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RECYCLING AND REUSING POLYAMIDE 6 EXTRUDED WASTE PRODUCTS TO MANUFACTURE CARBON FIBER BASED COMPOSITES

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Abstract: *The work presents a study regarding the recycling of polyamide 6 products processed by extrusion/injection molding to be used as matrix in laminated composites reinforced with carbon fiber fabric (as-received and surface oxidized in laboratory). The results highlight the similarity between the recycled PA6 based carbon fiber composites and the reference samples based on pure PA6 and the two carbon fiber variants, in terms of mechanical performance at tensile and flexural loads, physical-chemical and morphological characteristics as well as fracture behavior. This confirms that PA6 waste products can be harnessed into products with high performance for different applications.*

Keywords: thermoplastic polymer, plastic materials recycling, carbon fiber composites, waste recovery.

1. Introduction

In the past decades, polymer based materials have found applications in more and more domains, from consumer goods and sport to construction, automotive and aeronautics industries. As expected, most products based on polymers do not have an endless lifetime of use and inevitably at some point they become plastic wastes. Considering the environmental issues of our millennium generated by waste, as most polymeric materials are not biodegradable or their degradation is very slow and can persist for hundreds of years [1], researches focus on limiting the generation of plastic waste, with the aim to minimize the use of resources and maximize recovery [2]. This signifies recovering both mechanical and feedstock

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(chemical) as well as energy [2]. The terminology for plastics recycling includes four categories: primary (mechanical reprocessing into a product with equivalent properties), secondary (mechanical reprocessing into products requiring lower properties), tertiary (recovery of chemical constituents) and quaternary (recovery of energy). Chemical or feedstock recycling has the advantage of recovering the petrochemical constituents of the polymer, which can then be used to re-manufacture plastic or to make other synthetic chemicals [3].

In case of polymeric based materials recycling and recovery, the polymer nature plays a very important role. The two basic types of polymers, as a function of the way they respond to heat are: thermoplastic polymers - that by definition can be heated and formed then heated and formed again and again, the shape of the polymer molecules being generally linear or slightly branched, therefore they can flow under pressure when heated above their melting point and thermoset polymers – that undergo a chemical change when they are heated, creating a three-dimensional network, therefore after this process the molecules cannot be re-heated and re-formed, and when heated this type of polymers simply burn. Obviously, this characteristic makes thermoset materials poor candidates for recycling while thermoplastic polymer based materials are much easier to adapt to recycling [4], as a major useful attribute of thermoplastics is that they can be heated to their melting point, cooled, and reheated again without significant degradation [5].

Among thermoplastic polymers, polyamide (PA), also known as Nylon, is one of the most used in creating products from all kind of domains. Polyamide is a semi-crystalline thermoplastic polymer with low density, excellent wear resistance, good coefficient of friction, very good chemical resistance (especially in contact with oils), very good strength and hardness and very good temperature and impact properties. This excellent balance of properties makes the PA polymer an ideal material for metal replacement in applications, such as automotive parts, industrial valves, railway tie insulators and other industry uses, whose design requirements include high strength, toughness and weight reduction [6]. Depending on its structure, polyamide comes as two types: PA6 and PA66, that by modification of chemical structures (length of chains and chemical organization), several others families of polyamide can be obtained (PA11; PA12; PA4,6; PA6,10; PA6,12; PA10,10) [7], which are used for specialized applications [8]. The thermoplastic nature of polyamides allows them to melt (at approximately 220-250°C), making them suitable to be thermoformed into different shape products by specific techniques (extrusion, injection molding) but also, recycled by the same methods. It is important to mention that there is a distinct difference between nylon shapes produced by extrusion and those produced by casting [6]. Extrusion method typically provides for smaller, higher volume machined parts, while casting method typically allows for low volume, larger parts containing lower levels of internal stress [6]. However, the nylons obtained by both of these techniques can be modified through the use of fillers to enhance certain properties. The adjustable properties offered by this fact along with the wide variety of polyamide families this polymer adaptable to various applications and uses across a range of industries: consumer goods (e.g. toys, weather proof coatings, carpets etc) furniture accessories (e.g. in points of impact), gears, bushings, plastic bearings etc.[9].

Recently, a life-cycle assessment led by a consortium composed of a Nylon producer, a car manufacturer and car component supplier has underlined that the use of recycled polyamide in automotive applications carries a significant environmental benefit [10], according to the study "using recycled polyamide averts the generation of greenhouse gases equivalent to that produced by 400 000 cars or photochemical oxidation (responsible for ozone peaks) comparable to that made by 2 200 000 vehicles all travelling around Paris's ring-road" [11]. This data is extremely important as 20 % of a vehicle is made of plastic products parts [11], the thirteen top polymers used in automotive hardware being: polypropylene, polyurethane, poly-vinyl-chloride (PVC), ABS, polyamide (PA6 and PA6,6), polystyrene, polyethylene, polyoxymethylene, polycarbonate, polymethylmethacrylate (PMMA), polybutylene terephthalate (PBT), polyethylene terephthalate (PET), acrylonitrile styrene acrylate (ASA) [12].

When processing polyamides, waste generated during molding process and along the equipment areas can be reground and mixed with the virgin materials in up to 20% without generating mechanical properties or material appearance modification [2]. This is due to the good melt stability of polyamide that allows it to maintain its molecular mass and mechanical properties even after having been subjected to several reprocessing cycles [2, 13]. Mechanical recycling generally causes some reduction in physical properties such as tensile and impact strength [2], but this does not hinder the possibility to use valuable material in other applications where standards allow its new properties. Chemical recycling methods (e.g. depolimerization by acid or base hydrolysis, solution separation by neutral hydrolysis, ion exchange and alcoholysis) are most useful for high purity waste [2]. The recycling of polyamide has the potential for considerable impact on the use of non-renewable resources, and on waste disposal, as the collected waste products can be processed to produce various products, depending on the composition.

The current paper presents a study regarding the recycling of polyamide 6 products (in form of test specimens) that were processed by extrusion/injection molding (the same type and processing method used to produce different accessories such as screws, rods or plates in different applications from automotive industry or more [14, 15]) to be used as matrix in carbon fiber fabric reinforced composites. The carbon fiber reinforced PA6 composites were obtained in a previous study by a technique involving solvent dissolution of pure PA6 pellets, fabric impregnation (using as-received carbon fabric and chemically oxidized in the laboratory, respectively) and thermal pressing of the laminated structure [16]; the materials exhibited high mechanical performance in terms of tensile and flexural strength and stiffness [17] supported by a strong mechanical interlocking between the phases as well as chemical connection between the polymer and the sample with surface oxidized carbon fiber. The aim of this paper was the comparison of the mechanical performance of the carbon fiber reinforced PA6 composites obtained using the same technique, but starting not from pure PA6 pellets, but from PA6 recycled from a product processed previously by extrusion/injection molding.

2. Materials and methods

2.1. Materials

The materials used in the study are presented in Table 1:

Table 1. The materials used in the study, their source and properties

Matrix	Polyamide 6 (from test parts processed via extrusion/ injection)	The mechanical properties were determined by the authors and reported in [18]: Tensile strength: 79.4 MPa; Young's modulus: 3.18 GPa; Tensile elongation: 18.3 % (ISO 527); Flexure strength: 78.6 MPa; Young's flexure modulus: 2.31 GPa (ISO 178); HDT: 70 °C (ISO 75)
Reinforcement	Carbon Fiber Fabric as-received (CF)	Produced by Chemie Craft, France; purchased from Polydis, Romania: Twill weave, 3K warp; Fabric areal weight: 193 g/m^2; Fiber density: 1.7 g/cm^3
	Carbon Fiber Fabric activated by surface chemical oxidation (CF_{ox})	The carbon fiber fabric (CF) was surface oxidized using a mixture of $K_2Cr_2O_7/H_2SO_4$, at room temperature and higher temperature, to create functional groups on the surface that can interact with the polymer groups. The mixture ratio and oxidizing conditions (reaction time, temperature) were reported by the authors in [17].
Reagents	Formic acid HCOOH (FA)	Polymer dissolution solvent- purchased from Chemical Company, Romania; Concentration: 85%
	Potassium dichromate ($K_2Cr_2O_7$)	Carbon fiber fabric chemical oxidation agent- purchased from Chemical Company, Romania
	Sulfuric acid (H_2SO_4)	Carbon fiber fabric chemical oxidation agent- purchased from Merck; Concentration: 95-97%

2.2. Recycling of PA6 and manufacturing carbon fiber reinforced PA6 composites

The materials development stage was composed of two main stages: PA6 recycling from extruded products followed by carbon fiber fabric laminated composites formation. The processes of waste recycling and reprocessing into new products (consisting of as-received and surface oxidized carbon fiber reinforced composite materials based on the recycled PA6 matrix) were connected, as the final recycling stage consisted is the first stage of the new products development: the PA6 waste was dissolved in formic acid, and the obtained solution was used to impregnate the carbon fiber fabric layers that were subjected to thermal pressing to obtain the final laminated composites.

The PA6 extruded products consisting of test parts (specimens) that were processed into specific shapes by extrusion followed by injection molding were chopped into small pieces using technological cutters bench. The products were 5 years old (processed by extrusion/ injection 5 years before recycling) and this was the first and only time the material was subjected to reprocessing/recycling.

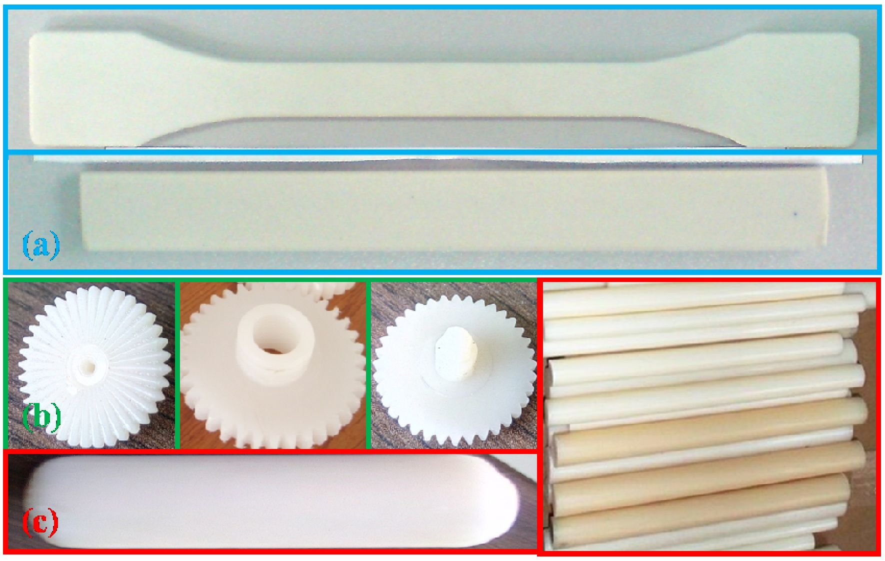

Fig. 1. (a) PA6 test samples processed by extrusion/ injection (same procedure used for finite products used directly into industry) that were subjected to recycling process, (b, c) example of finite products (gears, bars) made from PA6 manufactured through extrusion/injection

The PA6 pieces were dried at 95°C for 16 hours and afterwards, they were added into formic acid solvent and dissolved under mechanical stirring (250 rpm, at room temperature) until full polymer dissolution (homogeneous solution).

The obtained solution was used to impregnate 5 layers of carbon fiber fabric (CF) and 5 layers of surface treated carbon fiber fabric (CFox). The solvent was then removed at room temperature and 80-100°C and “semi-preg” samples were obtained. The two samples were afterwards subjected to a thermal pressing program using a hydraulic press, by heating the samples gradually until 230°C and then applying 5-10 min dwell periods between 230°C–250°C, and then cooling the samples gradually down to room temperature. The carbon fiber laminated composites obtaining technology is described in detail in the previous work [16, 17, 19].

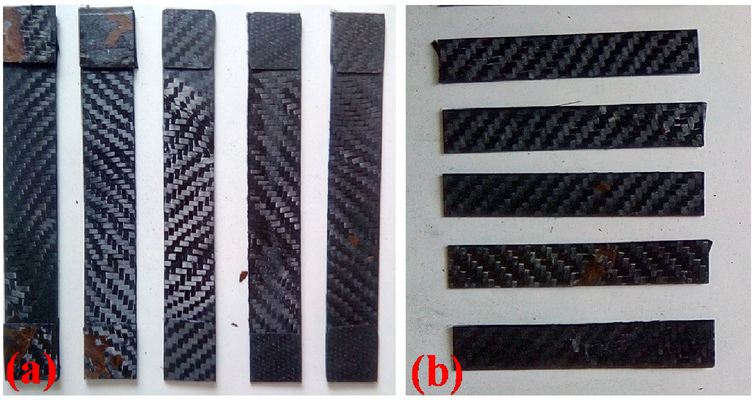

Fig. 2. (a) Recycled PA6/Carbon Fiber laminated composites specimens (rectangular with tabs) for tensile testing; (b) Recycled PA6/Carbon Fiber laminated composites specimens (rectangular) for flexural testing

The samples were obtained in form of plates with 1.7 mm thickness, that were cropped into specimens with specific geometry for mechanical tests (Fig. 2). The samples were named $PA6_{recycled}/CF$ and $PA6_{recycled}/CF_{ox}$, corresponding to the composites based on recycled PA6 and as-received carbon fiber fabric and surface oxidized by $K_2Cr_2O_7/H_2SO_4$ mixture carbon fiber fabric, respectively.

2.3. Materials characterization and testing

FTIR spectroscopy was performed using Spectrometer Nicolet iS50 (operated in ATR mode) on the PA6 samples (pure, extruded and recycled).

Scanning electron microscopy was performed using QUANTA 250 FEI scanning electron microscope equipped with an EDS module.

Optical microscopy was performed using MEIJI 8520 microscope, equipped with video camera, at 40x magnification on the fracture cross section of the mechanically tested specimens.

Tensile testing was performed using INSTRON 5982 mechanical testing machine, according to SR EN ISO 527 [20] standard specification, using 5 mm/min tensile rate, on the carbon fiber reinforced polyamide 6 samples.

3-point bending (flexural) testing was performed using INSTRON 5982 mechanical testing machine, according to SR EN ISO 14125 [21] standard specification, using 2 mm/min speed, and nominal span length (calculated as 16x specimen thickness), and conventional deflection (the test was carried out until deflection reached 1.5x specimen thickness) on the carbon fiber reinforced polyamide 6 samples.

3. Results and discussions

3.1. FTIR spectroscopy

FTIR spectroscopy was performed on a sample from pure PA6 pellet, samples from PA6 processed by extrusion/injection, a sample from PA6 (from pure pellets) processed by dissolution in formic acid and thermal pressing and a sample from PA6 (from extruded PA6 scrap) processed by dissolution in formic acid and thermal pressing (recycled).

As PA6 absorbs moisture readily, the extruded PA6 chips were subjected to FTIR analysis before and after drying. As the FTIR spectra in Fig. 3 show, the OH groups from moisture water can be observed by the wide peak at 3600 cm-1 in the un-dried PA6 sample, while in the dried extruded PA6 sample and pure PA6 pellet, the peak is not visible, confirming that the moisture uptake was eliminated.

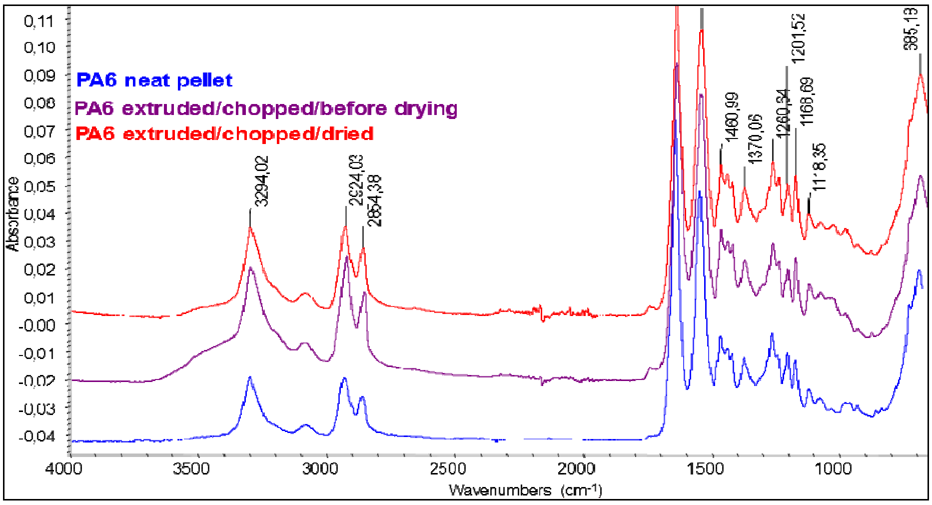

Fig. 3. FTIR spectra of pure PA6 sample, PA6 processed by extrusion/injection samples before and after drying

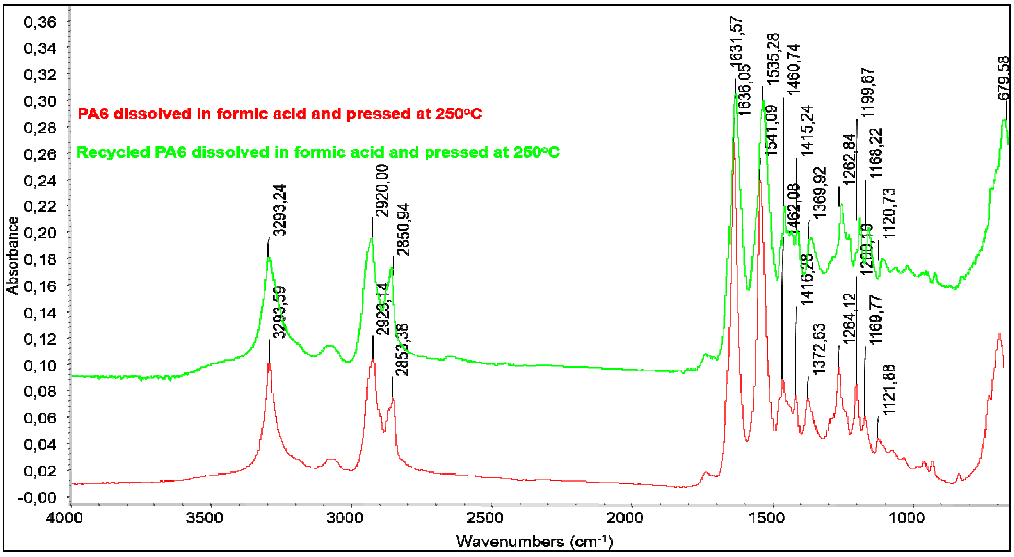

Fig. 4. FTIR spectra of PA6 (from pure pellets) processed by dissolution in formic acid and thermal pressing and PA6 (from extruded PA6 scrap) processed by dissolution in formic acid and thermal pressing (recycled)

Comparing the spectra of the samples processed by dissolution in formic acid and thermal pressing of PA6 from pure pellets and PA6 from extruded chips respectively, no significant change is observed, indicating that the polymer did not suffer any chemical structure modifications during reprocessing stages. This was expected as the polyamide 6 thermo-formable nature and good compatibility with the formic acid solvent allows several cycles reprocessing of this polymer. The absence of modifications in the FTIR spectrum indicates also that the polymer characteristics did not change by reprocessing stages.

However, it is very important to mention that, comparing extruded PA6 spectrum with thermal pressed PA6 spectrum, some small modification can be noticed in the 1200 and 1410–1470 cm-1 regions, that could be assigned to the restructuring of the polymer as a result of solubilization followed by crystallization [22]. The 1200 and 1465 cm-1 peaks correspond to the amide V and CH2 bending vibrations respectively, in polyamide α or β form, which is commonly obtained when processing PA6 involves slow cooling [23], as the thermal pressed samples were cooled gradually until room temperature. Therefore, FTIR analysis suggests that the two methods (extrusion/ injection vs. solvent dissolution/thermal pressing) lead to the formation of PA6 with different cristallinity. This fact was expected, as studies [24, 25] show that the polymorph forms of PA6 are very sensitive to the polymer processing conditions. The monoclinic α form is thermodynamically stable, monoclinic γ form is less stable [26], while the mezomorph β is partially disordered and studies attest that the latter can be obtained by fast cooling of the melted samples [25], as it is the case in the extruded/injected sample (samples were injected at 250°C and quickly cooled in a mold down to 50°C). Studies attest that α-PA6 is generally obtained by slow cooling [23], β-PA6 is generally obtained when cooling from melted state, while γ-PA6 can be transformed into α-PA6 by thermal treating by slow heating and cooling [25].

Thus, FTIR spectroscopy analysis of the recycled PA6 showed that subjecting the polymer to the extrusion– injection– chopping– solvent dissolution– thermal pressing cycle did not affect the chemical structure of the polymer. This indicates that recycled PA6 properties when used as matrix in fiber composites should also not present significant changes compared with the pure PA6 used as matrix.

3.2. SEM analysis

Scanning electron microscopy was performed in the fracture cross-section resulted after mechanical tests (Fig. 5). The images illustrate the good interface between the recycled polyamide matrix and the fibers. It can be observed that through solvent impregnation of the fabric and thermal pressing of the composite within the polymer melting temperature range, the recycled polymer embedded the fibers that constitute the fabric, creating a thin polymer layer around the fibers. This leads to an extended contact area between polymer and fibers of the fabric, which allows an efficient mechanical load transfer within the composite.

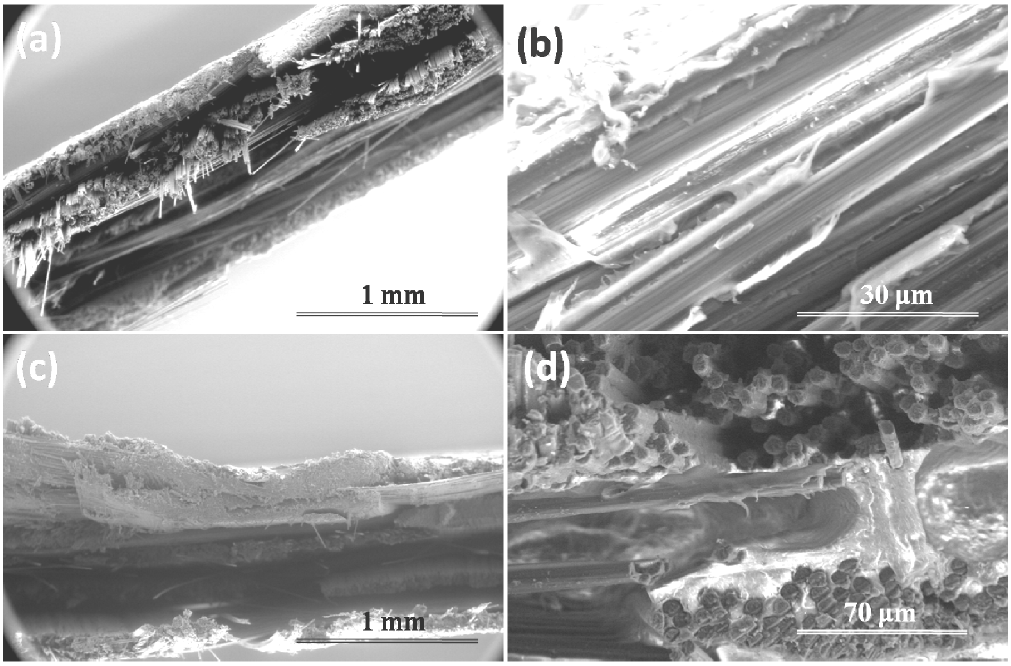

Fig. 5. SEM images of the fracture cross section of (a), (b) $PA6_{recycled}/CF$; (c), (d) $PA6_{recycled}/CF_{ox}$

In the case of $PA6_{recycled}/CF$ (Fig. 5- a, b), it can be noticed that there are areas where the thin polymer layer partially detached from the fibers, indicating low chemical interaction between the polymer and fibres as well as the mechanical interlocking failed in those regions.

In the case $PA6_{recycled}/CF_{ox}$ (Fig. 5- c, d), the composites based on recycled PA6 and oxidized carbon fiber, the polymer layer is visibly more strongly attached to the fibers that constitute the carbon fabric, suggesting that the mechanical loads were not able to detach it from the fibers, due to a stronger connection between the phases, established both by mechanical interlocking and physico-chemical bonding created between the functional groups of the recycled PA6 and functional groups generated on the oxidized fiber surface. Hydrogen-bonding is the most important interaction between the two phases meaning amidic groups of polyamide and carboxylic and hydroxyl groups from the surface of carbon fiber fabrics.

3.3. Mechanical testing

Both tensile and flexural tests were performed on a minimum of 5 specimens per sample and the mechanical strength, stiffness and elongation were averaged taking into account the medium range values. The average values are presented in Table 2. The properties of the samples based on recycled PA6 (PA6recycled/CF and $PA6_{recycled}/CF_{ox}$) were compared to reference samples based on pure PA6 (PA6/CF and $PA6/CF_{ox}$), that were previously developed within the previous experimental study conducted by the authors [17].

Table 2. Mechanical properties of the carbon fiber fabric reinforced composites based on recycled PA6 matrix compared to the reference ones based on pure PA6 matrix

Sample / *Material properties*	*PA6/CF*	$PA6/CF_{ox}$	$PA6_{recycled}/CF$	$PA6_{recycled}/CF_{ox}$
	Reference materials Results presented in [17]		*Materials developed within the study starting from recycled PA6*	
Tensile strength (MPa)	339.2	588.9	332.2	572.4
Young’s modulus (GPa)	45.5	69.1	46.2	70.5
Tensile strain (%)	0.91	0.99	0.86	0.9
Flexural strength (MPa)	436.7	911	431.6	902.5
Young’s flexural modulus (GPa)	38.3	69.3	37.2	68

Analyzing the results, it can be noticed that the mechanical performance at tensile and flexural stresses of the composites based on recycled PA6 presents insignificant changes in terms of both strength and elasticity modulus. Average values in Table 2 show that both tensile and flexural strength as well as Young’s modulus and Young’s flexural modulus of the recycled PA6 based samples have an insignificant variation between 0.8 % and 3 % compared to the reference samples based on pure PA6 matrix. The maximum 3 % variation of the mechanical properties can be considered almost unnoticeable.

The slight decrease in the elongation at break in both recycled PA6 based samples can be correlated with the fact that literature reports this phenomenon as usual consequence of reprocessing polyamide [13, 27-29], as all reprocessing cycles are believed to generate a decrease in the drawing ability and the elongation at break of the recycled samples [13].

The absence of change in the elasticity modulus and strength values suggests the maintaining of ductile nature of the PA6 subjected to recycling process. These results confirm the recycling ability of PA6 based materials and the fact that through the used method, PA6 waste based products can be successfully reprocessed and valorized into other products with different applications and destination of employment [13].

3.4. Optical Microscopy

Fig. 6- a and b illustrate the fracture area of the tensile tested specimens, and Fig. 6- c and d illustrate the fracture area of the ones tested at flexural stress.

In case of tensile tested specimens, it can be noticed that for $PA6_{recycled}/CF$ the main failure mechanism was crack propagation that led to matrix debonding from the fiber and by extending on longitudinal direction, led to delamination. It can be noticed that the external fiber layers did not break in the same area, in the visualized area and that matrix micro-cracking phenomenon is present, showing that the matrix lower mechanical strength probably lead to inefficient load transfer between matrix and fibers and consequently lower mechanical strength and stiffness of the composite.

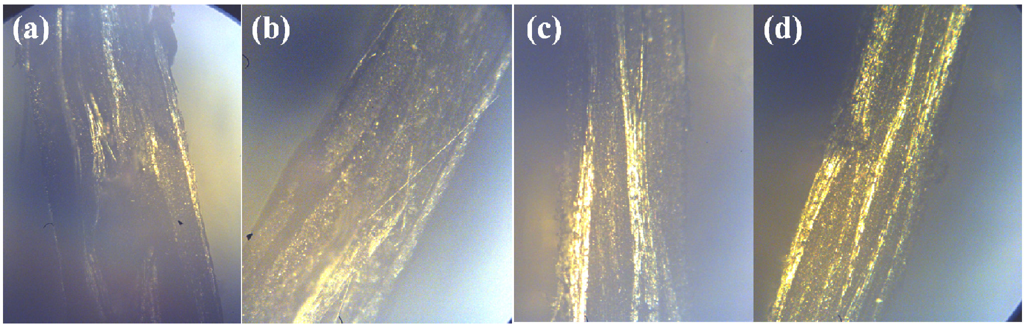

Fig. 6. Optical microscopy images of the fracture area of tensile tested samples (a) $PA6_{recycled}/CF$, (b) $PA6_{recycled}/CF_{ox}$ and flexural tested samples (c) $PA6_{recycled}/CF$, (d) $PA6_{recycled}/CF_{ox}$

In the case of $PA6_{recycled}/CF_{ox}$, the failure occurred fiber breakage that determine crack propagation in a lateral area of the sample, causing some debonding on a shorter length and only of two external layers, and only in the fracture area, but the rest of composite layers were not damaged.

In the case of flexural tested specimens, it can be noticed that the materials did not break until conventional deflection was reached, in the case of $PA6_{recycled}/CF_{ox}$, the bending point can be distinguished, appearing to have caused a micro-crack in that area, with no propagation; this can be correlated with the higher rigidity of the sample with oxidized carbon fiber.

Thus, mechanical testing of the carbon fiber composites showed that the mechanical performance in tensile and 3-point bending of the recycled PA6 based composites presents insignificant changes in terms of mechanical strength and elasticity modulus, the absence of significant modifications along with the fracture cross section analysis suggesting that the PA6 subjected to recycling process maintained its ductile nature and mechanical properties. The fracture behavior was in accordance with the mechanical performance results and presented similarities with the behavior noticed in the reference samples.

Conclusions

The paper presents a study regarding the recycling of polyamide 6 specimens/products processed by extrusion/injection molding to be used as matrix in carbon fiber fabric (as-received and surface oxidized) reinforced composites, processed by fabric solvent impregnation and thermal pressing of the laminate. The experimental study intended to highlight both the recyclability capability of PA6 into fiber reinforced composites as well as comparing the characteristics of the obtained composites based on recycled PA6 with the reference ones, obtained from pure PA6. The materials were subjected to physico-chemical and morphological analysis as well as mechanical testing.

FTIR spectroscopy analysis of the recycled PA6 showed that subjecting the polymer to the extrusion– injection– chopping–solvent dissolution– thermal pressing cycle did not affect the chemical structure of the polymer, indicating the properties of the recycled PA6 did not suffer modifications from physico-chemical point of view.

Mechanical testing of the carbon fiber composites showed that the mechanical performance at tensile and flexural stresses of the composites based on recycled PA6 presents insignificant changes in terms of strength and elasticity modulus, also suggesting the preservation of the PA6 properties subjected to recycling process. The fracture behavior during mechanical testing, observed by optical and scanning electron microscopy was in accordance with the mechanical performance results and presented similarities with the behavior noticed in the reference samples.

The results highlight the similarity between the recycled PA6 based carbon fiber (as-received and chemically oxidized) composites and the reference samples based on pure PA6 and the same two carbon fiber variants, in terms of mechanical performance, physical-chemical and morphological properties as well as fracture behavior. The results confirm that using recycled PA6 in the carbon fiber composites did not affect their performance; therefore using recycled PA6 in these composites can be a viable option. Therefore, PA6 products than become waste can be successfully reprocessed and harnessed into other products with different applications and destination of employment.

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