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Mechanical recycling of an end-of-life automotive composite component

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Abstract

This paper investigates the effect of mechanical recycling on an end-of-life automotive component based on PA66 reinforced with glass fibers. The material was pelletized and injection moulded three times and compared with the composite material currently used to produce the same component. The study is focused on the comparison between the microstructural and rheological behaviour of the component and its final mechanical properties. The results reveal that mechanical recycling leads to the breaking of the fibers, decreasing their contribution to the mechanical strength. Despite the degradation suffered by the material, it preserves mechanical characteristics that are acceptable for other automotive applications. Therefore, mechanical recycling can be a solution to the problem of disposing of composite materials in landfills, as the products obtained still show satisfactory characteristics.

Keywords: mechanical recycling, automotive composite, end-of-life component, polyamides, glass fibers

1. Introduction

In the last few decades sustainable development and environmental issues have assumed a key role in the worldwide community [1,2]. As a result, the European Union has established a series of directives and regulations to reduce emissions of carbon dioxide [3]. This has led to a progressive replacement of conventional materials with thermoplastic reinforced composites in order to obtain lighter components with the same performances [4]. Inevitably, this results in the production of a higher amount of waste from the manufacturing process and a growing challenge to develop economically sustainable recycling methods for end-of-life components [5–7].

Recycling of thermoplastic matrix composites is now a mandatory challenge in the automotive sector. In fact, according to European directives, manufacturers have to reuse and recover at least 95% in weight per vehicle [8]. Different strategies have been adopted for recycling intrinsically inhomogeneous materials, such as composites [9–11]. The most common method involves mechanical recycling which consists in grinding the material and reusing the granulate obtained instead of the virgin one [12]. This approach is particularly suitable for short fiber reinforced polymers, for which the fiber breakage induced by grinding and the subsequent reprocessing has a minor effect on the mechanical properties of the material. Other approaches, such as thermal and chemical recycling, allow the recovery of fibers and matrix in the form of organic substances [13–15]. However, the high energy consumption of these methods compared to the mechanical one makes them only sustainable for composites with high commercial value fibers [16].

In the automotive sector, fiber reinforced polymeric composites are used for structural or semistructural applications of components, such as radiators, door beams, drive shafts and

tanks [17–19]. Most of these components are reinforced with short glass fibers that allow the thermo-mechanical characteristics required for many applications to be achieved at a lower cost than carbon fibers based ones. Usually, the recycling of this type of composites is studied by reprocessing the material several times [12,20] or by inducing an artificial aging that simulates the degradation to which the component is subjected during its life [21]. However, until now, few recycling attempts have been performed starting from glass fiber reinforced polymer components at the end of their life.

The aim of this work is to recycle end-of-life components through the mechanical method and to establish the possible applications of the materials obtained on the basis of the comparison between the mechanical, rheological and morphological properties of the recycled materials and the reference ones. In particular, end-of-life radiator parts, taken from waste usually landfilled, made of glass-fiber reinforced polyamide 66 have been used. The component was subjected to 3 steps of grinding and injection moulding and compared to a reference material made of PA66 reinforced with 35 wt. % glass fiber. This article shows how the mechanical recycling of end-of-life car components is one of the most recommended and simplest methods to obtain a material with mechanical properties useful for different applications.

2. Materials and Methods

Radiator parts coming from an end-of-life vehicle (more than 10 years of use) and made of PA66 reinforced with 35.7% of short glass fibers were used as starting composite materials. These were reduced in size by using a band saw GLOBE KB-45 and then pelletized with a granulator PIOVAN S25-30. Through the injection moulding process dog-bone tensile test bars and bending specimens (called R, as recycled) were obtained.

Finally, some of the specimens obtained from the first recycling step were re-pelletized and re-moulded (RM) two times, following the procedure sketched in Figure 1. The samples thus obtained, called RM1 and RM2, differ from the recycled product R as they have not undergone natural aging due to the 10-year use of the component.

Unfortunately, being no longer on the market, it was not possible to recover the same material used to produce the component more than 10 years ago. For this reason, commercially available RADILON A RV350W pellets, purchased by Radici Group and used at present to produce the same component, were chosen as reference material (Ref) to make a comparison with the recycled one. These composite granules consist of PA66 reinforced with 36.2% short glass fibers. Table 1 shows all the abbreviations used in this paper to indicate the composite materials at the different recycling steps

Table 1 Abbreviations used to indicate composite materials at the different recycling steps

Abbreviation	Material
EoL	End of life
R	Recycled
RM1	Remoulded one time
RM2	Remoulded two times
Ref	Reference

The injection moulding of both reference and reprocessed materials was carried out using a BABYPLAST 6/10P machine. The temperatures used along the screw profile were 290 °C for the

reference material and 285 °C for the reprocessed ones; a pressure of 100 bar in the injection filling phase, and of 80 bar in the injection pressure phase maintained for a total time cycle of 40.5 s were adopted.

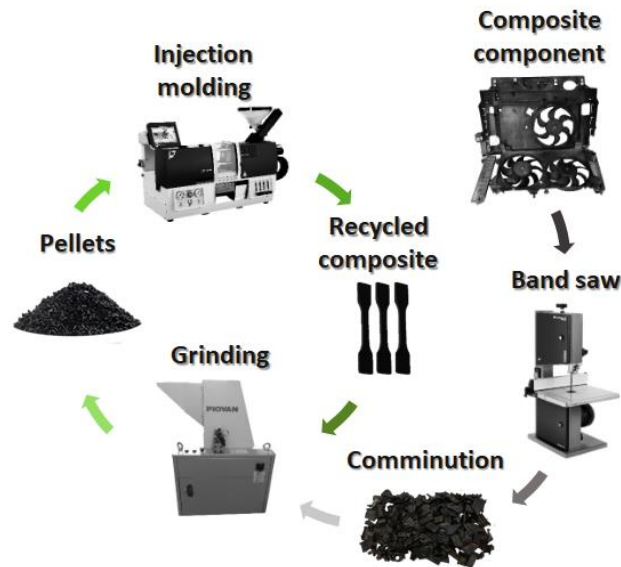


Figure 1 Schematic illustration of the mechanical recycling method

Tensile and three-point flexure tests were performed on the injection moulded samples using a MTS Criterion Model 43 machine. Before being subjected to mechanical tests, the samples were dried at a temperature of 80°C for 16h. For tensile tests, 5A type dog bone specimens were used according to ISO 527. Elastic modulus, tensile strength and percentage deformation at break were evaluated using a gauge length of 25 mm and a crosshead speed of 1 mm/min. The bending tests were performed according to ISO 178 using a crosshead speed of 2 mm/min.

Rheological tests were carried out on a strain-controlled Rheometer Ares (TA Instruments) with parallel plates of 25 mm. The measurements were performed in a nitrogen atmosphere at a temperature of 290°C and a deformation of 0.25%.

To determine the fiber length and their distributions, the composites were firstly burned at 700°C in order to decompose the matrix. The recovered fibers were observed with an optical microscope Leica DMI 5000 M (Leica Microsystems).

The microstructure of injection moulded samples was analysed by sectioning them along a plane perpendicular to the injection direction. Several images were recorded at different magnifications and then analysed by using a MATLAB program developed by our team able to determine the orientation of the fibers with respect to the specimen axis. Starting from optical microscope images, the software allows to recognize the fibers based on grayscale contrast. A degree of orientation is assigned to each fiber based on how much the fiber section deviates from being a perfect circle. A fiber exactly perpendicular to the examined surface should have a perfectly circular section to which an orientation degree equal to zero is assigned. While, a misalignment leads to a much more elongated elliptical cross-section as much as the fiber is misaligned.

The x-ray diffraction analyses were performed by using Panalytical X'PERT PRO PW3040/60 diffractometer, with Cu K α radiation at 40kV and 40mA, Panalytical BV, The Netherlands. The

used program involves the scan of composite materials in 2 theta range from 10° to 60° with a step size of 0.013°. HighScore software (Malven Panalytical) was used for the elaboration of XRD spectra and the identification of crystalline phases.

Calorimetric analyses were performed with the Perkin Elmer Pyris 1 DSC instrument under argon atmosphere and in a temperature range from 25°C to 300°C with a heating rate of 10° C/min. For each sample, two heating-cooling cycles were performed in the above-mentioned conditions, as the first cycle was used to eliminate the thermal history of the sample resulting from the forming and use processes.

The thermal behaviour of the material in oxidative atmosphere was evaluated with a thermogravimetric analysis using the Mettler Toledo TGA/SDTA851e instrument in the temperature range from 25°C to 800°C, a heating rate of 10°C/min, under synthetic air flow.

3. Results and discussion

The purpose of this work was to obtain a 100% recycled thermoplastic composite through the mechanical recycle of an end-of-life (EoL) car component, composed of PA66 reinforced with 35.7 wt. % of short glass fibers. The degradation due to natural aging and mechanical recycling has been evaluated by comparing the mechanical properties of the recycled material with that of a reference material. The mechanical properties have been correlated to the rheological behaviour of the material and the length and distribution of the fibers.

The thermoxidative behaviour of PA66GFs was evaluated by TGA analysis performed in air (Figure 2). There are no relevant differences between the curves in terms of degradation temperature and solid residue (Table 2) due to the recycling. The initial degradation temperature $T_{2\%}$ corresponds to the temperature at which there is a weight loss of 2%. The degradation always occurs in one step, according to the thermoxidative degradation mechanism of PA66 which leads to the cleavage of the chain due to the formation of radicals [22,23]. For the reprocessed materials, the residues at 800°C are around 33-35wt.% of the initial weight, slightly less than the 36.2% of the reference one and the 35.7% of the EoL component.

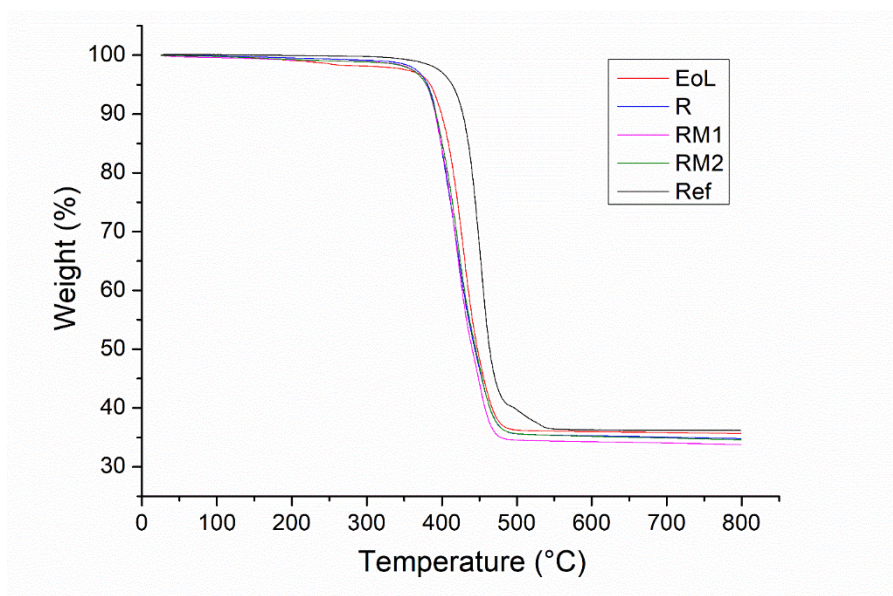


Figure 2 TGA analysis performed on air of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

Table 2 Thermal properties of PA66GF Composites

Sample	$T_{2\%}$	Residue (%)	T_m	X_c
EoL	322,1	35,7	251,8	36,6
R	358,8	34,8	251,5	40,7
RM1	353,2	33,8	252,0	40,0
RM2	351,3	34,6	251,7	34,0
Ref	389,2	36,2	252,8	33,9

Figure 3 shows the X-ray diffraction patterns of the reference, end-of-life, recycled and remoulded composites. All the spectra exhibit a broad hump in 2theta region from 15° to 30°, indicating that the samples contain a portion of highly disordered material, which corresponds to the amorphous component of semicrystalline PA66 matrix. The spectra of all the samples investigated are comparable; the two main diffraction peaks at 2theta of 20,45° and 23,26° are distinctive of the α -crystal form of PA66 [24–26]. A less intense peak at 2 theta of 25,28° is evident in the XRD spectra of the end-of-life and all reprocessed materials. This peak is characteristic of the quartz phase and for this reason is related to the glass fibers.

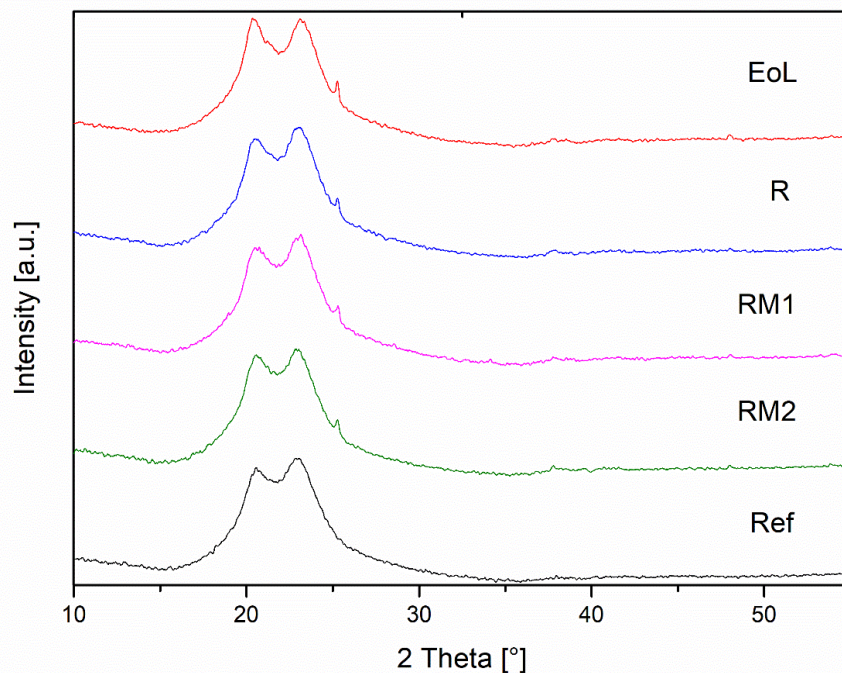


Figure 3 XRD spectra of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

Figure 4 shows the DSC thermograms related to both the first and the second heating/cooling cycle of the different products. The first heating/cooling run shows that all the samples present a single endothermic peak which can be associated to the melting of α -crystal form of PA66, according to XRD results. On the other hand, a different thermal history of the materials can

result in different DSC traces. In fact, all the DSC curves referring to a second heating/cooling run display a double endothermic peak in the same temperature range respect to that observed for the first run. The presence of a double melting peak in the polyamides can be attributed either to the polymorphism (α and β crystalline phases [27,28]) of this class of polymers or to the cooling rate which, during crystallization, can lead to the formation of small, imperfect and disoriented crystallites [29,30], which melt at a lower temperature [31]. The degree of crystallinity (X_C) was evaluated taking into account the melting enthalpy (ΔH_m), the weight fraction of the glass fibers (%GF) and the theoretical melting enthalpy of a 100% crystalline material ($\Delta H_{m100\%}$), according to the equation:

$$X_C = \frac{\Delta H_m}{\Delta H_{m100\%} \cdot (1 - \%GF)} \cdot 100$$

The value of 199 J/g used as $\Delta H_{m100\%}$ was obtained by averaging literature data [32–34]. The X_C values reported in Table 2 show that the natural aging, due to the use of the component, promotes matrix crystallization. However, this behaviour, due to the increasing number of reprocessing steps, can be balanced by the thermo-mechanical degradation of the matrix. In fact, the breaking of the polymer chains during recycling probably leads to a decrease in the molecular weight and formation of crystallites of smaller dimensions [21].

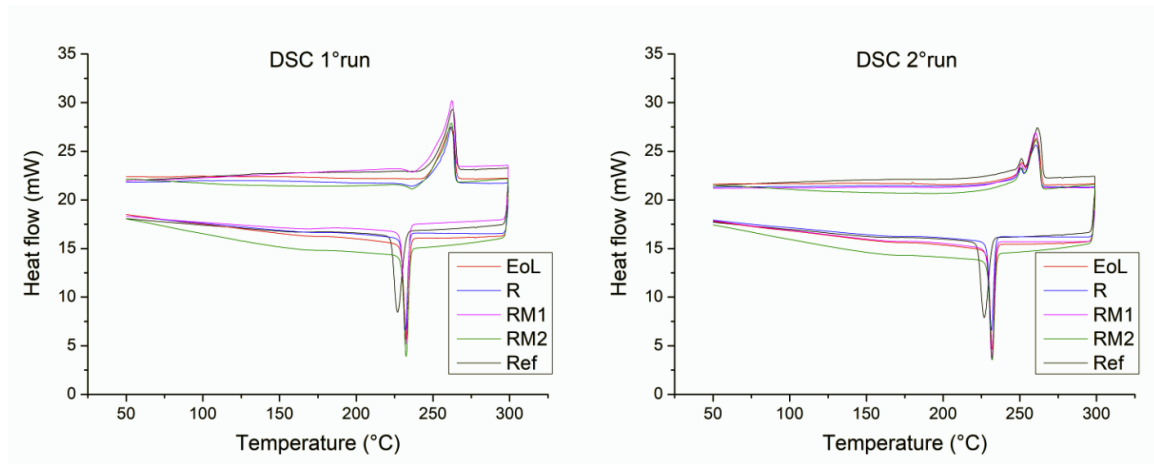


Figure 4 DSC curves related to first and second heating/cooling run of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

To analyse the fiber length and its variations after the reprocessing step, a composite scrap for each type of sample was burned in a furnace at 700° C. The fibers obtained after the matrix degradation were observed by optical microscope and analysed individually to evaluate their length. As can be seen from Figure 5 there is a decrease in fibers length from end-of-life fibers in (a) to R fibers in (b) up to RM1 fibers due to the mechanical degradation that occurs in the recycling process.

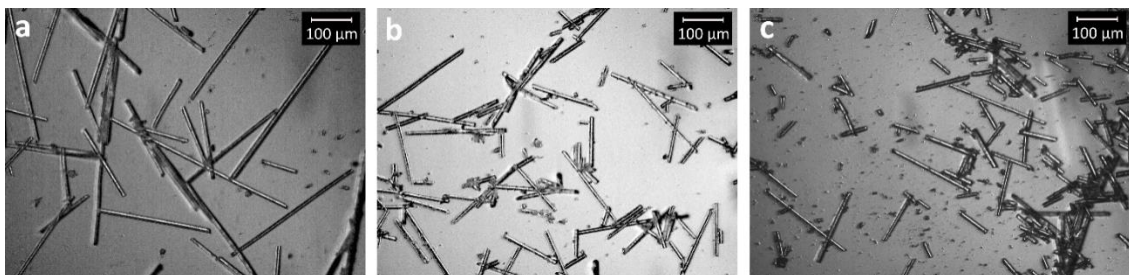


Figure 5 Glass fiber length evaluated by optical microscope at 100X for EoL fibers in (a), R fibers in (b) and RM1 fibers in (c)

The results of the fiber length analysis are reported in Table 3 in term of average values and in Figure 6, which shows the distribution of lengths for the different types of products.

Table 3 Average fiber length for end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref).

Sample	Average fiber length (μm)
EoL	253 ± 107
R	175 ± 87
RM1	152 ± 87
RM2	124 ± 65
Ref	344 ± 219

Table 3 clearly shows that the decrease in average fiber length grows with the number of reprocessing steps. The fiber length difference between the reference and the end-of-life material is mainly due to the use of fibers with different initial length and, only to a lesser extent, to the mechanical damage which occurred during the manufacture of the component.

In addition, with the progressive reduction of the fiber size, it becomes increasingly difficult to break shorter fibers, which leads to a homogenization of fiber length towards lower values and a narrow length distribution. The variation in fiber length distributions is clear in Figure 6, in which the distribution in the passage between R and RM1 materials moves considerably towards short fibers with length smaller than $100 \mu\text{m}$. For the reference and end-of-life distribution, there is a prevalence of fibers around $200\text{-}300 \mu\text{m}$ long, while the RM1 and RM2 materials show more than 60% of fibers with a length less than $100 \mu\text{m}$.

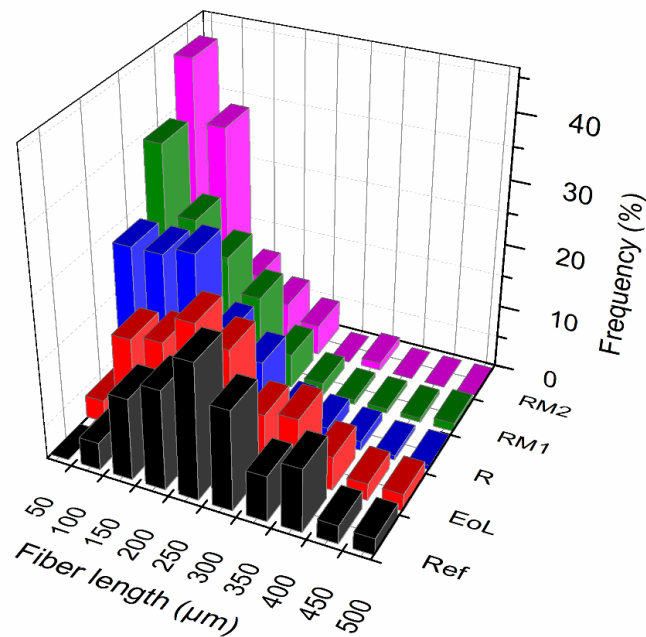


Figure 6 Fiber length distribution of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref). For each length range the frequency is normalized and expressed as a percentage.

These variations also affect the rheological measurements in Figure 7. The difference in the complex viscosity value of one order of magnitude between the reference and the end-of-life material is very likely caused by the degradation that the matrix has undergone over the years. The drop in viscosity continues in the three steps of reprocessing, but with different trends. The first recycling process of the EoL material results in a rather small viscosity decrease. On the contrary, there is a similar and more important fall (with respect to both the EoL component and material resulting from the first recycling R), for samples submitted to the remoulding process (RM1, RM2), which can be associated to the breakage of the fibers. In fact, it is well known that, in addition to the percentage reinforcing content, also the length of the fibers affects the rheological properties [35]. With the increase in the length of the reinforcement and therefore of its aspect ratio, the mobility of the polymer chains decreases due to the formation of a rheological percolation network which determines the increase in viscosity [36]. The length of the fiber for the EoL and R materials is sufficient to justify the formation of the percolation network. However, after the remoulding, the significant increase in the percentage of the fibers with length less than 50 μm suggests that the system is below the rheological percolation threshold [37]. Once the percolative network has been lost, the degradation of material due to the breakage of fibers becomes progressively less important with the repetition of recycling, as very short fibers are unlikely to can break again, and for this reason the viscosity of the material after the second and the third remoulding is not very different. Generally speaking, the progressive decrease of viscosity with the increasing number of regrinding and remoulding processes can be justified by considering both matrix degradation and the fiber length distribution. In fact, the presence of increasingly short fibers makes them less effective in resisting the motion of the matrix [38].

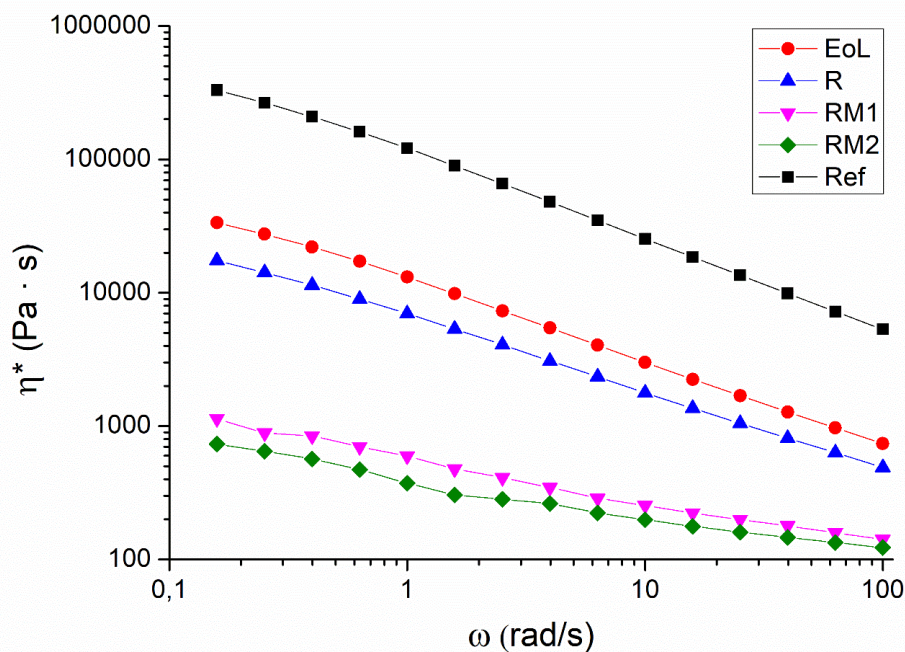


Figure 7 Complex viscosity measurements for end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

The orientation and the distribution of the glass fibers in the PA66 matrix was evaluated by using an optical microscope. The micrographs in Figure 8 show that almost all the fibers, about 11 μm in diameter, are aligned in the extrusion direction, as confirmed by the average orientation angle obtained from the MATLAB analysis (Table 4). Therefore, the fiber length variation, from about 350 μm to 125 μm (Table 3), does not influence the fiber orientation during the injection process.

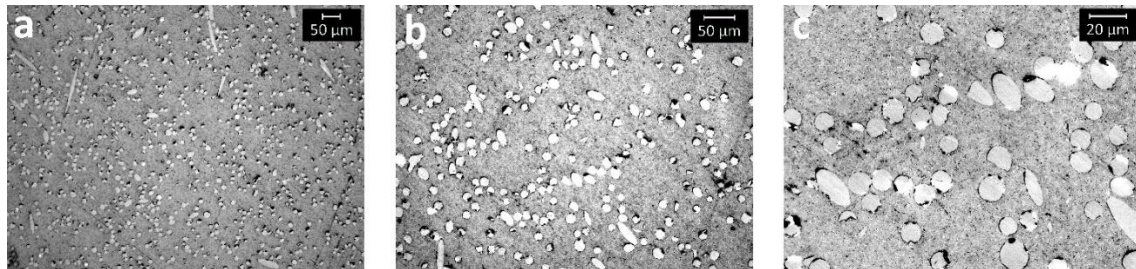


Figure 8 Optical micrographs of the section of a PA66GF composite at different magnifications: (a) 100X, (b) 200X, (c) 500X magnification

Table 4 Average orientation angle θ , with respect to the injection direction, of recycled (R) and remoulded samples (RM1, RM2)

Sample	θ
R	3,11°
RM1	3,74°
RM2	3,14°

The mechanical properties of the injection moulded specimens were evaluated with tensile and bending tests. As reported in Table 5, the results of the tensile tests showed that natural aging leads to a decrease of both elastic modulus and tensile strength. At the same time, a slight increase in the deformation percentage was detected. The results of the bending tests show the same trend as presented in Table 6. The greatest difference in term of mechanical behaviour was observed between the samples derived from the reference pellets and the samples R, which have undergone both natural aging during their lifecycle and reprocessing steps. In particular, a decrease of 23% to 29% can be seen in the elastic modulus and tensile strength, respectively. The worsening of mechanical properties is also related to the different average fiber lengths. In fact, according to the shear-lag model, the mechanical properties of a composite containing short fibers is related to the load transfer efficiency between the matrix and reinforcement. The end parts of the fibers are not able to completely withstand the tensile stress and, consequently, as the aspect ratio decreases, the efficiency of the fibers in the stiffening of the material worsens [39]. On the basis of literature data, it can be stated that the reference system consists of fibers with an aspect ratio higher than the critical one. On the other hand, all the materials deriving from the end-of-life component have average fiber length lower than the critical one, and therefore they are less effective in reinforcing the matrix [40]. A much smaller reduction in mechanical properties was found between the samples R, RM1 and RM2 which differ by the number of recycling processes (pelletizing and injection moulding) undergone by the material. In particular, there is a decrease in tensile strength of 16% from R to RM1 and 11% from RM1 to RM2. These results agree with the Bernasconi et al. paper concerning the mechanical

reprocessing of PA66 + 35% glass fibers [12]. In fact, in this work there was a 11% reduction in tensile strength between the starting material and the 100% reprocessed one. Despite the recycling processes leading to a deterioration of the mechanical properties compared to the reference material, these still remain far higher than those of the unreinforced matrix. The last row of Table 5 shows the tensile properties from the technical data sheet of RADILON A ESL128, a polyamide 6,6 (UR) marketed by the same company that produces the reference material [41]. It can be seen that, even after the last reprocessing step RM2, the tensile strength is almost double and the elastic modulus is more than triple that of the unreinforced material. Therefore, the recycled material can be used in the automotive sector for those components made with unreinforced PA66 or reinforced up to 15% in glass fibers, such as carbon canisters, connectors, fasteners, headlight bezels and turbo air ducts [42].

Table 5 Tensile test results of PA66GF Composites (R, RM1, RM2, Ref) compared to unreinforced (UR) PA66 mechanical properties

Sample	Elastic modulus [GPa]	Tensile Strength [MPa]	Deformation [%]
R	7,8 ± 0,3	120,0 ± 2,3	3,0 ± 0,3
RM1	7,4 ± 0,1	113,5 ± 0,2	3,4 ± 0,1
RM2	6,7 ± 0,2	100,8 ± 1,3	4,2 ± 0,3
Ref	10,2 ± 0,5	170,5 ± 5,2	2,6 ± 0,1
UR	2,05	55	7

Table 6 Bending test results of PA66GF Composites

Sample	Elastic modulus [GPa]	Bending Strength [MPa]	Deformation [%]
R	6,83 ± 0,13	187,7 ± 7,4	3,7 ± 0,3
RM1	6,42 ± 0,04	186,5 ± 1,4	4,7 ± 0,2
RM2	5,87 ± 0,06	171,3 ± 2,5	5,2 ± 0,4
Ref	9,03 ± 0,33	263,6 ± 8,9	3,7 ± 0,1

4. Conclusions

The feasibility of the mechanical recycling of an end-of-life automotive component has been assessed. The PA66GF radiator part, coming from waste currently landfilled, has been reprocessed three times, always obtaining materials with higher mechanical characteristics than the same unreinforced matrix. However, a progressive worsening of mechanical features with reprocessing was observed. The deterioration of mechanical properties can be mainly related to the reduction of the fiber length caused by milling and moulding steps involved in the recycling process. The progress in the fiber breakage process can be observed in particular during the first and second reprocessing, while it becomes less important during further recycling treatments as the breakage of fibers with reduced length is more difficult. However, the recycled material can be used in the automotive sector for those components made of unreinforced polyamide 66 or reinforced with low percentage in glass fibers. This would offer a contribution to comply with the strict regulations of EU about the reuse of 95% in weight of each vehicle. In addition, chances for improving the characteristics of recycled composites by tailoring the moulding process to the modified rheological behaviour of recycled material and through the possible compounding with virgin materials exist.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests of personal relationships that could have appeared to influence the work reported in this paper.

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