CELLULOSE CHEMISTRY AND TECHNOLOGY

COMPATIBILIZED GREEN COMPOSITES BASED ON WOOD CHIPS AND THERMOPLASTIC POLYMER WASTE MATRICES

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The objective of this study was to obtain and evaluate the thermal, mechanical and morphological characteristics, as well as the stability towards moisture, of some new green composites made of wood chips (W), as natural filler, and recycled polyethylene (rPE) or recovered statistic aliphatic copolyamide (coPA) as matrix, as well as rPE matrix with small amounts of coPA as compatibilizer. Experimental data confirmed the better dispersion of particles inside the matrix, as well as the improvement in the interfacial adhesion and tensile properties of rPE-W composites containing 5-20% coPA.

Keywords: green composites, polymer waste, compatibilizer, properties

INTRODUCTION

The term "waste" projects a vision of a material with no value or useful purpose. Along with the growing production and consumption, plastic waste is one of the major components of global solid waste. Similarly, a large amount of wood waste is generated in different stages during wood processing and a proportion of this waste is generally meant for landfill, although most of the wood processing waste is used for energy.[1-4]

Green composites are, basically, obtained from raw materials that do not use petroleum as feedstock, but are based on sustainable resources, such as plants. Generally, there are two sorts of green composites: (a) wholly green composites, made exclusively of natural polymers and resins (such as modified starches and proteins) with natural fillers (ligno-cellulosic fibers or chips), and (b) green composites where either the matrix, or the filler, is natural (*i.e.*, a plastic matrix with natural filler or a natural polymer as matrix with plastic fibers/particles).[5-10] Significant amounts of research is being conducted to develop environmentally friendly and fully sustainable green composites suitable for applications that do not require high mechanical properties, such as packaging, product casings, housing and interior design, furniture, automotive panels, etc. It is estimated that the global bioplastics and green composites market is growing at more than 25% per year and experts predict that the production will exceed 50 billion pounds per year by 2015. Natural fillers are suitable due to their renewable character, relatively high strength and stiffness, low cost, low density, low CO_2 emission, and biodegradability. The main advantage of green composites is that, at the end of their life cycle, they can be recycled. Furthermore, they are susceptible of composting under various conditions.[11,12]

The development of wood-plastic composites (WPCs), aiming to use the already existing wood waste and recycled plastics, which would otherwise be added to landfills, is indispensable and offers the prospect of lessening waste disposal problems and lowering production costs. Nowadays, WPCs emerge as some of the most dynamic growth materials and become more and more commonplace with the development of new production techniques and processing equipment. A major advantage of these materials over wood is their ability to be molded, bent and fixed, which makes them able to meet almost any desired form and environmental conditions. At present, there is a wide variety of different applications where wood and plastics can be converted into high value materials.[1,13-16]

Many papers have reported on the hydrophilic nature of wood fillers causing poor adhesion towards hydrophobic thermoplastics in wood filled plastic composites.[17,18] The optimization of interfacial adhesion between cellulose-based fillers and thermoplastics, as well as the filler dispersion within the polymer matrix, are problems that can be solved by two methods: (1) a chemical pre-treatment of the natural filler, which yields an increased reactivity towards the polymer matrix,[19-22] or (2) the addition of a compatibilizer to the composite formulation, which can improve the interfacial adhesion between components.[23-25]

The objective of this study was to obtain and evaluate the mechanical and morphological characteristics of some new green composites made of wood chips, as natural filler, and recycled polyethylene (rPE) or recovered statistic aliphatic copolyamide (coPA) as matrix, as well as rPE matrix with small amounts of coPA as compatibilizer. Experimental data showed a better dispersion of particles inside the compatibilized matrix, as well as a slight improvement in the interfacial adhesion and bending strength of rPE-W composites containing 5-20% coPA.

EXPERIMENTAL

Materials

For the matrix, two kinds of recycled plastics were selected:

a) Recycled low density polyethylene pellets (rPE) were obtained by recovery and recycling of polyethylene films from agriculture. The material has a melt flow index of 0.55 g/10 min at 170 °C, a density of 0.92 g/cm^3 and a melting temperature ranging from 108 to 120 °C.

b) Recovered copolyamide (coPA) is a ternary statistic copolymer 6/6.6/6.10, with a melt flow index of 11.9 g/10 min at 190 °C and a melting temperature range from 125 to 135 °C. CoPA waste resulted after the synthesis/granulation process of the polymer.[26]

The plastic wastes were used after processing in the laboratory; they were thoroughly washed with water and dried at 70 °C for 12 h before mixing and compounding with wood chips.

As wood filler, pine chips of *Pinus radiata* – a waste collected from a local furniture manufacturer – were used. The chip dimensions varied from 0.1 to 7 mm. The wood chips were dried at 50 °C for 24 h in an oven up to a moisture content of 2-3%.

Preparation of wood-plastic composites

Prior to mixing, the coPA and the wood waste were dried in an oven for 24 h at 90±2 °C and their moisture content was controlled in order to be less than 2%.

The compounding process included two steps: (1) compounding of the wood filler and plastic, and (2) extrusion and compression molding of the compounded mixture to obtain a panel type product.[27,28]

All blends were made with a wood chips (W) to plastic (P) weight ratio of W/P=60/40. The plastic and wood filler were mixed, weighted for each formulation according to Table 1 and subsequently blended. A single screw extruder was employed and the barrel temperature was 155-160 °C (die temperature: 160 °C).

The mixing process took 5 min on the average. In the first stage, extruded samples were collected, cooled, and granulated into pellets of 2-3 mm.

The pellets were dried at 90 °C for 24 h before the panel sample production. Then, pellets were compressed into an oil-heated press at 150 °C for 3 min under a pressure of 20 kg/cm^2. Finally, the panels were transferred into a cold press, where they were cooled to room temperature under the same pressure. The dimension of the final composite panel was 165×150×5 mm. Prior to testing, samples were conditioned at constant room temperature (23±1 °C) and relative humidity (60%).

Table 1
WPCs formulations (%wt)

Sample	Code	Composition		
		Wood chips, %	Plastics, %	
			coPA	rPE
1	coPA	–	100	–
2	rPE	–	–	100
3	coPA(40)	60	40	–
4	rPE(40)	60	–	40
5	coPA(5)	60	5	35
6	coPA(10)	60	10	30
7	coPA(20)	60	20	20

Measurements

Granulometric study of wood chips and polymer particles

For the selected plastics waste, the granulation was 0.3-0.5 mm for coPA and 2-4 mm for rPE. As for the wood chips, they were separated on vibrosieves with size fractions of less than or equal to 0.2, 0.2-0.5, 0.5-1, 1-2, 2-3, 3-5, 5-7 and 7-10 mm (hereafter, the size of the fraction is marked by its upper limit). The yield of each fraction was defined by weighing with a microbalance.

For the wood filler, a packing factor (*F*) was defined and its values were determined by vibration compaction of the wood chips in a glass measuring cylinder with a diameter of 80 mm. A portion (P) of wood chips, selected by weight, was placed in the cylinder and its volume (*V*) was measured after vibration compaction. The value of *F* was calculated as follows (Eq. 1):

$$F = {}^{P}/_{V} \cdot \rho_f \tag{1}$$

where ρ_f is the density of the wood filler particles. Ten particles of each fraction were taken for measurements of weight and geometrical dimensions. The density of wood chips was calculated using the ratio (Eq. 2):

$$\rho_f = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} l_i b_i h_i} \tag{2}$$

where m_i, l_i, b_i, and h_i are the weight, length, width and thickness of a particle *i*, and *n* is the number of particles (n=10, in our case).

Thermal characterization

Thermogravimetric analysis (TGA): A thermogravimetric analyzer (a Paulik–Paulik–Erdely type Derivatograph, MOM – Budapest, Hungary) was used to characterize the decomposition and thermal stability of wood-coPA composites. The specimen was heated from room temperature up to 600 °C. The sample weight was 50 mg and the heating rate was set at 12 °C/min. During testing, the heating unit was flushed under a continuous air flow of 30 mL/min.

To separate possible overlapping reactions during measurements, derivative thermogravimetric (DTG) analysis was also conducted to measure the mass change of a specimen with respect to temperature (dm/dT) using the same TGA system.

Differential scanning calorimetry (DSC): A DSC analyzer (METTLER TA Instrument DSC 12 E calorimeter, Greenfield, Switzerland) was used to determine the thermal transitions of wood-polymer composites. A specimen pressed into an aluminum sample pan was placed in the heating chamber for DSC. The heating rate was 10 °C/min. During measurements, the heating chamber was flushed with a continuous nitrogen flow of 30 mL/min. The melting temperature of WPCs was estimated as being the temperature where the DSC thermograms exhibit the maximum of the thermal peak. Indium was used as a reference sample (T_m = 156.6 °C; ΔH_m = 28.43 J/g). The melting heat of WPCs (ΔH_m, J/g) was calculated from the endothermic peak area. The melting peak area was measured using a planimeter and was compared to the indium metal peak area (weight and heat of melting being known) to determine the melting heat of each sample.

Evaluation of mechanical properties

The mechanical properties of the WPCs were assessed through tensile and flexural properties and were determined according to ASTM D638–01[29] and ASTM D790–00[30] specifications. For the tensile strength measurements, a mechanical tensile machine (FU-1000; Rauenstein, Germany) was used. Crosshead speed was set at 20 mm/min. Dimensions of samples: 150x10x5 mm. The flexural bending properties were evaluated by three-point bending tests using a PM-400 testing machine (Ivanovo, Russia), at a crosshead speed of 3 mm/min and a span of 75 mm. The composite sample dimensions were 80x10x5 mm.

All samples were conditioned at a temperature of 23±2 °C and relative humidity (RH) of 50±5% for at least 40 h prior to testing. At least five samples were tested for each type of measurement.

Morphological study

Geometrical dimensions of the wood particles were measured with an optical microscope (MBS-9; Moscow, Russia). Their weight was determined with a Sartorius 4431 microbalance (Gottingen, Germany). Ten particles of each fraction were selected for measurements. Optical observation of the wood chips and polymer granules morphology were performed with an optical microscope (IOR type MC1, Bucuresti, Romania). The fractured surfaces of the samples were examined by a scanning electron microscope VEGA//TESCAN type instrument (Tescan, Brno, Czech Republic) at 30 kV. The samples were first dipped into liquid nitrogen and then broken in order to prepare fractured surfaces. Afterwards, the samples were mounted on the sample stub and sputtered with gold. For each composite formulation, 5 SEM images were taken and analyzed.

Water sorption and dimensional stability

The water sorption and dimensional stability tests were conducted in accordance with ASTM D570-98,[31] in which the specimens were immersed in water for preset intervals and temperature. Time of immersion in water: 24 h at room temperature (23±1 °C). The weight gain and thickness increase were measured 20 minutes after the samples were removed from water. After each water immersion test, samples were taken out of the water, dried on a filter paper, and then weighed on an analytical balance (± 0.001 g). Then, they were immersed for the next stage. The period of manipulating the sample out of water was no longer than 1 min. The water uptake was calculated for each sample (Eq. 3):

$$Water\ sorption = \frac{(m_t - m_0)}{m_0} \cdot 100\% \quad (3)$$

where m_o and m_t are the initial oven-dry mass (kg) and the mass (kg) after immersion time t, respectively. Equilibrium moisture content (EMC) of the samples is the moisture content when the daily weight change of the sample was less than 0.01% and thus the equilibrium state was assumed to be reached.

In the dimensional stability tests, the thickness of each composite sample was measured and the swelling (S) was calculated as follows (Eq. 4):

$$S(\%) = \frac{(h_t - h_0)}{h_0} \cdot 100\% \quad (4)$$

where h_o and h_t are the panel thickness values (mm) before and after the water immersion, respectively.

RESULTS AND DISCUSSION

Granulometric study of wood chips and polymer particles

The granulometric study is required in order to establish the relationship between the components' morphology and the composite properties. The granulometric distribution (percentage) of coPA and wood chips is presented in Table 2.

For the composites using rPE as matrix, wood chips with various sizes were used, whereas the composites based on coPA contained wood particles with size fractions of 2 mm or less.

In our study, the packing factor *F* of the wood filler was calculated for a statistic mixture of particles, according to Fig. 1, and its value was 0.71. For particles with determined length, L=1.0 and 0.20 mm, *F* was 0.57 and 0.58, respectively.

The yield of each fraction was defined by weighing and it is shown in Fig. 1.

In our case, a higher value for *F* indicated that the distance between particles increased, which is favorable for composites processing because it allows an increased amount of polymer to penetrate between wood chips and inside their tracheids, yielding composites with improved elastic properties.

The calculated value of ρ_f was 0.496 g/cm^3 for wood particles of each fraction.

The granulometric study was completed by the direct observation of wood and polymer particles and their images obtained by microscopy are shown in Fig. 2.

Table 2
Granulometric distribution of coPA and wood chips

coPA particles		Wood chips	
Fraction (mm)	Distribution (%)	Fraction (mm)	Distribution (%)
< 0.1	9	< 0.2	6
0.1-0.25	22	0.2-0.5	8
0.25-0.3	34	0.5-1	14
0.3-0.4	18	1-2	53
0.4-0.5	8	2-3	12
0.5-0.6	6	3-5	4
0.6-0.8	3	5-7	3

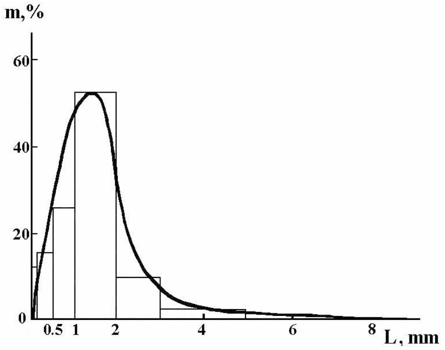
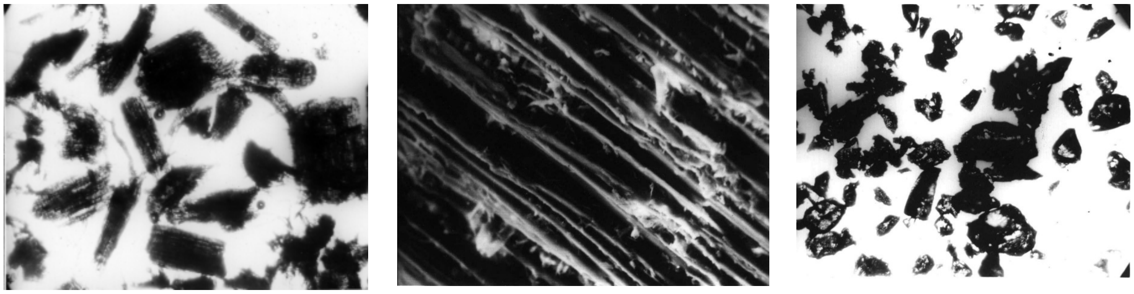


Figure 1: Differential curve of the weight distribution of the wood particles



a b c

Figure 2: Microscopy images of raw materials: a) wood chips (x15); b) wood chips – detail (x300); c) coPA powder (x30)

Images illustrate in detail the appearance of raw materials. Irregularities on the surface of the wood chips were highlighted: torn and/or broken fibers, asperities of different size (Fig. 1b). This roughness is due to the harsh conditions of the wood cutting process.

The coPA powder consists of particles with irregular polygonal contour, with roughness owing to the cryogenic grinding (Fig. 1c). This is a common feature for both recycled polymers. Due to the existing surface irregularities in all components, it is assumed that agglutination will occur during the preparation of the composites (with the contribution of small size wood chips with a length <1 mm), negatively affecting the mixture homogeneity. This is the reason why a preliminary mixing phase (vigorous mechanical stirring) is required prior to the extrusion homogenization stage.

Thermal behavior of raw materials and composites

For the TGA, testing conditions were the same for all the analyzed samples. Precautions were taken to maintain the same geometry or mass of the different samples. The range of temperatures of degradation was estimated from the DTG curves and the weight loss was read from the TG plots. Comparing the TG and DTG curves of the composites with those of each component, evidences on changes during the thermo-oxidative decomposition of materials were revealed.

Table 3 and Fig. 3 present TGA data and TG-DTG curves for wood, rPE and coPA.

Several parameters were evaluated: T_i – the onset degradation temperature (T_i was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve;[32] T_{max} – the maximum decomposition temperature of the main stage of the thermal degradation and ΔW – the weight loss (as percentage of the initial mass) in this stage; the residual char (ash) at 500 °C.

The most obvious issue was the rPE degradation that occurred in a one step process, from 315 to 500 °C, confirmed by the presence of only one peak at 468 °C in the DTG curve. The mass loss of rPE starts at 315 °C and continues very slowly at temperatures below 400 °C. Over 400 °C, this process evolves rapidly and the residue is very low (5.30% at 500 °C) due to the volatile emission.

On the other hand, the copolyamide decomposes in two stages. The initial stage of decomposition (in the range 5-15%) involves oxidation of the less thermally stable segments. The copolyamide begins to decompose only over 345 °C. The weight loss increased at 190 °C and the slow rate degradation in the range 20-340 °C proves the thermal stability of coPA. This behavior may be explained due to the high thermal resistance of methylene and amide groups. At higher temperatures, there is a sudden increase in the weight loss (second stage) caused by the enhanced thermo-oxidative processes. This generates emission of gaseous by-products, secondary compounds formed during previous stages, at lower temperatures, when they were not volatile. The coPA residue at 500 ºC was 11.66%.

As for the wood chips, the process is more complex: thermal degradation of wood can be regarded as the sum of the thermal degradation reactions of the individual components. It evolves in two stages (as shown in Table 3 and Fig. 3).

Table 3
TGA data of the raw materials used for WPCs

Material	Peak nr.	T_i-T_f, °C	T_m, °C	W_{Tm}, %	$W_{Ti\text{-}Tf}$, %	T_{10}, °C	T_{50}, °C	$Residue_{500}$, %
Wood	1st	40 - 150	110	5.39	9.24	–	–	–
	2nd	215 - 365	328	47.81	48.35	–	–	–
	–					125	335	16.63
rPE	1st	315 - 505	468	71.05	91.47	365	455	5.30
coPA	1st	38 - 135	100	2.31	3.08	–	–	–
	2nd	345 - 475	352	76.25	77.33	–	–	–
	–					383	415	11.66

where: T_{10}, T_{50} – temperature corresponding to 10 and 50% mass loss, respectively; T_m – temperature of the maximum degradation rate; T_i – temperature of the beginning of the decomposition; T_f – temperature of the end of the decomposition; W_{Tm}, $W_{Ti\text{-}Tf}$ – mass loss at T_m, and T_i-T_f ; $Residue_{500}$ – residue at 500 °C

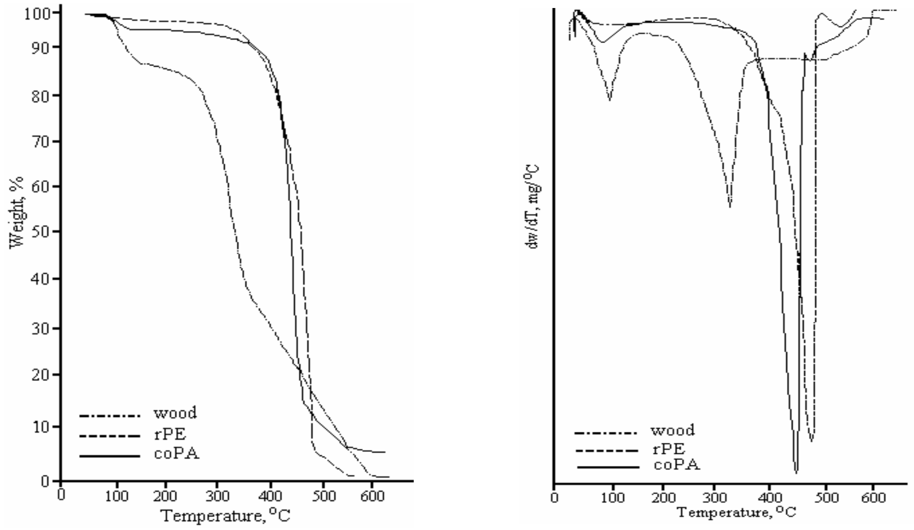


Figure 3: TG (left) and DTG (right) curves of the raw materials

Wood is a composite material mainly consisting of cellulose, hemicelluloses and lignin, and each of them displays a different behavior with respect to thermal degradation. Cellulose is highly crystalline, which makes it thermally stable. Hemicelluloses and lignin, on the other hand, are amorphous and start to degrade before cellulose. Hemicelluloses are the least thermally stable wood components, due to the presence of acetyl groups. Lignin degrades partly over a wide temperature range, starting at relatively low temperatures.[19] The first decomposition stage occurred below 80 °C, when a weight loss of 5-6% was registered, attributed to the evaporation of the adsorbed water from wood. Significant weight losses were noticed in two intervals, 200-360 °C and 350-500 °C, the degradation in the second stage being slower and gradual. The weight loss is due to the thermal decomposition of the wood constituents: hemicelluloses are degraded mainly between 150 and 350 °C, cellulose in the range 275-350 °C, and lignin in the interval 250-500 °C. The residue was 17% at 600 °C. These data are in good correlation with the literature.[19,21]

In conclusion, the preliminary thermal study of the raw materials showed that rPE had the highest thermal stability compared with coPA and wood chips.

Thermal characterization of the WPC samples was performed and thermogravimetric data are summarized in Table 4, whilst TG and DTG curves are presented in Fig. 4.

Three domains were identified. In the first temperature interval (~30÷150 °C), WPCs exhibit an initial mass loss of maximum 2.3%, when the adsorbed water is removed.

The addition of wood and coPA into the thermoplastic composites matrix, rPE, induced thermal degradation at lower temperatures. It was reported that thermal degradation of wood yields free radicals, which may be responsible for the decay of thermoplastic polymers at high temperatures, due to their capability to accelerate thermal degradation reactions.[33,34]

The thermal decomposition of WPCs occurred in a two-step process, as confirmed by the presence of two main decomposition peaks in the DTG curves (Fig. 4).

Composite materials started to degrade in the temperature range 215-230 °C. The first peak, at around 345 °C (interval 220-365 °C), may be attributed to wood constituent polymers and coPA degradation. In the second interval (380-480 °C), the peak was recorded at 455 °C and its value was close to the temperature of the maximum degradation rate of rPE (468 °C), which is an indication of the rPE decomposition prevalence in this stage.

The residual weight of WPCs at 500 °C showed that the addition of wood and coPA to the rPE matrix increased the remaining residues due to the charring of wood and copolyamide. In comparison with neat rPE and coPA (weight losses were ~95% and ~88%, respectively), the new composites displayed a higher thermal stability, as evidenced by the decrease to 75-80% of their corresponding weight losses.

Table 4
Thermogravimetric data for WPCs

Material	Peak	T_{peak}, °C		W_{peak}, %		T_{10}, °C	T_{50}, °C	$Residue_{500}$, %
		T_i-T_f, °C	T_m, °C	W_{Tm}, %	W_{Ti-Tf}, %			
rPE(40)	1st	30-175	100	1.54	3.85	–	–	–
	2nd	220-375	345	30.36	31.65	–	–	–
	3rd	375-480	455	69.10	38.47	–	–	–
	–	–	–	–	–	276	415	22.30
coPA(5)	1st	35-160	105	2.31	4.62	–	–	–
	2nd	220-365	345	32.58	33.10	–	–	–
	3rd	390-478	460	72.35	31.16	–	–	–
	–	–	–	–	–	270	415	21.30
coPA(10)	1st	30-145	95	2.31	5.59	–	–	–
	2nd	230-375	350	37.02	37.29	–	–	–
	3rd	390-480	455	67.80	19.34	–	–	–
	–	–	–	–	–	260	403	25.20
coPA(20)	1st	30-160	100	2.31	6.16	–	–	–
	2nd	215-360	340	30.14	36.70	–	–	–
	3rd	380-485	460	68.45	25.84	–	–	–
	–	–	–	–	–	250	395	25.20

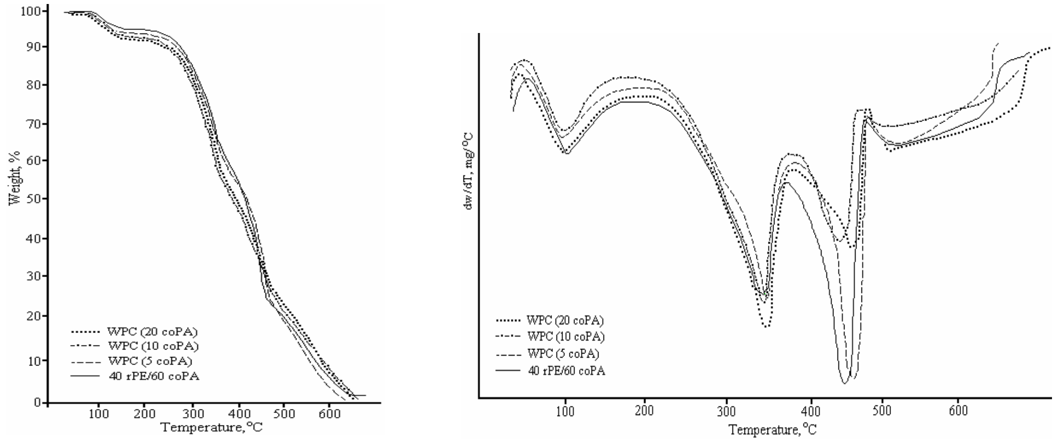


Figure 4: TG (left) and DTG (right) curves of WPC samples

Table 5
Mechanical properties of WPCs

Sample	Code	Mechanical properties	
		Tensile strength, MPa	Bending strength, MPa
1	coPA	23.0	-
2	rPE	10.2	-
3	coPA(40)	6.5 (±0.30)	42.5 (±0.33)
4	rPE(40)	7.8 (±0.30)	13.2 (±0.33)
5	coPA(5)	4.2 (±0.30)	15.3 (±0.4)
6	coPA(10)	4.6 (±0.30)	17.6 (±0.4)
7	coPA(20)	5.5 (±0.32)	20.5 (±0.45)

Standard deviations are given between parentheses

Mechanical properties of composites

It is well known that dispersion of the reinforcing agent and interfacial adhesion between matrix and filler are factors with the highest influence on the mechanical properties of the composites. Our study aimed to evaluate the variation of composites' tensile and bending strength with their formulation. Experimental data are presented in Table 5.

It is noticeable that the tensile strength of the composites with coPA matrix is lower than that of the composites with rPE matrix (about 17%). Adding coPA, and, subsequently, increasing the amount of coPA in the rPE matrix from 12.5% up to 50%, determined a modest increase in the tensile strength. Thus, for the coPA(20) sample, the breaking strength value was by 31% higher than that of the coPA(5) and by 30% lower than that of the rPE(40), while the tensile strength for coPA(5) was by about 46% lower than that for rPE(40).

This behavior is due to the different elastic modulus of rPE (0.11 GPa) and coPA (0.394 GPa), coPA displaying a superior tensile elasticity. The addition of defined amounts of coPA yielded composites with enhanced elasticity. Therefore, it is possible to obtain materials with preset properties by modulating the ratio of components in the formulation.

The dependence of the composites bending strength on their formulation confirmed that the plastic nature of components have a significant effect on the WPCs mechanical properties. The difference in bending strength values for composites coPA(40) and rPE(40) was significantly higher (about three times higher) at equal content of wood. The addition of coPA improved the bending strength with 16-55% compared to the composites with rPE matrix. This effect may be assigned to the increasing share of interfacial polymer–wood interactions due to the presence of coPA in the composite formulation, indicating that interfacial bonding between these two phases occurred through reactive moieties belonging to coPA and wood constitutive polymers. Finally, it can be concluded that coPA acted as a compatibilizer[35,36] and this led to composites with improved bending strength.

An interesting feature is the influence of the wood chip dimensions on the mechanical properties of these composites. It is known that WPCs filled with wood fine powder displayed high elastic properties, but poor tensile strength. On the other hand, plastic based composites filled with coarse wood chips (about 5 mm length) showed enhanced bending strength, due to the reinforcing effect of wood, but tensile strength was not as high as expected.[37] Therefore, we used a statistic mixture of wood chips, where the share of medium size (1-2 mm) particles was 53%. These particles are responsible for an improved load transfer from the polymer matrix and big wood slivers to small chips, thus favoring load dissipation and preventing the occurrence of stress concentrators.

Morphological study

The examination of the fracture surfaces of the composites by a scanning electron microscope offered information about how the copolyamide addition to the rPE matrix affects the morphology of the composite. The conclusion drawn from this study can be corroborated with the data obtained for mechanical properties, confirming the effect of coPA addition to the rPE-wood composite formulation.

SEM micrographs of the fractured surface of coPA(40) and rPE(40) composites are shown in Figs. 7a and 7b.

The coPA(40) sample (Fig. 7a) presented a very well-defined structure of wood cells organized in tracheids and vessels, which was not penetrated by the matrix polymer. It is easy to notice that there are voids at the wood-plastic interface, suggesting that coPA did not cover wood chips satisfactorily. This behavior might be explained by the poor wettability of wood chips and insufficient dispersion of the polymer. As a result, a phase separation occurred.

As for the rPE(40) sample, it showed an improved dispersion of the filler into the matrix and the wood chips were better covered by the polymer. Thus, the interfacial interactions between the matrix and the filler increased, probably due to the different grade of plastic and other impurities in the rPE, improving the tensile strength of the composites. These observations are in good agreement with the results obtained from mechanical tests.

The addition of defined amounts of coPA to rPE(40) composites entailed a significant effect on the morphology of the composites. The fractured surface images of the composites containing 5, 10 and 20% coPA are shown in Figs. 8a-c, respectively.

The SEM images of the coPA(5) and coPA(10) samples (Figs. 8a and 8b) – the composites with the lowest amount of coPA – showed numerous holes and cavities, with some fibers pulled out of the matrix, due to the weak bonding at the interface of the phases.

Fig. 8c, corresponding to the coPA(20) sample, showed that most of the wood chips were embedded into the mixed coPA-rPE matrix, displaying an improved polymer wetting, which was reflected in its better dispersion and adhesion. This study confirmed that coPA acts as a compatibilizing agent when added in certain amounts.

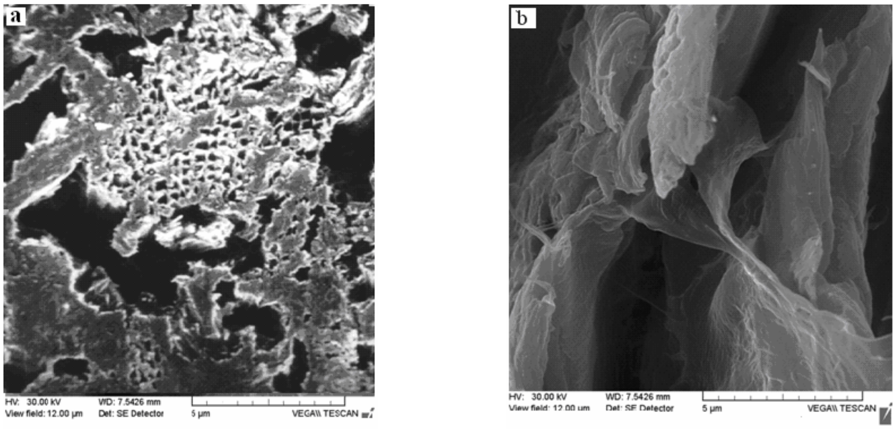


Figure 7: SEM images of composite samples: (a) coPA(40) and (b) rPE(40)

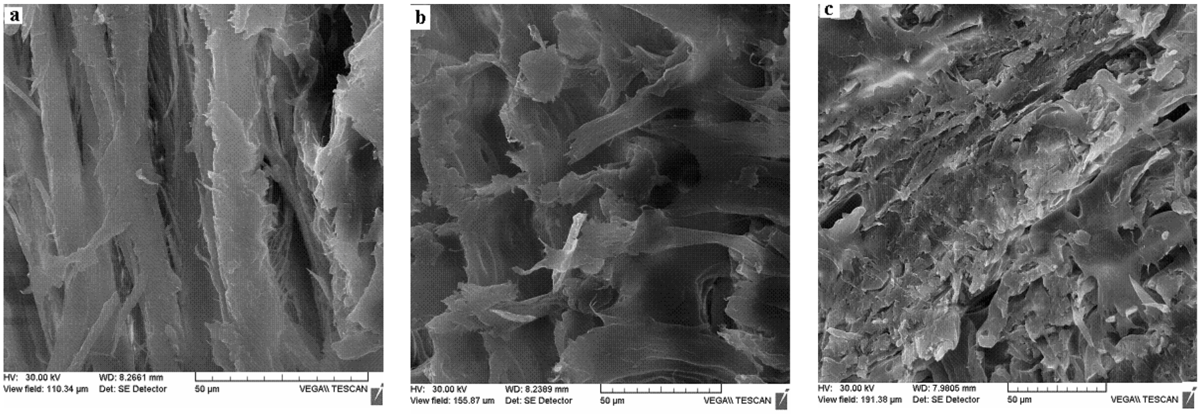


Figure 8: SEM images of composite samples: (a) coPA(5), (b) coPA(10) and (c) coPA(20)

However, an optimization of the composites formulation is required because cavities and some debonding can still be noticed at the wood-plastic interface. Improving the dispersion of the phases, the coverage of filler particles and the adhesion between the matrix and the filler will ensure a better load transfer and distribution to the network of the wood chips. This can be confirmed by mechanical tests, these compatibilized materials exhibiting superior bending strength. This behavior is due to the improvement of interfacial interactions between the wood and the mixed matrix, enabled by the presence of coPA in the composite formulation.

Water sorption and dimensional stability

The water sorption in wood-thermoplastic composites is mainly due to the presence of lumens, fine pores and hydrogen bonds in wood, gaps and flaws at the polymer-wood interface, and micro-cracks formed in the matrix during processing.[38] Generally, this complex phenomenon is governed by two significant criteria: the nature of the filler and matrix (hygroscopic for wood, hydrophobic for rPE) and the mechanism of water diffusion into composites.

On the other hand, polyamides are well known for their hydrophilic character, they are able to readily absorb water when placed in a saturated atmosphere or upon immersion. As a common feature, the water uptake of polyamides is 8-12% when immersed for 48 h, at 25 °C.

For the studied WPCs, the water absorption after 24 hours increased with the increasing amount of coPA, at constant wood content, as presented in Table 6. The difference in absorption between coPA(40) and the other composites with a mixed matrix, after an immersion time of 24 hours, is noticeable: 35% and 1.5-5%, respectively. Since the amount of wood is the same in all formulations, the disparities are due to the nature and ratio of coPA and rPE. In the case of coPA(40), the effect is cumulative, given by both coPA and wood contributions (the main wood polymers, cellulose, hemicelluloses and lignin, are mostly responsible for the high water absorption of wood chips).[39]

As for the rPE(40) sample, the water uptake is very low (0.9%) and reflects the highly hydrophobic character of rPE and its ability to cover wood chips and fill pores and lumens, so that the wood filler cannot absorb water, thus creating an insulating layer.

The composites with a mixed matrix absorbed more water than sample rPE(40) due to the lower content in rPE (35, 30, 20%) and increased amount of coPA (5, 10, 20%).

A factor strongly affecting the WPCs behavior towards moisture is the size distribution of the wood chips. The advantage of medium size particles lies in their relatively uniform distribution in the bulk. While small size particles are almost completely covered by the polymer, the big ones are scarcely wetted by the matrix, but their vessels and tracheids are more accessible to polymer filling during extrusion and compression molding. Medium size chips combine the advantages of both, minimizing the corresponding flaws.

The same behavior was observed for samples coPA(5-20) when their dimensional stability was evaluated: the thickness swelling was higher than that of sample rPE(40), but significantly lower compared to coPA(40).

WCPs water sorption might be considered as an indication of the potential biodegradability of these materials at the end of their service time, since a higher amount of water absorbed upon exposure readily promotes the UV/thermal/ enzyme-initiated degradation reactions that occur during composting.

Table 6
Dependency of water uptake and thickness swelling of composites on coPA content (after 24 h immersion)

Sample	Code	Composition, %			Water sorption, %	Thickness swelling, %
		Wood chips, %	Plastics, %			
			coPA	rPE		
1	coPA(40)	60	40	–	35	8
2	rPE(40)	60	–	40	0.9	0.85
3	coPA(5)	60	5	35	1.5	1.1
4	coPA(10)	60	10	30	2	1.3
5	coPA(20)	60	20	20	5	1.8

CONCLUSION

The objective of this study was to obtain some new green composites based on recycled polymer waste, rPE and coPA, and wood chips recovered from the furniture industry, and to investigate their properties. The effects of using coPA as matrix, as well as compatibilizing agent, on the thermal and mechanical properties of the composites, their morphology and water sorption were also studied.

Based on the results and discussion presented herein, the following conclusions were derived:

- given the nature and properties of the matrix polymers and of the filler, high amounts of wood chips (60 wt%) were incorporated, yielding higher rates of wood recovery;
- all composite samples have displayed improved bending strength due to a beneficial combination of factors: high content of wood resulting in increased stiffness, granulometric distribution of wood particles (medium size particles act towards load dissipation and prevent the occurrence of stress concentrators), the compatibilization effect of coPA that allowed enhanced interfacial interactions in composites with mixed matrices;
- results from SEM analysis showed a better dispersion of the wood chips in the compatibilized rPE matrix;
- the water absorption and thickness swelling of the composites with mixed matrices were significantly lower compared to those of coPA(40), confirming the ability of coPA to act as compatibilizing agent for wood-rPE composites.

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