves first a pyrolysis phase in an inert environment (N_2), then a gasification phase in an oxidizing atmosphere(O_2/N_2) at Tp.

All scrap samples were placed in ceramic crucibles within the chamber. For each experimental trial, the initial weight, post-pyrolysis weight, and post-gasification samples weight were measured using an analytical balance to calculate the weight loss. After the treatments, fibers were cleaned with a stream of N_2 and metalized with an Au/Pt coating to be analyzed by SEM to verify the absence of char and degradation phenomena and to measure their diameters.

Tensile tests of single fibers were carried out to determine the variation of mechanical properties of recycled fibers compared to virgin fibers, in particular the average values of Young's modulus, tensile load, and elongation at break. A total of 30 recycled fibers and 30 virgin fibers were tested with Remet TC10 dynamometer equipped with a 10N load cell. The carbon fibers have very small diameters, so they have been fixed on paper supports, which makes them easier to handle and fix in the machine. During the test, the long sides of the support are cut off to allow the testing of the fibers. The elastic modulus was calculated as the ratio of load to elongation at break. It has not been normalized with respect to fiber cross-section, which could vary depending on fiber degradation.

The fibers obtained from the selected treatments were analysed by SEM to characterize their diameters. The surface distribution of oxygen and carbon was analysed with the EDX detector coupled to the SEM. The high surface oxidation of rCFs compared with virgin fibers could indicate too long gasification treatments or at too high temperatures.

3 RESULTS AND DISCUSSION

For each type of scrap, three samples were tested and the average weight loss was calculated and reported in Table 1.

The cured scraps have shown an average weight loss of 28% after the pyrolysis stage, and an additional average weight loss of 9% after the gasification stage; the average fiber/matrix weight ratio of the samples is 63/37. An average mass loss of 25 % after pyrolysis and 8 % at the end of gasification was observed for the uncured material scraps; the fiber/matrix weight ratio was 67:33.

	Uncured	**Cured**
Temperature	T_p	T_p
Weight loss in Pyrolysis	25	28
Weight loss in Gasification	8	9
Weight loss Total	33%	37%

Table 1: TGA Results

The time intervals of pyrolysis and gasification stages were determined with TGA for both types of scrap. Table 2 shows the selected treatments for pyrogasification in the muffle furnace. Values for residence times in the pyrolysis and gasification stages cannot be reported for reasons of industrial confidentiality. The numbers in subscript follow the ascending order of the times to which they refer. Table 3 reports the experimental results of pyrogasification treatments.

Test ID	**Scrap**	**Pyrolysis time**	**Gasification time**
U1	Uncured	t_{p1}	t_{g1}
U2	Uncured	t_{p1}	t_{g2}
U3	Uncured	t_{p1}	t_{g3}
U4	Uncured	t_{p1}	t_{g4}
U5	Uncured	t_{p1}	t_{g5}
U6	Uncured	t_{p2}	t_{g5}
U7	Uncured	t_{p3}	t_{g5}
U8	Uncured	t_{p3}	t_{g6}
U9	Uncured	t_{p3}	t_{g7}
C1	Cured	t_{p4}	t_{g3}
C2	Cured	t_{p4}	t_{g4}
C3	Cured	t_{p4}	t_{g5}
C4	Cured	t_{p4}	t_{g6}
C5	Cured	t_{p4}	t_{g7}
C6	Cured	t_{p4}	t_{g8}
C7	Cured	t_{p5}	t_{g3}
C8	Cured	t_{p5}	t_{g4}
C9	Cured	t_{p5}	t_{g5}
C10	Cured	t_{p5}	t_{g6}

Table 2: Pyrogassification treatments

Regarding uncured scrap, there are no significant differences in weight loss in any of the tests performed, so it can be assumed that the optimal process time is the one that yields the same amount of degraded matrix in the shortest possible time.

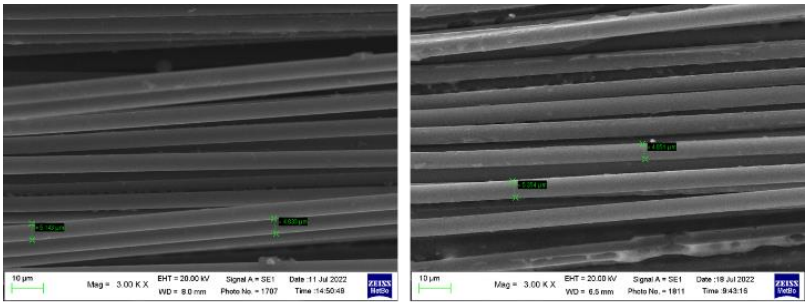
Sample U1 still has a non-negligible amount of undegraded matrix, making the CFs still joined together. The remaining samples, on the other hand, appear matrix-free and thus potentially suitable for reuse. Cured scraps have no significant difference in weight loss in the pyrolysis stage, while in the gasification stage there is a difference in weight loss between treatments as time increases.

Long gasification times, resulting in higher weight loss than the estimated fiber/matrix weight ratio, can cause possible degradation. An exception is the sample C1 which has some residual matrix in the pyrogassified fibers.

Test ID	Pyrolysis weight loss%	Gasification weight loss%	Total weight loss%
U1	28,7	6,4	33,3
U2	28,6	8,6	34,7
U3	27,9	10,3	35,3
U4	27,9	10,6	35,5
U5	27,8	11,2	35,9
U6	28,8	10,8	36,5
U7	30,6	8,7	36,6
U8	30,0	9,1	36,4
U9	29,6	8,7	35,7
C1	29,6	10,9	37,3
C2	29,8	11,9	38,2
C3	29,2	15,6	40,2
C4	29,5	19,7	43,4
C5	29,0	17,0	41,1
C6	29,4	16,6	41,1
C7	29,8	11,1	37,6
C8	30,0	11,6	38,1
C9	30,1	17,4	42,3
C10	30,5	17,7	42,8

Table 3 - Experimental results of pyrogasification treatments

Samples obtained from treatments that allowed for macroscopically clean fibers, and which are characterized by the shortest process times, were analysed by SEM. Figure 2 shows SEM images of samples U2 and C2. Both samples appear sufficiently clean, consequently, fibers obtained from longer processes can also be considered free of the polymer matrix. Small agglomerates are noted on the surface of the fibers, probably attributable to dust particles that were not removed during cleaning with N_2.



(a) (b)

Figure 2: SEM images, 3000X magnification, of fibers obtained from (a) U2 and (b) C2 treatments.

Figure 3, Figure 4, and Figure 5 show the results of mechanical characterization, especially the average values of elastic modulus, tensile load, and elongation at break. The values obtained for fibers recovered from cured and uncured scraps were compared with those of virgin fibers.

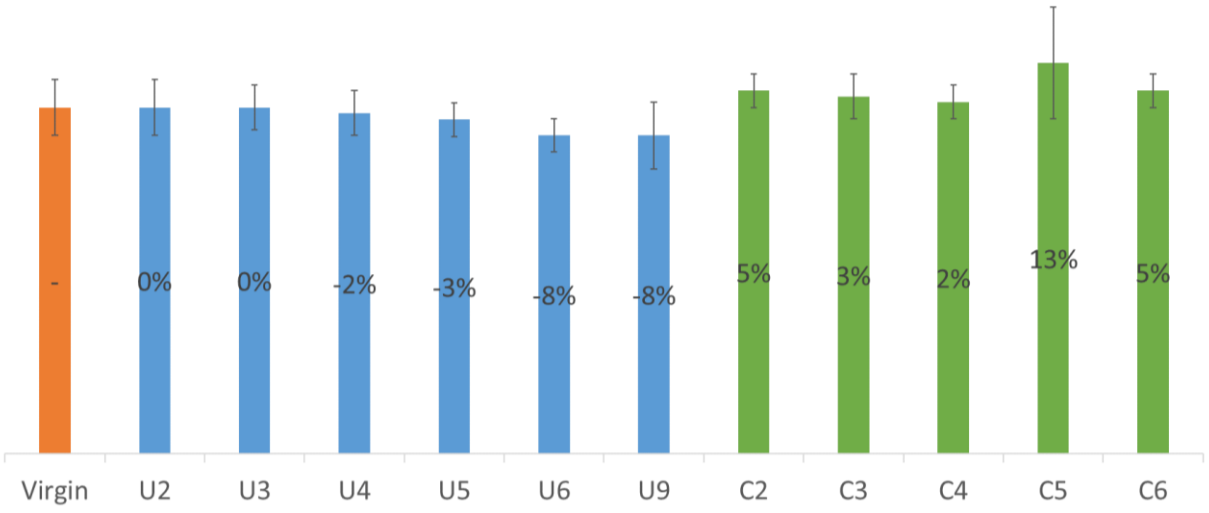


Figure 3: Elastic Modulus

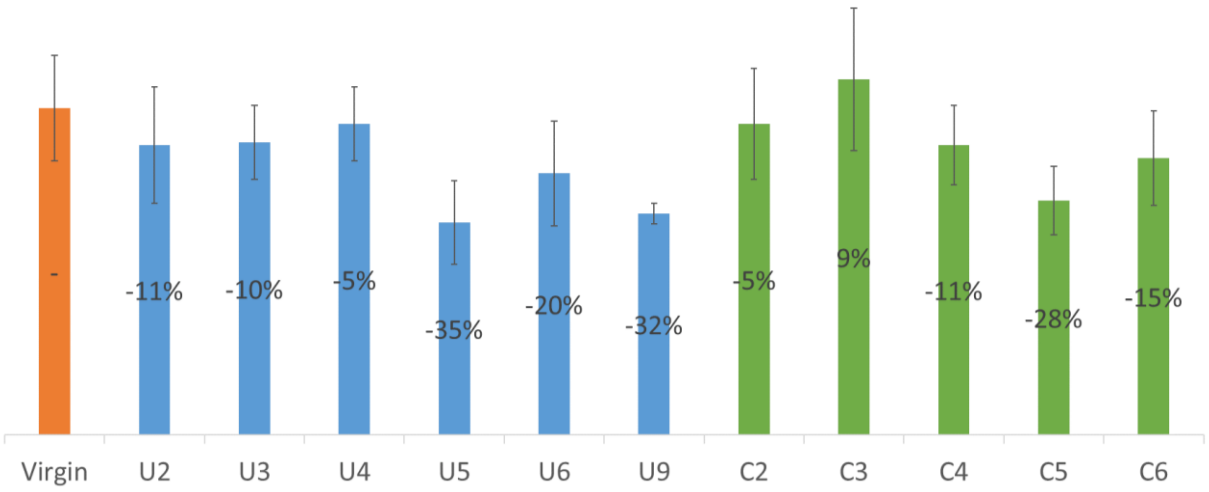


Figure 4: Tensile Load

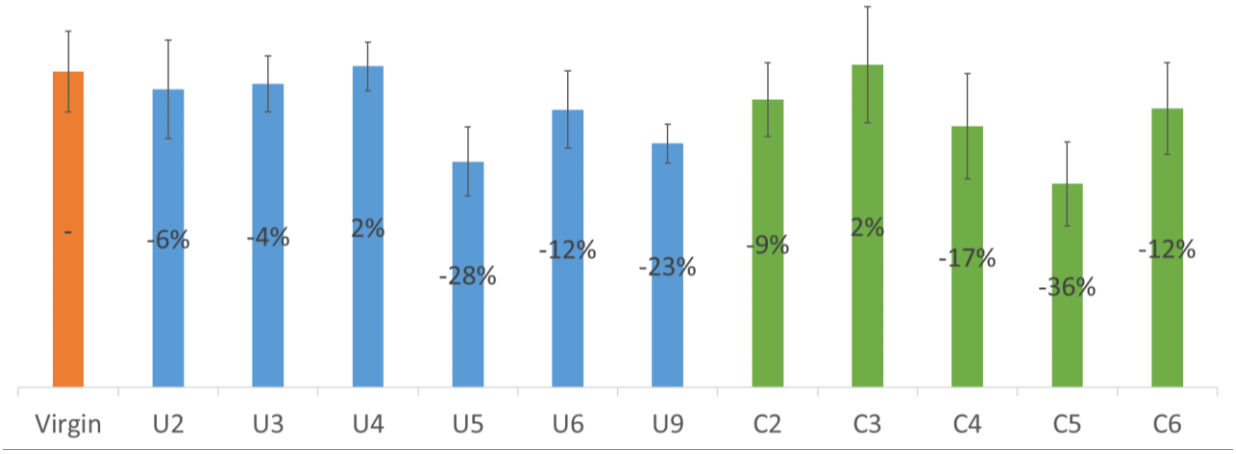


Figure 5: Elongation at break

As for uncured scraps, the modulus of all recovered fibers is comparable with virgin fibers. Focusing on both maximum stress and elongation at break, it is possible to see that the treatments that return the fibers having the best properties in comparison with virgin fibers are U2, U3, and U4. As for the cured scraps, again the elastic modulus of all treatments performed is in the order of magnitude of virgin fibers. For stress and elongation at break, the treatments that provide the rCFs with the best mechanical properties are C2 and C3.

Comparison with virgin fibers shows that rCF from both uncured and cured scraps have comparable average diameters, indicative of complete matrix degradation without fiber degradation (Figure 6).

The recovered fibers were analyzed with EDX and compared with virgin fibers to assess the change in carbon/oxygen atomic and weight element ratio (O/C ratio) on their surface. The results are reported in Figure 7.

Virgin fibers have oxygen percentages around 4%, which is still too high compared to graphitic fibers because of the hard-to-remove sizing, but comparable to treated fibers.

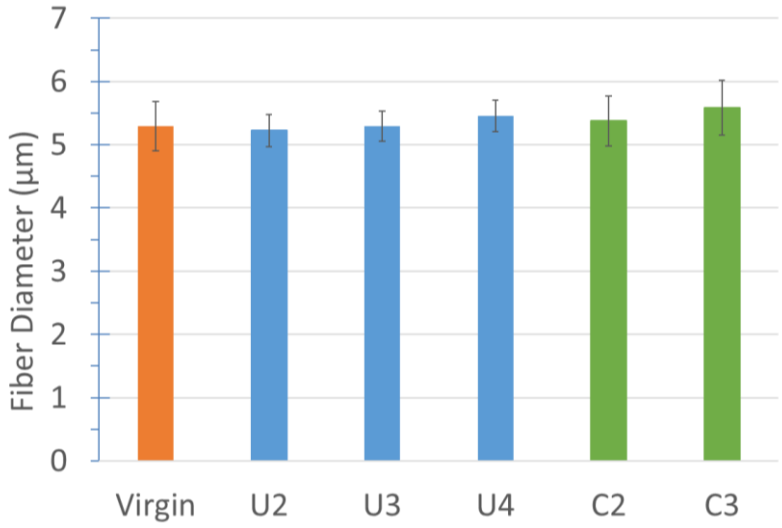


Figure 6: Average diameters (µm)

For fibers recovered from untreated material, the treatments that result in the lowest oxygen percentage are U2 and U4. The U3 process, on the other hand, returns fibers with an oxygen percentage

comparable to that of virgin fibers.

For cured material, the two best treatments have an oxygen content of 3 % similar to virgin fibers.

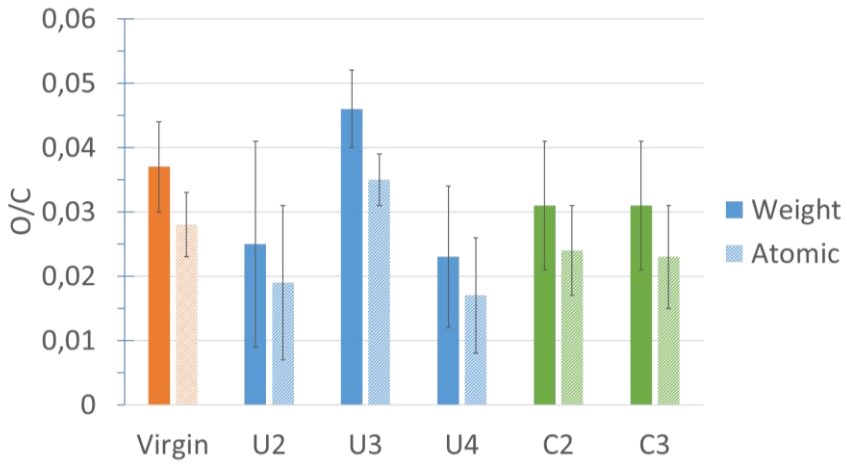


Figure 7: carbon/oxygen atomic and weight element ratio (O/C ratio) by EDX analysis

4 CONCLUSION

The work aims to optimize pyrogasification process parameters on CFRC scrap from the aerospace industry and recover carbon fibers with mechanical properties comparable to virgin ones. The composite scraps were studied by TGA to investigate thermal degradation kinetics of the polymer matrix and the weight loss as a function of time.

All samples were subjected to the pyrogasification process inside the reactor at the temperature of T_p, varying the residence time of both the pyrolysis and the gasification phase.

The rCFs with the different treatments were subjected to single fiber tensile tests to evaluate their elastic modulus, tensile load, and elongation at break %. Then the diameters and carbon/oxygen element ratio of the fibers obtained from the treatments considered best performing were measured by SEM and EDX analysis.

Characterization is necessary to determining process times and temperatures. Too long residence times or too high temperatures can cause degradation of the graphitic fibers; short residence times or too low temperatures do not ensure proper matrix removal, reducing the ability of the fibers to adhere to the new polymer matrix, affecting the mechanical properties of the final article.

The optimal treatments selected are those that allow obtaining clean, non-degraded fibers with properties comparable to those of virgin fibers while at the same time ensuring that process times are minimized.

From the analyses conducted, the optimal treatments appear to be the following:

- For uncured rejects, pyrolysis times are t_{p1}, and gasification times between t_{g2} and t_{g4}.
- For cured rejects, pyrolysis times are equal to t_{p4}, and gasification times between t_{g4} and t_{g5}.

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