Comparative mechano-morphological studies on polyamide 6 based single polymer laminate composites prepared by different reactive processing techniques

Shafagh D. Tohidi[a], Ana Maria Rocha[a], Nadya V. Dencheva[b], Bernhard Engesser[c], A. S. Pouzada[b], Zlatan Z. Denchev[b].

[a] *Centre of Textile Science and Technology (2C2T), Department of Textile Engineering, University of Minho, Guimarães, Portugal.*

[b] *IPC - Institute for Polymers and Composites, Department of Polymer Engineering, University of Minho, Guimarães, Portugal.*

[c] *Jakob Müller AG, Frick, Switzerland.*

ABSTRACT: Single polymer composites (SPC) based on polyamide 6 (PA6) are developed via nylon reactive injection molding (NYRIM) or powder coating/compression molding (PCCM) in the presence of PA6 woven textile plies. The effect of fiber volume fraction of textile on the tensile properties of the SPC resulting from both molding techniques were investigated and compared. Polarizing light microscopy (PLM) was applied to detect a transcrystalline layer at the fiber-matrix interface. The results showed that applying PCCM technique increased the tensile modulus of SPC by ca. 50% as compared to the neat matrix component. Some SPC were reprocessed and the resulting PA6 molded plates showed morphology and mechanical properties very similar to those of commercial hydrolytic neat PA6. The thermal stability and crystallizability of both NYRIM and PCCM laminate systems was studied by means of TGA and DTA in the temperature range from 30ºC-550°C.

1 INTRODUCTION

Thermoplastic composites are produced by combining chemically different organic and inorganic components that can be reshaped by reheating above their processing temperature [1]. Recycling of conventional thermoplastic materials is complex due to high costs, certain technical difficulties and the negative environmental impact [2-3]. Single polymer composites (SPC) are novel promising materials, in which oriented thermoplastic polymer reinforcing elements are embedded in an isotropic matrix of the same polymer [4]. Because of the identity of the matrix and reinforcement polymers, there is a better stress transfer between them that, depending on the chemical composition of the components, can be due to the presence of H-bonds or other specific interactions across the interface in SPC [5]. At the same time, conventional thermoplastic composites often display weak matrix-fiber interfaces. Other key benefit of SPC is their full recyclability by reprocessing. This feature attracts the interest of high value industrial sectors. To produce most SPC types, melt-processing techniques are frequently used, such as powder impregnation [6], hot compaction [7-8], partial melting [9], film-stacking [10], or co-extrusion [11]. A typical drawback of these methods is the narrow processing window, resulting in partial melting and loss of orientation of the reinforcements, unavoidably leading to insufficient mechanical properties.

Reactive processing help overcoming the said drawback because as a rule they are carried out at lower temperatures. Activated anionic ring-opening polymerization of lactams (AAROP) is one of these reactive processing routes. It is known as a chain-growth, anion-catalyzed process, in which a ring-shaped lactam monomer opens and transforms into high molecular weight polyamide without liberation of by-products [12-13]. The typical AAROP temperatures are between 160-180ºC, i.e., 40-60ºC below the melting point of the PA6 reinforcing textile plies determining a wide processing window in which the latter will remain intact.

Few studies are available describing the production and properties of PA6-based SPC [10,12-14]. Tohidi et al [15] investigated textile reinforced SPC laminates produced by compression molding of PA6 knitted textile structures powder-coated by PA6 microparticles obtained by AAROP. The tensile properties of these composites were studied as a function of the knitted reinforcement architecture (Rib or Jersey), fiber volume fraction V_f (15, 20 and 25%), ply orientation (wale and course) and stacking orders (0/45/0 and 90/45/90). Their results showed increased tensile stiffness and strength of composites reinforced with 15% fiber content, which constitutes an improvement factor of 11 % and 15% as compared to the neat anionic PA6 matrix and to commercial hydrolytic PA6 (HPA6), respectively.

The preparation of PA6-based SPC via in-mold AAROP using a semiautomatic prototype mold was studied by Dencheva and coworkers [16]. A wide processing window about 60ºC, tensile strengths over 130 MPa and Young´s moduli above 1.5 GPa using

only 20 wt% of fibers were obtained. This group investigated the production of all-polyamide laminate composites produced in two stages, namely (i) reactive microencapsulation of nanoclays in PA6 through AAROP, and (ii) compression molding of PA66 textile plies powder-coated by the microcapsules of stage (i) [17]. They reached an improvement of 73% in the Young's modulus, a 142% increase of the stress at break, and over a fivefold increase of the notched impact resistance compared to the PA6 matrix.

Notably, no studies on the mechanical behavior of PA6-based SPC and the type and architecture of the reinforcing textile plies were published. This study aims at the production of PA6-based SPC reinforced with plies of plain-woven textiles designated as WSPC. Two processing methods were used: reactive injection molding of PA (NYRIM), and a combination of compression molding and powder coating/compression molding (PCCM) with PA6 microparticles, previously synthetized by AAROP from the ε-caprolactam (ECL) in solution. These WSPC laminates were mechanically grinded and reprocessed by injection molding. The tensile properties and the morphological characteristics of the SPC laminate composites resulting from the NYRIM (N-WSPC) and PCCM (P-WSPC), as well as of the reprocessed samples were evaluated and compared. The reinforcement-matrix interface was investigated by polarizing light microscopy (PLM). The thermal stability of produced and recycled composites was studied by DSC and TGA methods in a wide range of temperatures.

2 MATERIAL AND EXPERIMENTAL

2.1 *Woven reinforcements*

Plain woven fabrics with air jet textured PA6 continuous-filament (CF) yarns (160 dtex) were fabricated and delivered from Jackob Müller AG (Switzerland) and pre-washed with non-ionic detergent solution at 30˚C for 30 min to diminish contaminations and then rinsed with reverse osmosis water for another 15 min. All woven reinforcements were immersed in acetone for 30 min and then dried for 120 min at 60˚C to eliminate any non-chemically bonded hydrophobic finish from the filament surface. To improve mechanical properties and geometrical stability, all reinforcements were extended biaxially to 30% of their original length using a specially designed metal frame and a screen stretching apparatus. The extended reinforcements were annealed with fixed ends at 170˚C for 90 min. The geometric characteristics of the textile reinforcements are tabulated in Table 1.

Table 1. Sample designation and properties of plain-woven reinforcements

Type	Treatment	Designation	Density*	Areal weight ($g.m^{-2}$)	Thickness (mm)
Plain	No	P	22×16	147.6±1.7	0.58±0.01
	Yes	P-A	20×12	111.0±2.1	0.42±0.01

* Density=Warps.cm^{-1} × Wefts.cm^{-1}

2.2 *Reagents*

The ECL monomer of reduced moisture (AP-Nylon® caprolactam) from Brüggemann Chemical, Germany was polymerized with the activator Brüggolen C20 (C20) from same company and sodium dicaprolactamato-bis-(2-methoxyethoxo)-aluminate (DL) from Katchem (Czech Republic) as initiator, all being used without further treatment. Acetone and methanol solvents (puriss grade) were purchased from Sigma-Aldrich (USA).

2.3 *Preparation of WSPC by NYRIM and PCCM*

To prepare the N-WSPC, a prototype equipment developed for reactive injection molding of polyamides was employed [21]. The required number of plain-woven textiles with dimensions 80×80×3mm were placed in the mold, aligned along the warp direction (0). Separately, 0.33 mol of ECL was heated to 90ºC under nitrogen flux and mixed with 1.5 mmol of DL. After several minutes at temperatures between 90-110°C, 0.75 mmol of the activator C20 was added to the mixture at once. The resulting activated monomer/initiator mixture was injected into the preheated to 120°C mold. The polymerization took place at 160-170°C during 15 min. Thereafter, the mold cooled to 65°C at a cooling rate of 40°C/min and the laminate molding was demolded. The preparation of P-WSPC laminates is described in detail elsewhere [15,17]. In a first stage, the PA6 microparticles (MP) are prepared by AAROP in suspension. In a second stage, the textile reinforcements are powder-coated with MP and consolidated in a hot press. All laminates were laser cut to standard dimensions according to ASTM D638. The sample designation is shown in Table 2.

Table 2. The designation and detail description of WSPC prepared by PCCM and NYRIM

WSPC designation	V_f, (%)	Number of plies (PCCM)	Number of plies (NYRIM)
P or N*-15	15	3	6
P or N*-20	20	4	8
P or N*-25	25	5	10

*P or N stand for PCCM or NYRIM.

2.4 *Reprocessing of WSPC*

The SPC samples fractured after the tensile test were separated into N- and P-series. All pieces of the same series were combined and grinded, then sieved and cleaned from contaminants. This material was fed into a BOY 22A injection molding machine with a clamping force of 220 kN and a maximum stroke volume of 2.05 in^3. The volumetric flow rate was set to 40 mm/s and the maximum injection pressure to 80 bars. The temperature profile from the hopper to the nozzle was set from 195ºC to 200ºC. A commercial PA6 Ultramid B35 (BASF, Germany) was also injection molded at the same conditions. Recycled N- and P-WSPC were designated with RN and RP respectively, the reference for comparison being the injection molded neat PA6 (designated as IN).

2.5 *Mechanical characterization*

The tensile behavior of plain-woven reinforcements was evaluated according to ASTM D5034 - grab test standard method using an Instron 4505 universal testing machine with a standard load cell of 2.5 kN at a constant crosshead speed of 2 mm/min. The woven sample sizes were 150×100 mm. The textiles were conditioned at 23˚C for at least 5 h before testing. The tensile properties of the N- and P- WSPC laminates were determined according to the ASTM D638 standard using a gauge length of 38 mm in an Instron 4505 testing machine, at 23±2˚C. The machine worked with a standard load cell of 50 kN and at a constant crosshead speed of 2 mm/min. At least five specimens of each sample were tested.

2.6 *Morphological characterization at interface*

An Olympus BH-2 polarizing light microscope equipped with a camera with image acquisition software (Leica Application Suite 4.4) were used to obtain PLM images of the samples.

2.7 *Thermogravimetric analysis*

The thermogravimetric analysis was performed on a modulated TGA Q500 from TA instruments. The TGA trace was obtained in the range of 40-600ºC under the nitrogen atmosphere with a flow rate of 20 mL/min, the heating ramp being 10C°/min. Before the test the samples were dried at 60ºC for 1 h. The TGA curve, its first derivative, as well as the DTA curve were obtained and analyzed for all samples.

3 RESULTS AND DISCUSSION

3.1 *Tensile tests*

The influence of the fiber volume fractions (15, 20 or 25%) and the type of the preparation techniques on the tensile behavior of N- and P-laminates is shown in Fig. 1a. All P-laminates showed higher tensile stress and strain values as compared to the neat matrix PN. The increase of the fiber content had no significant effect on the tensile strength of the P-composites although the textile ply increment from 15 to 25% increased their strain-at-break up to 12%. Fig. 1a shows also, that the in-mold polymerization of ECL (NN sample) caused an increase in its strain-at-break and tensile strength compared to the PN sample produced from compression molded MP. However, the tensile properties of all N-laminate composites were significantly lower. The reason was related with the existence of PA6 oligomers produced during the NYRIM processing. These elevated oligomer levels should be attributed to impediments in the matrix-forming AA-ROP that takes place in the presence of PA6 textiles, in which the filament finishing had not been removed completely by the acetone washing.

The stress-strain graphs of recycled WSPC (RP and RN) and of reference IN samples obtained from commercial PA6 granules are depicted in Fig. 1b. The latter sample showed lower tensile stiffness and yield strength than the neat NN and PN matrices, but a much higher strain-at-break. As to the recycled samples in Fig. 1b, the tensile properties of the RP sample were significantly higher than the RN material, evidencing a significant influence of the prior molding

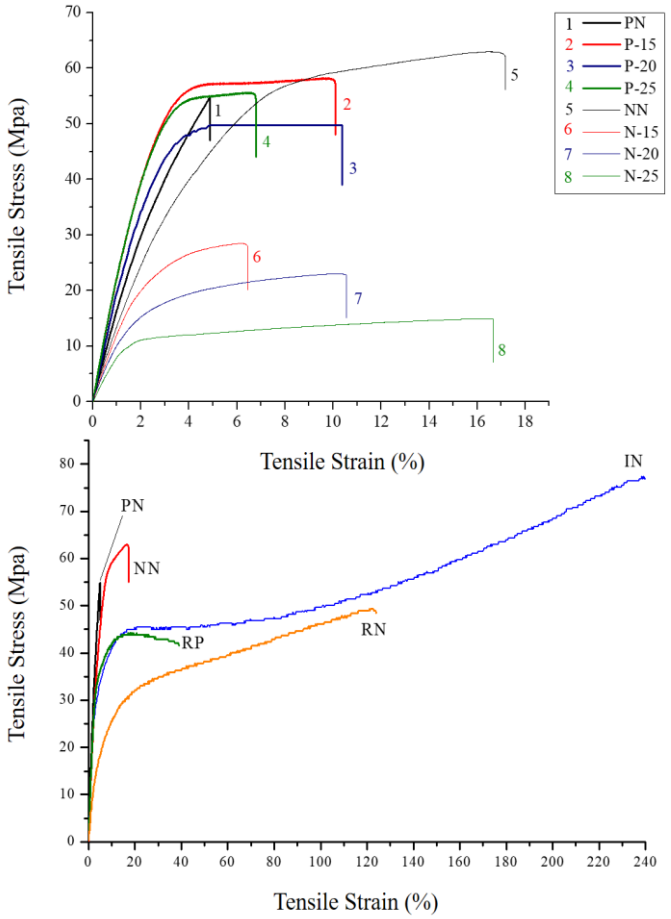

Fig.1. Stress–strain curves for: a - SPC with varying fiber volume fractions prepared by PCCM and NYRIM; b – reprocessed SPC. For sample designation see Table 2.

technique on the mechanical properties of the recycled composites.

The tensile properties of the N- and P-composites are tabulated in Table 3. The increase in the fiber volume fraction from 15 to 25 vol % did not improve the tensile stiffness and strength of P-WSPC. In case of N-WSPC, increasing the fiber content caused a clear growth in the strain-at-break, ε_{br}, together with a decrease in tensile strength, σ_{max}, and stiffness, E.

Table 3. Tensile test properties of WSPC prepared by PCCM and NYRIM

Samples	E (GPa)	σ_{max} (MPa)	ε_{br} (%)
P-A	0.02 ± 0.01	19.4 ± 1.0	28.1 ± 1.0
PN	1.73 ± 0.02	56.7 ± 1.8	5.2 ± 0.1
NN	1.38 ± 0.05	66.2 ± 2.9	12.1 ± 1.1
IN	1.30 ± 0.08	76.4 ± 1.1	225.7 ± 3.3
P-15	2.41 ± 0.05	61.7 ± 1.1	9.2 ± 0.5
P-20	1.64 ± 0.06	51.1 ± 1.9	8.5 ± 0.4
P-25	2.25 ± 0.05	54.3 ± 1.0	10.3 ± 0.1
N-15	1.28 ± 0.07	27.0 ± 1.4	7.8 ± 0.1
N-20	1.21 ± 0.01	23.4 ± 0.4	11.0 ± 0.0
N-25	0.94 ± 0.03	14.4 ± 0.6	16.2 ± 0.1
RP	1.80 ± 0.04	43.1 ± 1.2	38.0 ± 0.9
RN	0.60 ± 0.02	50.2 ± 0.9	122.5 ± 1.4

As seen from the averaged data in Table 3, the reprocessed RP material is significantly stiffer than RN and the PN and NN neat matrices. However, the σ_{max} and ε_{br} of RP and RN are clearly inferior than IN. The relatively large differences in the latter case should be attributed also to RP and RN being anionic PA6, and the IN reference hydrolytic PA6.

3.2 *Microscopy study*

The correlation of the mechanical properties of the composites to the characteristics of the reinforcement/matrix interface was based on PLM observations. In all SPC of this study, the isotropic matrix-forming PA6 crystallizes in the presence of oriented, crystalline PA6 filaments from the textile filaments. Under such conditions, a transcrystalline layer (TCL) is formed on the monofilament´s surface [18-19]. The thickness of the PA6 monofilaments of the woven textile reinforcement is measured before and after the formation of the matrix as in images in Fig. 2a-b.

Fig. 2a shows a stretched-annealed plain-woven textile, in which the average thickness of the monofilaments is 22-23 µm. After embedding the same textile into the PA6 matrix, the average thickness of the monofilaments is between 25-26 µm (Fig. 2b). This means that the TCL thickness in these systems is between 1-2 µm.

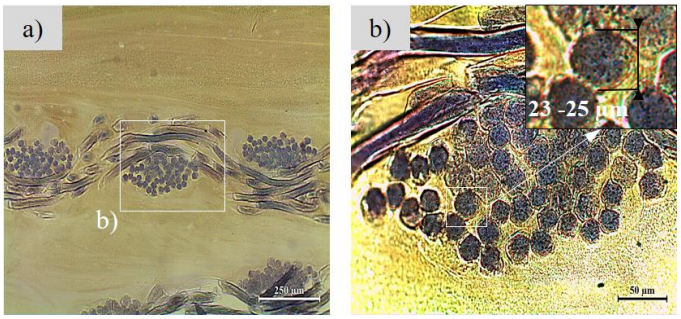

Fig.2. Microscopy surface topography of N-15 at two different magnifications.

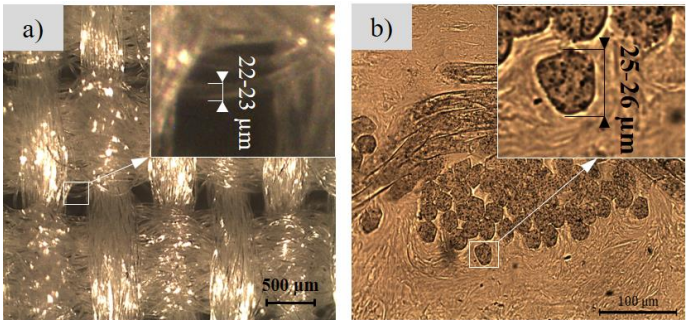

Fig.3. a) Stretched-annealed plain structure before lamination and measuring monofilament´s thickness (inset); b) Measuring the of embedded monofilament´s thickness in P-15 sample

Fig. 3a-b depicts the microscopy images of N-WSPC where the average thickness of the embedded monofilaments is 23-25µm. This means that in the N-laminates the thickness of the TCL is around 2 µm, *i.e.*, slightly lower than in the P-laminates. This may result from the pressure during the SPC consolidation being higher in P-WSPC. On the other hand, the cooling rate in N-WSPC is 10-15ºC/min lower, which could also influence the TCL thickness.

3.3 *Structural studies by TGA*

Differential thermal analysis (DTA) of WSPC and matrix components enables measuring the changes of enthalpy in an open system, while the sample mass is simultaneously altering. Combining TGA and DTA curves allows complementary evaluation of enthalpy and mass changes, providing in such a way better understanding of the crystallization, melting and degradation of the samples.

Fig. 4a-d represents the combined thermal studies of P-A, PN, P-15 and RP samples. They include three different plots as a function of the temperature, namely the weight loss (TGA, %), enthalpy/entropy changes (DTA, µV) and derivative thermal gravimetry (DTG, µg/min). As it can be seen in Fig. 4a, three characteristic points can be observed in each of the graphs. The initial decomposition temperature (IDT) represents the onset of the weight losses, TM is the melting temperature and MRD/MRDT the temperature of maximum degradation rate. The latter is determined as the inflection point of the integral TGA

curve (MRD), or as the peak of its first derivative (MRDT).

The DTA traces of P-A textile structure (red) showed a TM at 213ºC and a multiple endotherm of thermal degradation centered around 440ºC (Fig. 4a). The neat matrix from MP its DTA (PN, Fig. 4b) demonstrated a single TM peak at 200ºC and a strong thermal decomposition isotherm at 330ºC, i.e., a lower thermal resistance is registered as compared to the previous sample. The RP and P-15 sample (Fig. 4c and 5d) display a similar DTA behavior. The differences are being in the temperature position and the shape of the TM and thermal decomposition peaks.

The data from TGA/DTA analyses of all samples are tabulated in Table. 4. The thermal decomposition of NN and PN matrix (the IDT point) is around 250ºC, which is with 50ºC lower than the IDT of the neat textile reinforcement. Most probably, this difference is due to the orientation of the P-A sample. The TM points of the neat N- and P-sample matrices and of the respective laminates are lower than that of the IN-reference sample. Also, the MRDT points of all SPC before and after reprocessing are lower than in the IN and P-A samples. The carbonized residue at 550ºC in the NN matrix was with 6% higher than in the PN matrix, which may be attributed to the formation of cross-linked structures in the former case, that are more difficult to depolymerize.

As it can be seen in Table. 4, MP melted at lower temperature than the P-A textile, which is considered an advantage for the PCCM technique. The thermal stability of WSPC was higher than the matrix component but lower than the textile reinforcement. On the other hand, after reprocessing the P-composites, the PCCM technology produced 19% carbonized residue, more than two times higher than the PN samples.

Table 4. The designation and detail description of WSPC prepared by PCCM and NYRIM techniques

Sample	TM (ºC)	IDT (ºC)	MRDT (ºC)	MRD (Rad)	Degradation (%)
IN	220	331	451	1.08	98.2
MP	204	204	307	1.18	85.0
PN	198	249	330	1.54	98.0
NN	208	255	317	1.15	92.0
P-A	213	302	441	1.12	95.4
P-15	204	252	346	1.20	92.7
N-15	208	208	334	1.16	90.3
RP	207	239	353	1.13	82.9
RN	205	246	347	1.22	91.6

The explanation of the data in Fig. 4 and Table 4 should be related to small differences in the thermal degradation mechanisms in each of the samples studied. There exist six main degradation mechanisms including main-chain scission, side group scission, elimination, depolymerization, cyclization and cross-linking [20]. All these processes could occur in a different way and to different extent depending on the PA6 matrix synthetic route (hydrolytic polymerization or AAROP), the presence of oligomers, traces of catalysts and/or low molecular finishing substances and stabilizers related to the textile reinforcements.

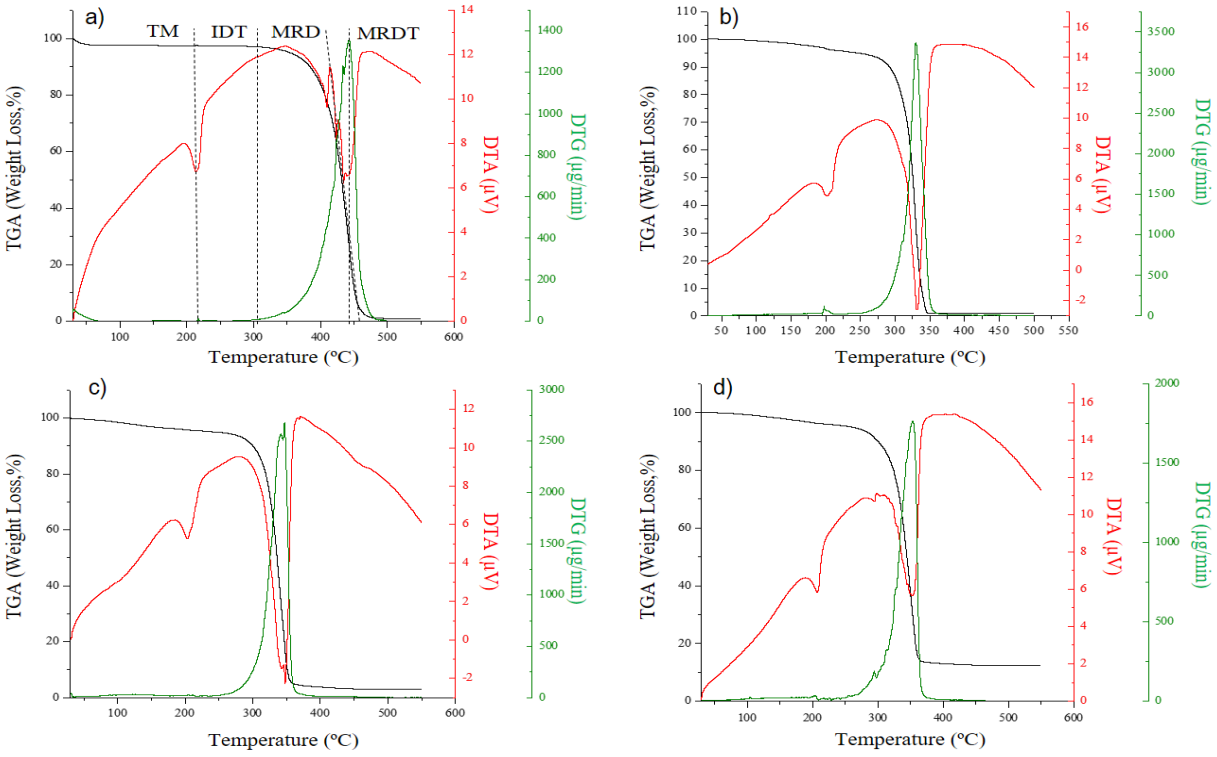

Fig.4. Combined thermal analyses in N_2 atmosphere at 10°C/min heating rate of: a) P-A; b) PN; c) P-15; d) RP. For sample designation see Tables 1 and 2.

CONCLUSIONS

Woven reinforced single polymer composites based on polyamide 6 were prepared by two molding techniques in the presence of the same plain-woven reinforcement: (i) a combination of powder-coating and compression molding (PCCM); (ii) reactive injection molding including the in-mold preparation of the PA6 matrix (NYRIM). The influence of fiber volume fraction on the tensile properties of WSPC prepared by the two techniques was evaluated. The two composite types were reprocessed by injection molding. Their mechanical and thermal properties were compared to the SPC composites, the two neat matrix types and to an injection molded neat commercial PA6.

Based on the study performed, the following conclusions can be drawn.

i) The PCCM technique can produce single polymer laminates with good mechanical properties in tension.
ii) The best tensile properties were obtained with 15 vol. % of textile reinforcements.
iii) Due to the formation of oligomers in the presence of the woven textile reinforcements, the NYRIM technique produced laminates with lower stiffness and strength, in spite of this technique being beneficial for the preparation of neat PA6 plates.
iv) The microscopy results indirectly evidenced the formation of a transcrystalline layer at the fiber-matrix interface in both NYRIM and PCCM materials.
v) Recycling the SPC prepared by PCCM produced neat PA6 materials (RP) with properties different from those of recycled NYRIM composites (RN).
vi) The RP samples showed better tensile properties than RN.
vii) The thermal behavior of RP and RN was quite different.

More research is necessary to explain these differences.

ACKNOWLEDGEMENTS:

This work was partially financed by FEDER funds through the COMPETE program and by national funds through FCT – Foundation for Science and Technology within the project POCI-01-0145-FEDER-007136. SDT thanks FCT for his PhD Grant SFRH/BD/94759/2013. NVD thanks for the financial support of FCT in the frames of the strategic project UID/CTM/50025/2013. Finally, ZZD is thankful to FCT for the SFRH/BSAB/130271/2017 personal research grant. All authors gratefully acknowledge the support of the project TSSiPRO-NORTE-01-0145-FEDER-000015 funded by the regional operational program NORTE 2020, under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund.

REFERENCES

[1] Mukhopadhyay, S. Deopura, B.L. Alagiruswamy, R. 2003. Interface behavior in polypropylene composites, *J. Thermoplast. Compos. Mater*. 16(6): 479–495.

[2] Netravali, A.N. Chabba, S. 2003. Composites get greener, *Mater. Today*. 6(4): 22–29.

[3] Rozman, H.D. Lee, M.H. Kumar, R.N. Abusamah, A. Ishak, Z.A.M. 2000. The effect of chemical modification of rice husk with glycidyl methacrylate on the mechanical and physical properties of rice husk-polystyrene composites, *J. Wood Chem. Technol*. 20(1): 93–109.

[4] Matabola, K.P. Vries, A.R. Moolman, F.S. Luyt, A.S. 2009. Single polymer composites: a review, *J. Mater. Sci*. 44: 6213–6222.

[5] La Mantia, F.P. Curto, D. Scaffaro, R. 2002. Recycling of dry and wet polyamide 6, *J. Appl. Polym. Sci*. 86:1899–1903.

[6] Lacroix, F. v. Werwer, M. Schulte, K. 1998. Solution impregnation of polyethylene fibre/polyethylene matrix composites, *Compos. Part A Appl. Sci. Manuf*. 29(4): 371–376.

[7] Hine, P.J. Astruc, A. Ward, I.M. 2004. Hot compaction of polyethylene naphthalate, *J. Appl. Polym*. Sci. 93: 796–802.

[8] Ward, I.M. Hine, P.J. 2004. *The science and technology of hot compaction, Polymer*. 45(5): 1413–1427.

[9] Gong, Y. Yang, G. 2010. Single polymer composites by partially melting recycled polyamide 6 fibers: Preparation and characterization, *J. Appl. Polym. Sci*. 118: 3357–3363.

[10] Bhattacharyya, D. Maitrot, P. Fakirov, S. 2009. Polyamide 6 single polymer composites, *Express Polym Lett*. 3(8): 525–532.

[11] Alcock, B. Cabrera, N.O. Barkoula, N.-M. Wang, Z. Peijs, T. 2008. The effect of temperature and strain rate on the impact performance of recyclable all-polypropylene composites, *Compos. Part B Eng*. 39(3): 537–547.

[12] Dan, F. Vasiliu-Oprea, C. 1998. Anionic polymerization of caprolactam in organic media. *Morphological aspects, Colloid Polym. Sci*. 276(6): 483–495.

[13] Vasiliu-Oprea, C. Dan, F. 1996. On the relation between synthesis parameters and morphology of anionic polycaproamide obtained in organic media. I. Influence of the Na [O (CH 2) 2 OCH 3] 2 AlH 2/ isophorone diisocyanate catalytic system, *J. Appl. Polym. Sci.* 62(10): 1517–1527.

[14] Gong, Y. Liu, A. Yang, G. 2010. Polyamide single polymer composites prepared via in situ anionic polymerization

of ε-caprolactam, *Compos. Part A Appl. Sci. Manuf*. 41(8): 1006–1011.

[15] Tohidi, S.D. Rocha, A.M. Dencheva, N.V. Denchev, Z. 2018. Single polymer laminate composites by compression molding of knitted textiles and microparticles of polyamide 6: Preparation and structure-properties relationship, *Compos. Part A Appl. Sci. Manuf.* 109: 171-183

[16] Dencheva, N.V. Denchev, ZZ. Pouzada, A.S. Sampaio, A.S. Rocha, A.M. 2013. Structure–properties relationship in single polymer composites based on polyamide 6 prepared by in-mold anionic polymerization, *J. Mater. Sci*. 48(20): 7260–7273.

[17] Dencheva, N.V. Vale, D.M. Denchev, Z.Z. 2016. Dually reinforced all-polyamide laminate composites via microencapsulation strategy, *Polym. Eng. Sci*. 57(8): 806-820.

[18] Quan, H. Li, Z.-M. Yang, M.-B. Huang, R. 2005. On transcrystallinity in semi-crystalline polymer composites, *Compos. Sci. Technol.* 65(7-8): 999–1021.

[19] Dencheva, N.V. Stribeck, A. Denchev, Z.Z. 2016. Nanostructure development in multicomponent polymer systems characterized by synchrotron X-ray scattering, *Eur. Polym. J*. 81: 447–469.

[20] Price, D. Hourston, D. Dumont, F. 2000. Thermogravimetry of polymers. *Encyclopedia of analytical chemistry*. 8094–8105.

[21] Dencheva, N.V. Sampaio, A.S., Oliveira, F.M. Pouzada, A.S. Brito A.M. Denchev, Z.Z. 2014. Preparation and properties of polyamide-6-based thermoplastic laminate composites by a novel in-mold polymerization technique, *J. Appl. Polym. Sci*. 131(8), 40083–40095.