The effect of mechanical recycling on the microstructure and properties of PA66 composites reinforced with carbon fibers

Giovanna Colucci,[1] Oxana Ostrovskaya,[1] Alberto Frache,[1] Brunetto Martorana,[2] Claudio Badini[1]

[1]Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[2]CRF, Centro Ricerche FIAT, Strada Torino 50, 10043, Orbassano (Torino), Italy
Correspondence to: G. Colucci (E-mail: giovanna.colucci@polito.it)

ABSTRACT: This article aims to prepare by injection molding recycled polymeric composites based on PA66 reinforced with short carbon fibers after artificial aging for applications in the automotive field. The aging cycles involves the combined action of UV radiation, moisture, and temperature in order to simulate the common outdoor conditions. The 100% recycled composites are obtained by the regranulation of the aged specimens followed by the remelting and re-injection molding. The study is focused on the comparison between the mechanical behavior and the microstructure of the composites before and after mechanical recycling. The results of mechanical, thermal, and morphological investigations reveal that the recycling process had no significant effect on the final properties and microstructure of the recycled composites. Therefore the recycled PA66CF30 composites could be successfully used for structural or semi-structural automotive applications guaranteeing good final performances and advantages from the environmental point of view. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42275.

INTRODUCTION

The future of the thermoplastic reinforced composites market looks like being extremely promising in the automotive sector because of their high strength-to-weight ratios, good chemical and impact resistance, and great design flexibility and processability.[1] Furthermore, their intrinsic recyclability and the ability to be reprocessed rapidly are recognized as driving forces for their industrial applications.[2,3]

In particular, fiber reinforced polymeric composites are engineered materials commonly used for structural or semi-structural applications for the production of automotive components, such as dashboard, rocker covers, radiator end tanks, air intake, and manifolds.[4] Although the majority of fiber reinforced thermoplastic composites contains glass fibers,[5–8] in the last years the attractive properties of carbon fibers have made them a good alternative choice. A key aspect for developing carbon fibers reinforced polymeric composites for automotive is their high stiffness and very low weight.[9–11]

In fact, carbon fibers are currently used in composites with a lightweight matrix, generally polypropylene[12–14] and polyamide,[15,16] with the purpose to improve significantly the final properties and reduce the energy consumption and the CO_2 emissions of vehicles. The polymer properties, the fiber length and content, the interfacial strength and the interaction between fibers and matrix play a crucial role on the final performances of the thermoplastic reinforced composites. Another important aspect that can explain why these materials are attracting so great interest is their capability to be recycled and reused. Looking at the literature, it is possible to find works regarding the reclaim of continuous fibers from thermoplastic and thermoset polymeric composites[17,18] and from ground tire rubber.[19] The effect of mechanical recycling on the final properties of recycled polymeric composites was investigated only with reference to glass fibre reinforced PA66 composites.[20–22]

The main purpose of the present work is the preparation of 100% recycled polymeric composites based on polyamide matrix reinforced with chopped carbon fibers that could be used as new starting materials for design and development same or similar structural or semi-structural components of vehicles.[14]

This choice was made on the basis of the poor previous studies on this topic present in literature. Specifically, this article is focused on the comparison between the microstructure and the mechanical behavior of composites, obtained by injection molding using polyamide 66 as polymeric matrix reinforced with 30 wt % of short carbon fibers, before and after mechanical recycling. In fact, as well-known in literature, the mechanical
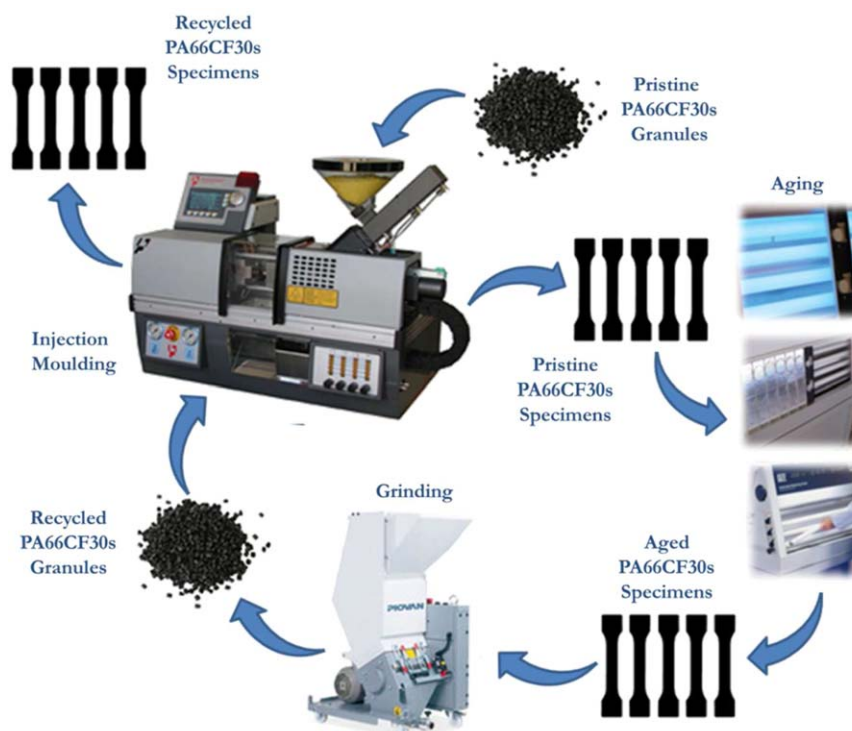
Figure 1. Schematic illustration of the mechanical recycling process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recycling of thermoplastic polymers is favorable with respect to other recycling processes in terms of overall energy consumption and emissions leading to the development of fully recycled materials in a very simple way. The process involves the regranulation and the remelting of the pristine materials, followed by re-injection molding.[22,23]

The mechanical, thermal, and morphological properties of the composites and the effect of the carbon fiber length on the final performance of the composites were studied. The effect of environmental aging on the properties of the PA66CF30 composites was also investigated in order to evaluate the changes occurred simulating the exposure to sunlight, rain, and moisture. This article shows a successful approach to easily obtain recycled composites with final properties comparable with those of the virgin composites maintaining the environmental and economic advantages of a recycled material.

EXPERIMENTAL

Materials and Methods

Commercially available TORAYCA® granules, obtained by compounding extrusion (PA66CF30), purchased by Toray Industries, were used as starting composite material, where polyamide 66 was reinforced with 30 wt % of short carbon fibers with an average size of 0.3 mm. The granules were melted and injection molded into dog-bone tensile test bars. Accelerating weathering test was carried out on the samples using fluorescent UV radiation simulating the damaging effects of terrestrial sunshine and reproducing outdoor moisture, by means of a QUV Accelerated Weathering Tester according to UNI EN ISO 4892-3 standard for plastics. Ten cycles of 8 h each were carried out alternating

periods of UV exposure followed by periods of no radiation, during which temperature changes occur and condensation takes place in order to reproduce accelerates moisture attack.

Tensile test and microstructure investigation were carried out on pristine and aged specimens. Finally samples of reprocessed materials were obtained by mechanical recycling of the aged composites, following the procedure sketched in Figure 1.

The recycling process involved the regranulation of the aged specimens by means of a RSP 15 open-type rotor grinder made by Piovan, followed by the remelting and re-injection molding. The tensile specimen preparation of pristine, aged, and recycled materials was carried out by using a Babyplast injection molding machine with a melt temperature of 280°C, injection time of 3 s at 90 bar and 7 s at 80 bar and a total time cycle of 20 s.

These processing parameters were selected according to the suggestions of the material supplier. The composites obtained were characterized by mechanical, morphological, and thermal point of view.

Characterization Techniques

Tensile tests were carried out at room temperature on ten dog-bone specimens for each kind of material (pristine, aged and recycled) by using an Instron Series IX testing machine. The experimental procedure and the sample dimensions were defined according to ISO 527 standard (specimens type 5A, 25 mm gauge length). All the specimens were preconditioned in an oven at 80°C for 2 h until their weight had stabilized and no further weight loss was observed. Young's modulus, yield strength, and elongation at break measurements were

Table I. Mechanical and Rheological Properties of PA66CF30 Composites

Sample	Elastic modulus[a] (GPa)	Tensile strength[a] (MPa)	Deformation[a] (%)	η^* (Pa s)
Pristine	23.5 ± 0.6	236.4 ± 3.8	1.7 ± 0.1	4263.1
Aged	20.2 ± 0.2	198.5 ± 4.6	2.0 ± 0.1	1231.9
Recycled	20.5 ± 0.7	188.2 ± 1.3	1.7 ± 0.1	3757.4

[a] The errors are given as standard deviations.

determined by using an extensometer with a gauge length of 50 mm at a crosshead speed of 10 mm/min.

Rheological measurements were carried out on a strain-controlled Rheometer Ares of TA Instruments, Waters LLC. The samples characterization was performed at 275°C with initial strain of 0.01% at a frequency of 6.28 rad/s. The specimens were previously preconditioned in a vacuum oven at 80°C for 12 h in order to remove the moisture eventually present.

To determine the fiber length, carbon fibers were taken out from the composite matrix according to a method previously described.[14,15] A burning treatment was performed in a muffle furnace in inert atmosphere at 700°C in order to burn out the polymer matrix. Single fibers were extracted from the ash obtained, dispersed in water, and dried. The carbon fibers were then placed on a glass microscope. Photographs showing the fibers distribution and length were finally collected by using an optical microscope Leica DMI 5000 M. The carbon fibers aspect ratio was measured analyzing optical micrographs with an image analysis software, Image Pro Plus®.

The microstructure of the polymer composites was investigated by scanning electron microscopy (SEM) after metallization with chromium; both cross section and fracture surface of the tensile samples were examined. A SEM-FEG Assing SUPRA 25 coupled with energy dispersive spectroscopy (EDS Oxford INCA X-Sight analyzer) was used.

Morphological analyses were also performed on the sample sections taken near the fracture surfaces using the optical microscope Leica DMI 5000 M.

The fiber/polymer interfaces were investigated by using a MERLIN Field Emission Scanning Electron Microscope (FE-SEM) from Carl Zeiss.

X-ray diffraction (XRD) measurements were performed on the injection molded specimens, using a Siemens D5000 diffractometer (Cu Kα radiation; 2ϑ range: 5–50°; Δ2ϑ step: 0.02°; step time: 2 s).

Differential scanning calorimetry analyses (DSC) were performed with a Netzsch DSC 204 F1 Phoenix System in the temperature range from −30°C to +300°C with a heating rate of 10°C/min under nitrogen flow (50 mL/min). For each experiment the sample was heated from −30°C to 300°C, then cooled from 300°C to −30°C for two times. The first heating/cooling cycle was recorded in order to eliminate the thermal history of the samples. The thermal transitions of the materials studied were measured on the second heating/cooling cycle.

Thermal gravimetrical analysis (TGA) was performed in argon with a Mettler-Toledo TGA/SDTA 851e instrument in the temperature range between 25°C and 700°C with a heating rate of 10°C/min in order to evaluate the thermal behavior of the composites. All curves were normalized to the unit weight of the sample.

RESULTS AND DISCUSSION

The purpose of the present work was to evaluate the effect of mechanical recycling on the final properties of thermoplastic composites based on PA66 as polymeric matrix reinforced with 30 wt % of short carbon fibers that could be used in structural or semi-structural applications for automotive components.

As well known, the fiber reinforced thermoplastic composites for outdoor applications, like automotive, encounter ambient moisture, and ultraviolet radiation in addition to the mechanical stresses and temperature which can affect significantly their final properties.[23–26]

So that, the PA66CF30 composites under investigation were aged before and recycled later by mechanical recycling. The effect of the artificial ageing as well as that of the recycling process was studied by comparing the characteristics and final properties of the specimens.

Mechanical Properties

The results of the tensile tests for PA66CF30 composites clearly showed that the aging treatment leads to a decrease of both elastic modulus and tensile strength with respect to the values for the pristine composites, as reported in Table I. A slight increase of the deformation percentage was also observed. This change can be explained considering the detrimental action of moisture and UV light. Actually, the UV irradiation causes photo-oxidative and thermo-oxidative reactions that can degrade the polymeric matrix. In particular, polyamides are susceptible to this degradation phenomenon that affect significantly the final properties in terms of discoloration and above all in terms of mechanical properties.[23–26]

Rheological measurements were carried out on the composites before and after the aging in order to have indication about the effect of the aging treatment on the molecular weight of the composites. The results, reported in Table I, showed that the complex viscosity slightly decreases, from 4263.1 for the pristine composites to 1231.9 Pa s for the aged ones, very likely because of the polymeric chain scission that occurs in the composites matrix because of the combined action of UV irradiation and moisture. This result confirms that the aging treatment has
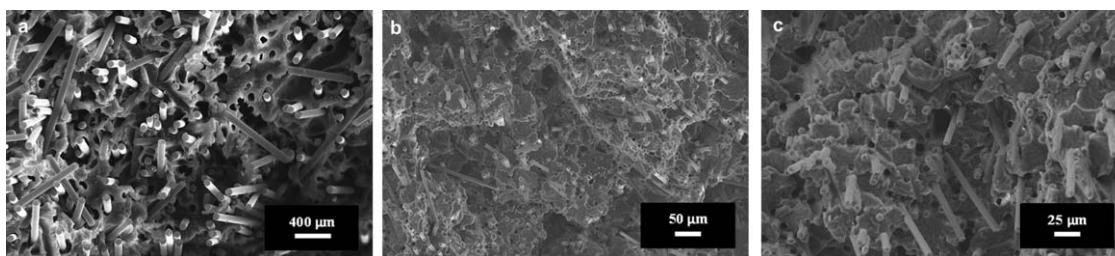
Figure 2. SEM micrographs at 1000× of the fracture surfaces of (a) pristine, (b) aged, and (c) recycled PA66CF30 composites.

remarkable effects on the mechanical properties of the composites, as previously discussed.

A different situation is observed comparing the viscosity of the pristine composites with that of the recycled composites. The value of the viscosity of the composites after the mechanical recycling is 3757.4 Pa s, lower than the value of the pristine one, but higher with respect to the complex viscosity of the aged composites (see Table I). The increase in the complex viscosity after recycling can be explained considering that polyamides have a high sensitivity with respect to heat treatments.[30]

The second injection molding process carried out to recycle the aged composites causes an increase of the weight average molecular weight (Mw), whereas the numeral average molecular weight (Mn) does not reveal any significant change. The increase in weight average molecular weight can be the result of solid-state polymerization.[30] This aspect can also explain why the mechanical behavior does not change significantly after the recycling process, as revealed by the tensile properties.

We also observed a further reduction of the tensile properties after the recycling process of about 20%. The elastic modulus and the ultimate strength of the pristine composites decrease after recycling, more than 3 GPa for modulus and almost 50 MPa for strength values, as summarized in Table I.

As the worsening of mechanical behavior mainly occurred during artificial ageing, it is clear that the recycling process does not have a significant effect on the final mechanical properties of the recycled composites. In spite of the degradation caused by aging and mechanical recycling, the composites still showed good properties, suitable for automotive applications.

Morphological Analyses

Morphological investigations of the fracture surface were also carried out by SEM analyses.

Figure 2 shows SEM micrographs at 1000× of the fracture surfaces for pristine, aged, and recycled composites in the middle of the specimens. The fracture surfaces were perpendicular to the injection flow direction. The composites showed almost the same feature of the fracture surface independently from the process undergone, indicating that the aging treatment and above all the mechanical recycling do not have remarkable effects on the failure mode. The pictures of Figure 2 evidence that the carbon fibers are aligned preferentially along the injection flow direction and that the dispersion of the fibers within

the polymeric matrix is not completely homogeneous on the fracture surface. Actually bundles of fibers together with defects, like voids, can be appreciated. The lack of homogeneity and the presence of defects are probably responsible for the failure at that sample section.

The pull out and the presence of fibers, completely extracted and lying on the fracture surface, are well evident at so high magnification, as Figure 2(a–c) reports. Moreover, the length of the fibers affects the morphology of the fracture since, as reported in literature, the pull out effect is much more evident in the presence of shorter carbon fibers.[13,27–29]

This last feature can explain the decrease on the elastic modulus and tensile strength values of the composites after the mechanical recycling process.
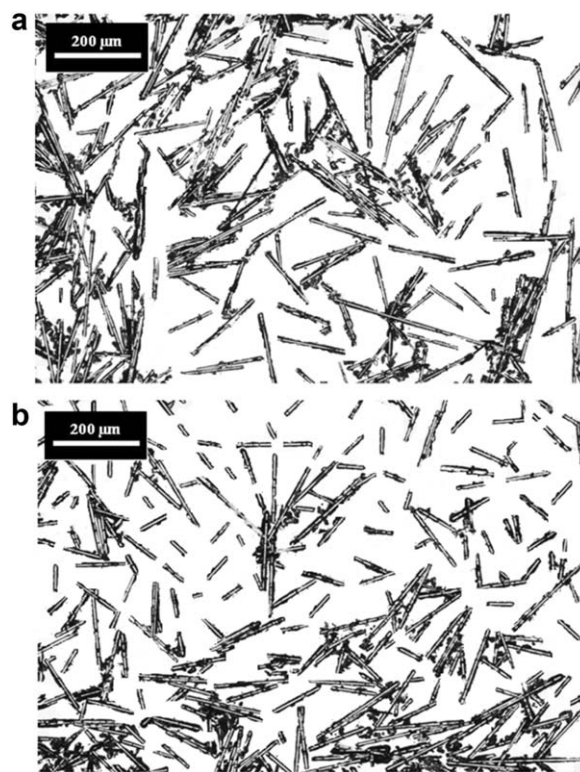

Figure 3. Carbon fibers length evaluated by optical microscope before and after recycling of PA66CF30 composites.
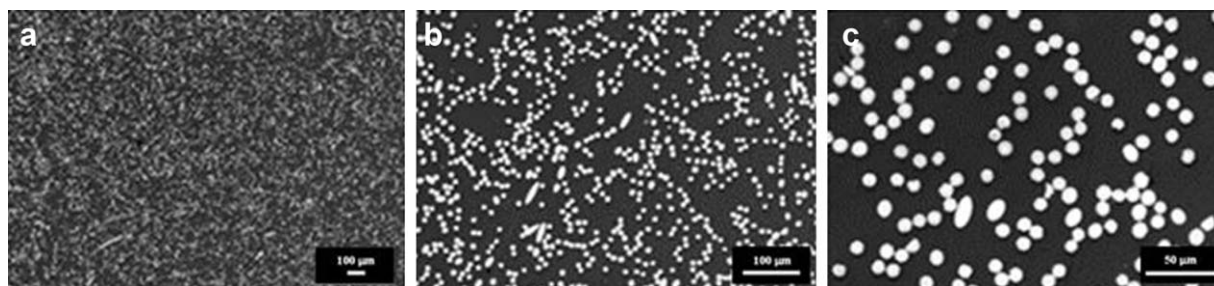
Figure 4. Optical micrographs of the section near the fracture surfaces of a typical PA66CF30 composite at different magnifications: (a) 50×, (b) 200×, and (c) 500×.

The carbon fibers lengths of the PA66CF30 composites were determined by burning a scrap polymer composite in a muffle furnace at 700°C in the presence of argon. In these conditions, the polymer matrix breaks down into lower molecular weight substances leaving a carbon char product and the fibers in a fluffy form. The carbon fibers obtained were then washed with water and dried but, in spite of this treatment, they still show traces of the carbon residue on the surface, as evident in Figure 3.

The fiber length was then optically observed analyzing the single fibers on a glass microscope. The optical image, reported in Figure 3(a), shows the presence of carbon fibers with an average length of 0.3 mm for virgin PA66CF30 composites.

On the contrary, the micrograph of Figure 3(b) reveals for the recycled PA66CF30 composites the presence of many shorter fibers with an average length lower than 0.3 mm.

The carbon fibers aspect ratio, before and after mechanical recycling, was also measured working on the optical micrographs of Figure 3 using an image analysis software (Image Pro Plus®). The counts showed values of 24.8% and 18.3% for the fibers coming from virgin and recycled composites respectively. The reason why these values are different with respect to the theoretical ones is probably because of the presence of fibers with lower length, the presence of over lopped fibers, and also to traces of carbon residues obtained after the polymeric matrix degradation in inert atmosphere, as previously discussed.

The orientation and distribution of the carbon fibers within the PA66 polymeric matrix were also optically studied evaluating the section of the tensile specimens taken few millimeters far

from the fracture surface. The optical images of Figure 4 show that in any case carbon fibers are generally aligned along the injection flow direction but their distribution within the matrix is often inhomogeneous.

Optical micrographs are reported in Figure 5 for a typical PA66CF30 composite. Defects like holes, aggregates, and vortexes are visible for virgin, UV aged, and recycled composites, probably because of the plastic flow of the materials during the injection molding process. Morphological investigations were also carried out by FE-SEM analyses in order to study the fiber–matrix interfaces in PA66CF30 composites.

The image of Figure 6(a) evidences the presence of a high number of carbon fibers with a good adhesion with the polymeric matrix. Furthermore, areas where the adhesion between the matrix and the fibers is rather poor are evident. In fact higher magnifications (200 KX) reveal the presence of phenomena of partial debonding between the polymer and the reinforcement, perhaps because of the scratches during the polishing step, as shown in Figure 6(b).

Nevertheless also at these damaged interfaces the interfacial bond is not completely lost since residual polymeric ligaments still connect the matrix to the carbon fibers. The SEM micrographs also evidence the presence of microholes and voids on the matrix surface.

Crystallization and Thermal Behavior

XRD analysis was used to investigate the possible changes in the crystalline structure after the aging treatment and the mechanical recycling. The XRD spectra of the PA66CF30 composites are reported in Figure 7. As previously observed by many
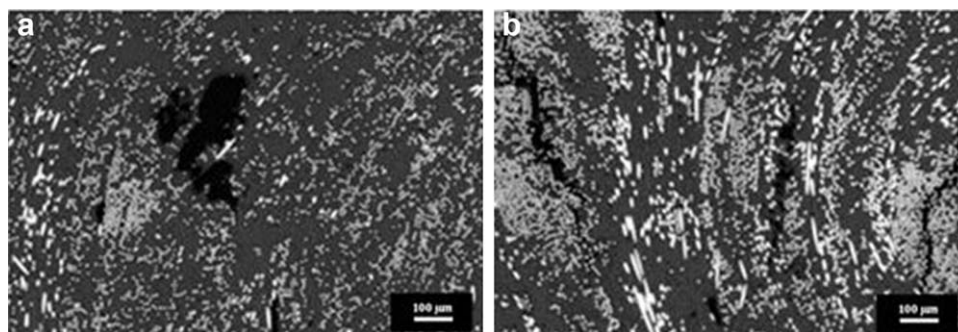

Figure 5. Example of defects on the tensile fracture surface of a typical PA66CF30 composite optically revealed like (a) voids, (b) vortexes and aggregates.
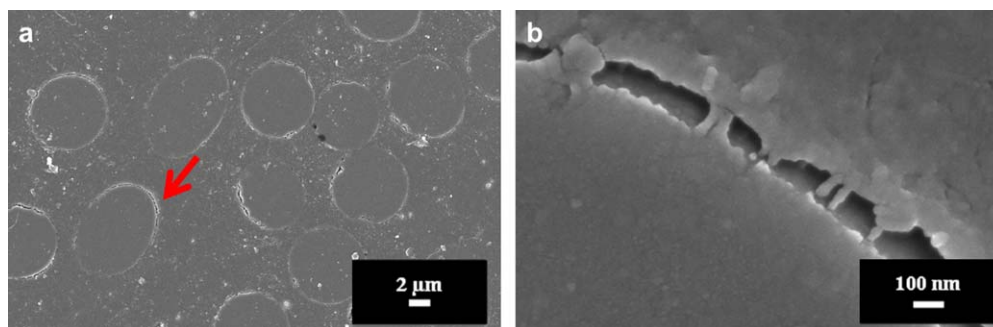
Figure 6. FE-SEM micrographs of the polyamide 66 and carbon fibers interface for a typical PA66CF30 composite at different magnification: (a) 8 KX and (b) 200 KX. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

researcher, PA66 composites exhibit two main peaks related to α crystalline form, located at around $2\vartheta = 20°$ and $24°$, because of the distance between sheets of hydrogen bonding chains with sheets stacked upon another along the chain direction, and to the separation of the hydrogen bond sheets, respectively.[31–33] The Υ crystalline form, less stable than the α form, does not appear in the XRD spectra. Comparing the diffraction patterns of the different PA66CF30 composites, it can find that the crystal structure does not change significantly neither after the aging treatment nor after the mechanical recycling. The comparison of both peaks position and intensity suggests that the pristine composites show higher crystalline degree than the aged and recycled ones.

Finally, the thermal properties of the composites were investigated by means of DSC and TGA analyses in order to evaluate the effect of the recycling process. The Figure 8(a) reports the DSC thermograms of PA66CF30 composites relative to the second heating/cooling cycle, which gives information about the thermal behavior of the composites.

The DSC curves reveal almost the same behavior for all the specimens studied, independently from the aging treatment or the mechanical recycling process. The cooling scans for PA66CF30 have one exothermic peak with a maximum at around 231°C [see Figure 8(a)]. Looking at the second heating
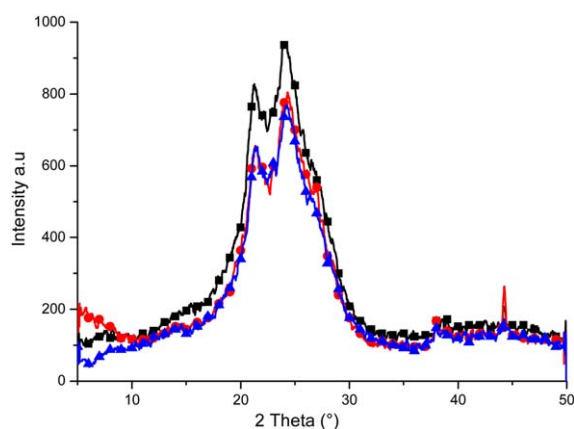
run [see Figure 8(b)], it is possible to observe that the polyamide 66 has a bimodal melting peak where the shoulder at lower temperature can be attributed to the thermally less stable Υ crystalline form, whose melting point is around 255°C, no longer visible in the case of recycled composites. Instead, the main melting peak of the α crystalline form has a maximum at around 266°C for pristine, aged, and recycled composites. The formation of the Υ phase seems related to the thermal history of the material, as this phase was not detected by DSC during
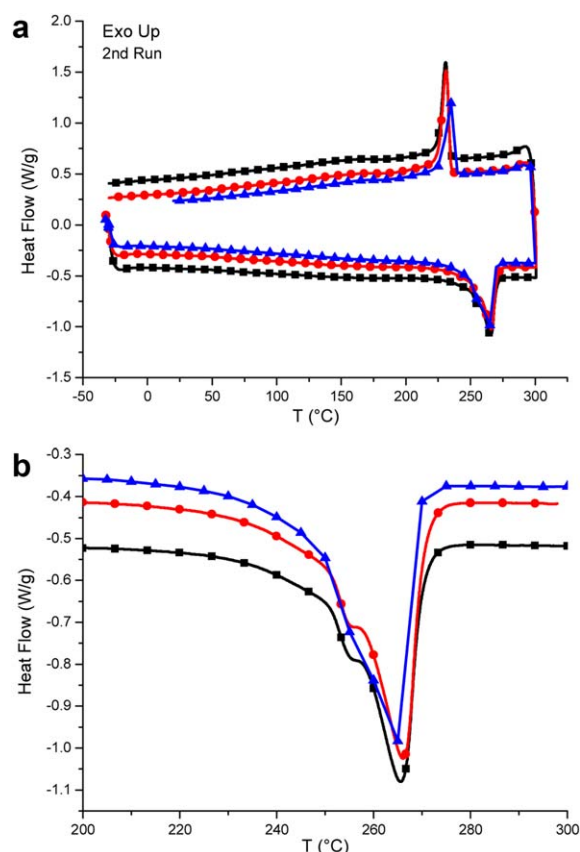

Figure 8. DSC curves corresponding to (a) the second heating/cooling run and (b) the enlargement of the melting peak of pristine (black curve ■), aged (red curve •), and recycled (blue curve ▲) PA66CF30 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. XRD spectra of pristine (black curve ■), aged (red curve •), and recycled (blue curve ▲) PA66CF30 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermal Properties of PA66CF30 Composites

Sample	T_g^a (°C)	T_m^a (°C)	T_c^a (°C)	ΔH_c^a (J/g)	X_c^b (%)	Residue (%)	T_5^c (°C)	T_{50}^d (°C)
Pristine	45	266	231	36.1	26.2	30	378	441
Aged	45	266	231	41.5	30.1	30	385	437
Recycled	45	265	234	33.9	24.6	29	381	435

[a] Determined by the second heating/cooling DSC run.
[b] Degree of crystallinity calculated considering $\Delta H_m^0 = 197$ J/g for 100% crystalline PA66.
[c] Temperature at which 5 wt % loss is achieved.
[d] Temperature at which 50 wt % loss is achieved.

the first heating/cooling run and by XRD carried out on injection molded specimens.

From the DSC curves it was also possible to investigate the crystallization occurring during cooling. The crystallization percentage values for the composites studied can be measured by using a wellknown equation from the literature.[34]

The degree of crystallinity (X_c) of PA66CF30 composites was determined from the heats evolved during the cold crystallization (ΔH_c), taking as a reference the enthalpy of theoretically 100% crystalline PA66 ($\Delta H_m^0 = 197$ J/g) and taking into account the weight fraction of the carbon fibers present in the composite. The ΔH_m^0 value reported in this study for 100%

Figure 9. (a) TGA and (b) DTG curves performed in argon of pristine (black curve ■), aged (red curve •), and recycled (blue curve ▲) PA66CF30 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystalline PA66 is an intermediate value among the several values proposed for polyamide 66 matrix having polymorphic forms.[35,36]

The Tg, Tm, Tc, and ΔH_c values and the degree of crystallinity of the specimens, obtained from the analysis of the DSC thermograms after the second heating/cooling run, are listed in Table II. The results clearly indicate that the aging treatment leads to a little increase of the polymeric matrix tendency to crystallize. In particular, it is evident an increase from 26.2% to 30.1% moving from pristine to aged composites. On the contrary, the crystallinity decreases to 24.6% after the recycling (see Table II).

This could be probably because of the recrystallization of crystals of lower sizes formed during the second injection molding, as a consequence of the polymer chain scission occurring during the recycling process, which leads to the formation of shorter polymer chains with lower molecular weight.[36,37]

The thermal stability of the PA66CF30 composites was also studied by TGA analysis.

The TGA and DTG curves, performed in argon, do not show a significant difference in the degradation temperatures for the pristine, aged, and recycled composites as reported in Figure 9(a,b).

The thermal degradation consists of only one step and the maximum degradation rate temperature is at around 378°C and 385°C for the PA66CF30 composites.

The initial degradation temperatures, useful for assessing the thermal stability, were measured evaluating the temperatures at which 5% of weight loss occurs together with the degradation temperatures at which the 50% of weight loss is achieved. T_5 and T_{50} values are summarized in Table II. TGA measurements were also performed to determine the real amount of carbon fibers dispersed within the polymeric composites.

After the degradation of the polymeric matrix, it was possible to detect at 700°C residue values near 30% for all the composites studied. The amount percentage of carbon fibers experimentally determined is in good agreement with the theoretical content for the pristine composites reported in the supplier datasheets (see Table II).

In conclusion, the thermal analyses results indicate that there is not a significant modification in the characteristics of the composite matrix passing from the pristine to recycled composites.
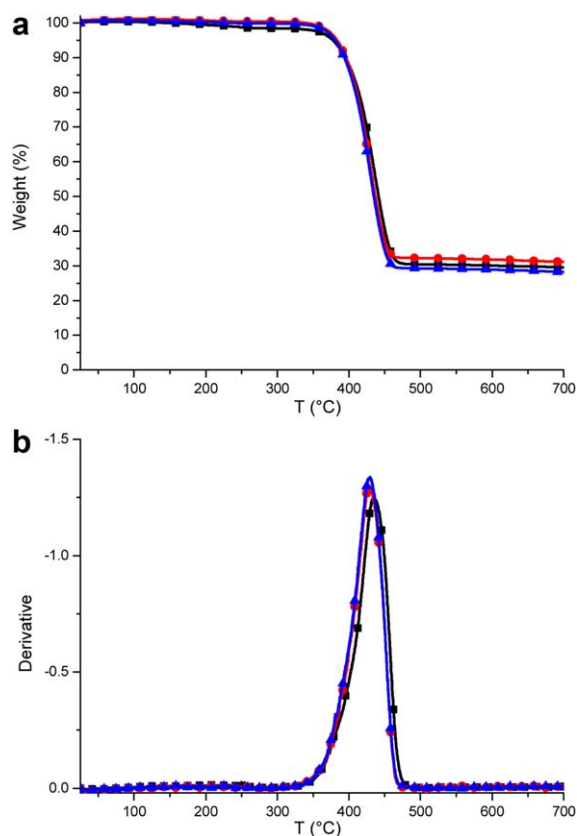
As known polyamides feel significantly the effect of UV irradiation and moisture in terms of discoloration, because of formation of chromophoric chemical species; in terms of plasticization because of the presence of water molecules between the polymeric chains which lead to a stiffness reduction; and again in terms of the formation of microcracks on the sample surface, which can cause surface roughness leading to polymeric chain scissions.[23–26]

Despite this, the results obtained reveal that no significant changes occur for PA66 reinforced with carbon fibers composites after recycling, indicating that the presence of carbon fibers, transparent to the radiation for their intrinsic nature, acts as a "protecting" agents for the polyamide matrix preserving the microstructure and the final properties of the composites.[38]

CONCLUSIONS

The effect of mechanical recycling of artificially aged PA66CF30 composites on the final mechanical properties and microstructure was investigated in the present work. Young's modulus and tensile strength did not change in a significant way after the recycling process. In spite of some reduction of average fiber length occurring during the grinding step, the recycling process caused only negligible decrease of tensile strength, being the mechanical behavior of the recycled composite almost the same of the aged one. The failure mode of all the composite specimens (pristine, aged and recycled) was very similar. Fracture occurred at sample sections where fiber agglomeration could be observed; fiber pull out was always observed on the fracture surface. In addition, a certain weakness of the interfacial bonds between fiber and matrix was put in evidence by SEM analysis on the sample cross-section, which is beneficial for toughness. Rather good alignment of fibers in the molding direction was observed for pristine, aged, and recycled composites. This feature seems mainly responsible for the mechanical behavior of the composites. The recycling process only slightly affected the mechanical strength of the composites that, instead suffered more degradation during aging.

The mechanical behavior of recycled composites should be further improved by optimizing the injection molding process. Nevertheless the final properties found in this work for recycled composites are not significantly different with respect to the pristine ones currently used for vehicles. Thus, they are suitable for semi-structural applications in the automotive industry.

ACKNOWLEDGMENTS

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