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ScienceDirect

Procedia Manufacturing 12 (2017) 203 – 220

Procedia MANUFACTURING

International Conference on Sustainable and Intelligent Manufacturing, RESIM 2016, 14-17 December 2016, Leiria, Portugal

Optimization of a wood plastic composite for architectural applications

Martins G.[a,*], Antunes F.[a], Mateus A.[b], Malça C.[b,c]

[a]*Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal*
[b]*Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, 2430-028 Marinha Grande, Portugal*
[c]*Department of Mechanical Engineering, Polytechnic Institute of Coimbra, 3030-199 Coimbra, Portugal*

Abstract

The actual demand for sustainable construction has fostered the research of alternative products made of new materials, such as composites based on renewable resources obtained directly from nature or, most importantly in this context, from the wastes of industries thus encouraging the implementation of recycling processes.
This study reports the optimization of wood plastic composites (WPC) made of industrial residues of pine sawdust, high density polyethylene (HDPE) and maleic anhydride-grafted-polyethylene (PE-g-MA) as coupling agent. These composites were specifically designed for the production of an innovative shading system to apply in the forefront of buildings, thus requiring an adequate combination of material properties concerning resistance to weather conditions, with mechanical and functional performance of the final products. The composites were optimized to enable their production and the fabrication of the shutter units through sequential extrusion processing. The optimization of the composites started with a thorough characterization of the raw materials and the mixtures were prepared after analysing the effect of the concentration of pine sawdust in the polymeric matrix, with variable amounts of the coupling agent. Torque rheometry was used to determine the most adequate viscosities for extrusion processing. The composites with optimized contents of pine sawdust and additives were characterized using SEM, FTIR, DSC-TGA, tensile testing, measurements of water contact angle and water absorption capacity. This allowed determining the respective microstructure, chemical interactions, thermal stability, mechanical properties, surface wettability and swelling capacity.

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Peer-review under responsibility of the scientific committee of the International Conference on Sustainable and Intelligent Manufacturing

* Corresponding author. Tel.: +351 239 852080; fax: -.+351 239 827703
E-mail address: agtmartins@gmail.com

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Peer-review under responsibility of the scientific committee of the International Conference on Sustainable and Intelligent Manufacturing
doi:10.1016/j.promfg.2017.08.025

Keywords: Wood Plastic Composite; Pine Wood Particles; High Density Polyethylene; Coupling Agent; Extrusion; Wood Residues.

1. Introduction

The concept of Wood Plastic Composite (WPC), created around the 1970´s, traditionally corresponded to a material primarily composed of wood particles and a thermoplastic polymer. At present days, the concept is broader and the term WPC refers to any composites that contain plant fibres and thermoset or thermoplastic polymers [1–5]. Since the chemical and physical properties of the main components are very different, this type of composite usually contains additives to promote the compatibility between the polymeric matrix and the fibres.

Concerning selection criteria of polymer types for the composites, thermoplastics are usually preferred because they offer the advantage of enabling repeated melting processes, unlike thermosetting polymers which become irreversibly in the solid state after a single processing cycle that leads to polymerization after an initial increased temperature. Thermoplastics are most adequate for blending the vegetable fibres and obtaining the composites in a twin screw extruder, for instance, followed by the extrusion or injection moulding of the composite previously obtained to achieve the intended final products. The great evolution of the WPCs has occurred together with the development of new processing methods and technologies, as well as development of new designs for most traditional products. Thus, the innovative WPCs have inspired new solutions for the surrounding industries in the fields of construction, architecture, automotive, decoration, among many others [1–5].

The WPC concept has been continuously evolving, addressing innovative solutions to the challenges derived from growing environmental impacts of hazardous chemical substances and excessive energy consumption. Awareness of these problems, which may be associated to a variety of industrial, scientific and political options, as contributed to the development of "*green chemistry*" solutions to maximize the efficiency of use of raw materials and to minimize the creation of waste. This involves the use of cleaner/non-polluting technologies, the use of biodegradable and recyclable materials (particularly from natural resources), the reuse of wastes generated from conventional industries, among other options that ultimately promote the preservation and protection of the environment for future generations. Clearly, the WPCs constitute eco-sustainable green materials, starting with the fact that the plant fibres components are annually renewable raw materials and their availability is more or less unlimited. Additionally, it has been reported that the CO_2 footprint of a WPC submitted to a combustion process or landfill disposal is neutral. At the end of its life cycle the released amount of CO_2 of the fibres is neutral with respect to the assimilated amount during their growth. The popularity of the WPCs is also due to the high durability, low maintenance, acceptable relative strength and stiffness, and lower prices relative to other competing materials, particularly when recycling of residues or other raw materials is applied. For instance, when the polymeric matrix is based on natural polymers, the WPC becomes a fully natural material. Other advantages which have been strength points include the resistance to the natural conditions, as biological deterioration, especially for outdoor applications where untreated timber products are not suitable. Moreover, in opposition to wood product, the WPCs generally have no need for surface treatments as polishing, painting or others [1–13].

In the last years a considerable amount of industrial wood wastes from many sectors that use wood, such as building construction, furniture and pulp and paper industries, has had a great increase. These wastes may be applied in the synthesis of composite materials, originating sustainable and added-value products [4,7,14]. The natural fibres incorporated into the wood plastic composites (WPC) may act as fillers or as reinforcement agents of the polymeric matrix, particularly if the interfacial adhesion between the components is promoted by the use of coupling agents. The low interaction between the hydrophobic polymers and hydrophilic natural fibres may be increased by the addition of adequate maleic anhydride grafted (-g-MA) polymers [8,10,15–18]. Chemically modified polymers with maleic anhydride, possessing a backbone compatible with the main composite polymer, become entangled in the matrix while the anhydride groups react with the hydroxide bonds of the cellulosic components of wood [8,10,15–18]. Through the use of these compatibilizers, also named as coupling agents, not only the interfacial adhesion and the mechanical properties may be increased, but the susceptibility to water adsorption, thickness swell and bio-deterioration may be limited to lower levels. Other additives, such as minerals as talc or calcium carbonate, are frequently used as fillers mostly for economic reasons or with the purpose of enhancing the stiffness and the mechanical resistance of the composite [1,4,5,17,19,20]. The addition of pigments and UV protectors may also be needed, usually in small quantities, being these additives commercially available in polymeric formulations. Through the use of pigments, surface treatments (painting or polishing) of the final products may be excused and

UV protectors may decrease the aging usually denoted by stains and micro-fissures at the product surface. Furthermore, advantages as low weight, biodegradability and recyclability of the resulting WPCs also depend on the combination of the composite constituents and processing methods. The selection of raw materials to obtain such WPCs must observe the chemical and physical properties of all components, with particular emphasis on their thermal characteristics because the vegetable fibres degrade at relatively low temperatures and the processing methods often require melt blending of the components for posterior extrusion or injection moulding, among other techniques [12,13,18,21–28].

The wide variety of polymers and fillers, including fibre types, fibre preparation techniques and possibilities for fibre surface modifications, open up opportunities to tailor the WPC materials to specific end-product requirements. Depending on the selected raw materials, additives and processing techniques, many of the advantages of a WPC result primarily from the low density and relative high strength of the plant fibres, their non-abrasive nature, biodegradability/recyclability and low cost [3,5,7,12,13,18,20–32]. Given the huge diversity of commercially available polymers, even having a same base composition, and the particular properties of each type of wood fibres, the optimization of composites for a certain application requires the specific study of the selected components, before and after being blended and processed as composite materials, in order to obtain the adequate final physical, chemical and mechanical properties.

In this work composites based on a selected grade of High Density Polyethylene (HDPE), pine wood sawdust (residues from a local furniture industry) and a coupling agent composed of PE-g-MA were produced. The objective of this study was focused in a particular application developed by a team of architects: an innovative shading system composed of shutter units that should be produced by extrusion [13]. The material requirements for this application included not only the low environmental impact (provided by the selection of a WPC with high content of wood filler), but also adequate mechanical properties and resistance to outdoor weather conditions, particularly to water absorption.

Nomenclature

HDPE high density polyethylene
WPC wood plastic composite
PE-g-MA maleic anhydride-grafted-polyethylene

2. Materials

The pine wood sawdust of variable and mixed mesh sizes was supplied by a local industry of production of furniture and of other indoor and outdoor wood commodities. The sawdust corresponded to residues which were obtained at different moments and at different spots of the factory, so as to obtain a reliable representation of the characteristics of this raw material.

The synthetic polymers were acquired to industrial suppliers: two different grades of HDPE traded under the designations HMA 035 from Exxon Mobile and KS 10100 UE from Dow Chemicals, and two coupling agents based on PE-g-MA supplied by Fusabond under the references E-226 and E-265. These polymers were selected based on the technical data from the producers, being the most relevant information (d=density, HDT=heat deflection temperature, T_m=melting temperature, MFR=melt flow rate (in standard tests with 2.16 Kg at 190 ºC), σ_y=tensile stress at yield, δ_y=tensile strain at yield, δ_b=tensile strain at break) summarized in Table 1. All polymers were in pellet form.

Cellulose and lignin, both with 99% purity, were acquired to Sigma Aldrich and used as received. These chemicals were used as references relatively to the wood samples.

Table 1 – Synthetic polymers used in this study: some thermal and mechanical properties from the respective Product Data Sheets.

Polymer	d (g/cm^3)	HDT (ºC)	T_m (ºC)	MFR (g/10 min)	σ_y (MPa)	δ_y (%)	δ_b (%)
HMA 035	0.964	72	134	8	26	9	>100

KS 10100 UE	0.955	128(Vicat)	-	4	25	-	>1600
E 226	0.93	95	120	1.75	-	-	-
E 265	0.95	-	131	12	-	-	-

3. Materials preparation and characterization

Wood particles

Two different batches (A and B) of pine wood sawdust were submitted to identical preliminary treatments to eliminate the moisture and to evaluate the variability of the residues supplied by the industry, namely regarding chemical composition, particle size distribution, apparent density and morphology.

The sawdust was dried in at 70 ºC for at least two days, being periodically turned over and weighed until constant weight was attained. Then, each batch was sequentially sieved through meshes of 2.8 mm, 1.4 mm and 0.7 mm. The obtained fractions were named as Fine (F), Medium (M), Coarse (C) and Extra (X), corresponding to the following particle sizes: F< 0.7 mm, 0.7 mm<M<1.4 mm, 1.4 mm<C<2.8 mm and X> 2.8mm. Each group of wood particles was weighed and the respective percentage was used to determine the particle size distribution of the supplied wood residues.

Moreover, the apparent density of each of the obtained fractions was estimated using an empirical method. Samples from each type (F, M, C, X) of wood particles were inserted in a graduated cylinder of 100 cm^3, slightly tapping the sawdust, but not compressing it. Then, the respective mass values were divided by 100. These tests were made in triplicates.

The characterization of the wood particles also involved FTIR analysis, DSC-TGA and SEM.

Synthetic polymers

The acquired polymers were dried at temperatures around 50 ºC to eliminate moisture from the pellets surface while avoiding thermal transitions that, typically, star to occur around 70 ºC in the selected polymers.

All of these materials were initially characterized using FTIR and DSC-TGA. Latter, as they were applied in the synthesis of composites, the polymers were also characterized as reference samples through torque rheometry, tensile testing, water contact angle and swelling in water.

Optimization of composites

The decision about which polymers should be selected to apply as matrix and coupling agent of the projected composite, as well as which size of wood particles, had to rely not only on the main properties of the isolated raw materials but, above all, on the diverse forms of interaction between such different materials. Being the viscosity of the melted composites a very strong limiting factor for the resulting quality of the final products, torque rheometry was selected as an essential technique for this study [3,33–35]..

Torque rheometry was used not only in the optimization of the composition of the WPCs, but also to prepare the composites and monitor the stability of the blended components. The measuring principle of this technique is based on the resistance that the material inside the chamber opposes to the rotation of the blades. Thus, the measured torque corresponds, in practical terms, to the viscosity of that material. As expected, torque values depend on the temperature of the material and on the rotation speed of the blades.

In this study, the composites were prepared as a function of the mass percentage, and not of the volume percentage of each component, because the wood particles constitute dynamic materials that deform and collapse during the mixing operation. Previous tests helped to determine that a rotation speed of 60 rpm was adequate to achieve the best commitment between the time required to stabilise the mixing torque and the effort needed to obtain an efficient mixture. This technique enabled to monitor the viscosity of the melted blends and to determine the critical concentration of solids (wood particles in this case), above which the blends cannot be processed or will result in composites with structural defects.

For each size range of wood particles (F, M, C), the optimization of a chemical composition for a composite involved the measurement of the effect of wood concentration in the viscosity of the melted blend containing each of the selected polymeric matrices. The methodology was based on the gradual addition of controlled amounts of wood particles to a certain amount of a melted polymer inside the mixing chamber [13,36,37]. Starting, for instance, with the addition of 10 g of HDPE HMA 035 inside the chamber at 160 ºC, after the stabilization of the temperature,

a fraction of 1 g of Fine wood was added after each 5 minutes of mixing. The wood particles addition continued until the torque variation shows that the wood concentration is excessive. In some cases, it is acceptable to make a first addition corresponding to a larger concentration of wood, e.g. 4 g, followed by successive fractions of 1 g. At all times, the concentration of wood particles in the system is well known and provided that the variables are controlled and the method is applied under similar circumstances to the systems at study, these adaptations of protocol normally provide reliable results. Moreover, the graphical representation of torque and temperature *versus* time from the equipment may be presented as function of the concentration.

After optimization of the chemical composition of the composites to a limited range of concentrations of some of the initial raw materials, the synthesis of composites was made using the same equipment of torque rheometry. This way, the experimental conditions were precisely the same, with the advantage of having a way to measure important parameters as torque and temperature.

In the synthesis of composites, the main polymer of the matrix was melted together with the coupling agent in the beginning of the process. Then, the wood particles were added in three steps, letting the torque stabilize between each addition. The melted composites were removed from the mixing chamber after the viscosity was stable for five minutes following the last wood particles addition. The melted composite material, removed with a spatula, was transferred to a surface where it had to be fragmented before turning cold and very hard to break. The small fragments were then used to prepare probes for other tests. The techniques applied in the characterization of the composites were the following ones.

Instrumental techniques

FTIR analysis

The vibrational spectra were obtained using a Nicolet Magna IR-750 spectrometer (Nicolet, Madison, WI, USA) in the attenuated total reflection (ATR) mode. The spectra were registered in the 500–4000 cm^{-1} region using 64 scans and a spectral resolution of 4 cm^{-1}. FTIR spectroscopy was used mainly to provide a qualitative analysis of the samples.

DSC-TGA

Simultaneous Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used to characterize the thermal properties of the reference samples and of the synthesized composites. These tests were performed using a SDT Q600 equipment (TA Instruments, New Castle, DE, USA), under nitrogen flow at a heating rate of 10 ºC/min from 25 ºC to 600 ºC. Samples ranged from 4 to 6 mg.

Torque rheometry

This technique, which provides an indirect measure of the viscosity of a material, was performed using a Plastograph Brabender equipped with a mixing chamber of 55 cm^3. The rotation speed was set to 60 rpm and the temperature to 150-190 ºC, depending on the selected polymers.

SEM

Scanning Electron Microscopy (SEM) observations were carried out in a Philips XL30 microscope (Philips, Amsterdam, Netherlands) operating at 20 kV. The samples prepared for SEM analysis were isolated wood particles and composites of diverse chemical compositions. The composites were immersed into liquid nitrogen and subsequently fractured so as to expose the interior section without deformations from cutting tools. The samples were coated with a thin layer of gold by plasma sputtering during 5 to 10 seconds.

Tensile testing

Specimens with a mean rectangular cross-section of 3.3x2.5mm and 63.5mm of length were produced using a compression moulding technique and submitted to tensile tests using an INSTRON 4505 equipment. Experimental tests are performed with a velocity of 1mm/min in accordance with ASTM D 638-2a. Tests were run in triplicates.

Water contact angle measurements

The surface wettability was determined with contact angle system OCA from Dataphisics, using distilled water as test liquid and Sessile Drop Dispense at medium velocity, using a Hamilton syringe of 10 µl. The results were averaged from 10 measurements for each sample.

Water immersion tests

The swelling capacity was determined by immersion of the probe samples in water for a 24 hours period. The probe samples, with an identical configuration to that of the tensile tests, were periodically weighted after removing the surface moisture with a cloth and the weight variation was expressed as a percentage of the initial value. These tests were performed in triplicates.

4. Results and discussion

Wood particles

The pine wood residues from two different batches (A and B) which were sieved and weighed had the particle size distribution that is represented in Figure 1. In both cases, almost 50% of the supplied sawdust corresponded to particles inferior to 0.7 mm. These were classified as Fine (F), while the other size ranges which corresponded to around 35 %, 10% and 5% were respectively named as Medium (M), Coarse (C) and Extra (X). The X fraction was discarded from this study because the particles were too heterogeneous.

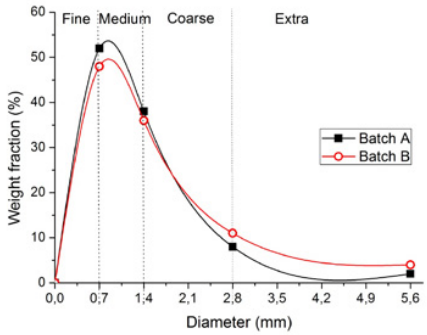

Fig. 1 – Particle size distribution of the supplied pine wood particles. The sawdust residues from batches A and B present similar profiles.

The FTIR spectrum of the pine wood samples is shown in Figure 2, together with the spectra from cellulose and lignin, the reference samples corresponding to the main components of wood. The wood spectrum results from the contribution of these two components, being some of the main features of the wood spectrum very similar to those of cellulose, as the intense band around 1206 cm^{-1}. The peaks at 1263 and 1511 cm^{-1} are mainly derived from the contribution of lignin. The 500-2000 cm^{-1} spectral region contains the bands assigned to the functional groups of these samples while the region of 2500-4000 cm^{-1} contains the large bands typically originated by elongation of C-H, N-H and O-H bonds of small chemical groups. Thus, the first region is more important regarding the use of vibrational spectra to identify chemical components from a material as, for instance, a composite.

The DSC-TGA results from pine wood presented in Figure 3 show a weight loss of about 10 % wt. in an endothermic process occurring at temperatures inferior to 100 ºC. This event is consistent with the loss of bond water from the wood sample. Between 100 and 300 ºC, the weight changes with temperature were neglectable. However, from 300 to 380 ºC, the sample lost around 60% wt in another endothermic process. The residue of 30 wt% at 380 ºC still decreased to 20 wt% at 600 ºC. These results agree with a 10% content of water, 60% of

cellulose and hemi-cellulose and 20% lignin in the analysed pine wood samples.

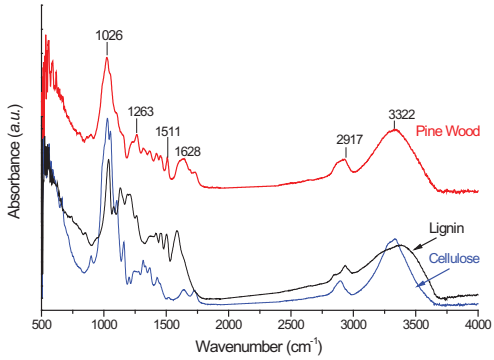

Fig. 2 – Vibrational spectrum of pine wood compared to cellulose and lignin, the main components of wood.

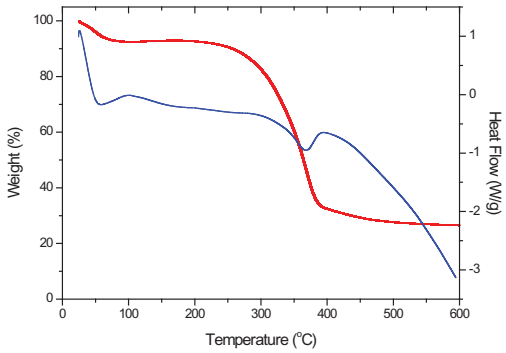

Fig. 3 – Thermogravimetry results of pine wood under inert atmosphere.

The physical appearance of the pine wood particles may be observed in Figure 4 at images obtained using SEM at low magnification values. The size range of the particles is relatively narrow since the sample under observation corresponds to a sieved fraction, the Fine range in particular. The wood particles present its traditional tri-dimensional structure with hollow lumen spaces visible in the cross-section.

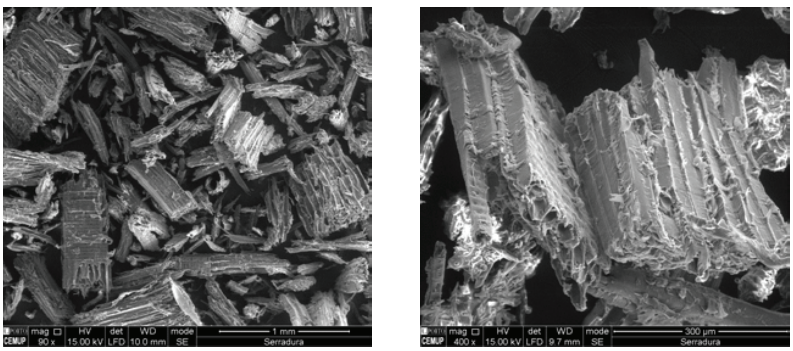

Fig. 4 – Size and morphology of the pine wood particles observed through SEM.

Synthetic polymers

The main results from the characterization of polymers are presented in Figures 5 and 6, respectively from FTIR spectroscopy and DSC-TGA.

The most interesting observation relative to FTIR results is that all spectra were identical with a medium intensity peak at 720 cm^{-1} assigned to CH_2 rocking, another at 1466 cm^{-1} due to C-C-C bending deformation and two intense peaks at 2842 and 2917 cm^{-1} which were attributed to CH_2 asymmetric and symmetric stretching respectively [38]. The fact that both of the modified polymers (E-226 and E-265) did not originate any vibrational bands from the maleic anhydride grafted moiety shows that the extent of chemical modification of the Fusabond polymers was very low in both cases. This result indicates that the use of these polymers as coupling agents between HDPE and wood may require high concentrations in order to have enough maleic anhydride groups to react with hydroxide bonds from the cellulosic components of wood [8,17].

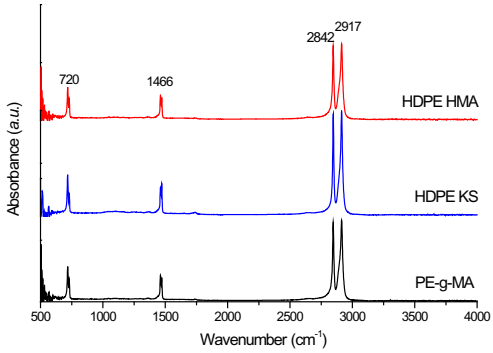

Fig. 5 – Vibrational spectra of two grades of HDPE (HMA 035 and KS 10100 UE) and of PE-g-MA (E-226 and E-265).

The HDPE polymers previously selected for this study, HMA 035 and KS 10100 UE, were chosen based on their thermal and mechanical properties. Regarding the physical and chemical transitions with temperature, DSC-TGA results (Figure 6) showed that the behaviour of both polymers is very similar but the softening, melting and degradation temperatures of HMA 035 (52, 138 and 488 ºC, respectively) were slightly superior to those of KS 10100 UE (50, 136 and 483 ºC, respectively). The obtained values did not match but were close to those provided by the manufacturers. Both polymers were very stable until 450 ºC and the degradation was complete before reaching 500 ºC. This set of results, together with data from MFR, indicates that the HMA 035 polymer should be more adequate to the application proposed in this study. The higher transition temperatures are important in a final product that is meant to be exposed to a wide range of environmental conditions. On the other hand, the higher MFR of HMA 035 (8g/10 min, according to the supplier) enables to anticipate an easier processing of the composites with this polymeric matrix.

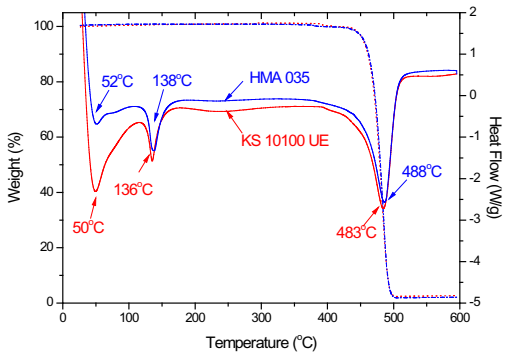

Fig. 6 – Heat flow and thermogravimetric graphics from HDPE HMA 035 and HDPE KS 10100 UE, showing the temperatures of the main transitions (softening, melting and degradation) by DSC and weight variations by TGA.

Optimization of composites

In order to select the main HDPE polymer to constitute the composite matrix and to select the size range of wood particles, diverse tests of torque rheometry were performed. These tests were also essential to determine which polymer could be mixed with a larger amount of wood particles and find the most appropriate concentration of wood filler regarding processing conditions and final properties of the composites. The objective was to maximize this filler content since this enables the substitution of the synthetic polymers for sustainable and recyclable materials.

As previously described, the optimization was performed through the gradual addition of known amounts of wood particles to a constant amount of melted polymer, recording the torque values and temperature across the assays. Figure 7 illustrates the form of the graphics resulting from this methodology. In this particular experiment, the test started as 10 g of HDPE HMA 035 was added to the mixing chamber at 160 ºC and with the blades rotation speed at 60 rpm. The torque value reached 9 Nm for some seconds and then stabilized at about 6 Nm, being this value nearly constant from 10 to 25 min of mixing. The temperature inside the chamber decreased when the polymer pellets were introduced inside it, increasing again to the initial value as the polymer melted. Next, a fraction of 4 g of Fine wood particles and following fractions of 1 g were added at each 7 minutes. The steps observed in the torque graphic show that each addition of sawdust caused an increase in the effort made by the rotating blades, meaning that the viscosity increased gradually and reached a state of equilibrium until a concentration of 11 g of wood in 10 g of HDPE was reached. The melted blend could support 2 g more of wood particles but the torque variation was inverted. This corresponded to having over crossed the critical concentration of filler content. In this test, the last addition corresponded to 1 g of E-226 causing a slight stabilization of the torque variation, which agrees with the expected effect of enhancing the interaction between the main polymer and the wood filler. In general, the temperature variation along the test corresponded to a decrease at each moment of fraction addition, but to a global increase due to the augment of friction between the wood particles in the melted blend.

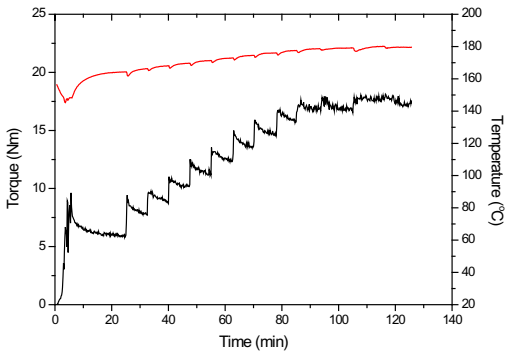

Fig. 7 – Torque and temperature measurements in the optimization of composites of HDPE HMA 035 and Fine wood particles.

After performing similar tests with both HDPE polymers and sawdust from batch A and B, of Fine, Medium and Coarse particle size ranges, the obtained graphics from the plastograph equipment were expressed as function of the filler content, as exemplified in Figure 8. The graphic is relative to blends of HMA 035 and sawdust from Batch A. The results show that the Fine particles enabled to prepare composites with higher filler content and with lower viscosity than with Medium and Coarse particles that revealed an opposite tendency with the particle size variation. The torque rheometry applied to KS 10100UE provided very similar results regarding the global behaviour of the blends with the diverse wood samples, as presented in a previous work [13]. However, the subtle differences were enough to allow the use of a larger filler concentration under more favourable experimental conditions to obtain, according to the expectations, composites with better performance for the projected applications.

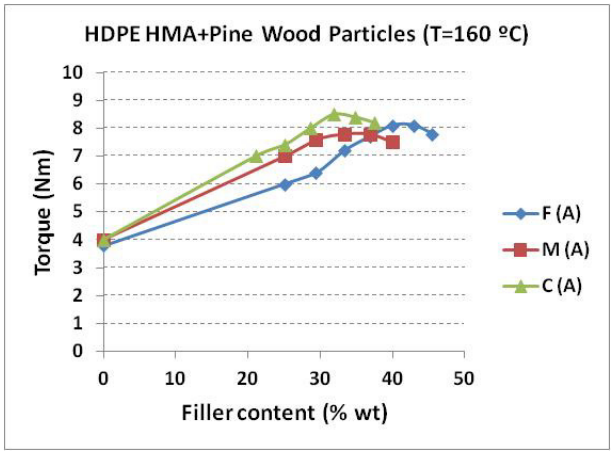

Fig. 8 – Torque rheometry applied to the optimization of composites made of HDPE HMA 035 and wood particles of diverse size ranges (Fine, medium, Coarse) from batch A.

In order to show, in practical terms, what happens to the polymer-filler blends before and after the critical concentration is reached, Figure 9 illustrates the appearance of the materials inside the plastograph mixer during the implementation of optimization tests for the composites of HDPE and wood particles: the left picture shows a white material which is an isolated melted HDPE polymer. It has a smooth appearance and forms a continuous layer over the blades. The picture in the middle corresponds to a blend of HDPE and wood particles in such a concentration that the resulting material is dark brown and the texture is still continuous and smooth. The picture at the right side corresponds to a blend where the critical concentration of wood particles was over crossed. The texture of the material is different from the latter examples, with a broken appearance.

In the case of the blends of HMA 035 with Fine wood particles from the rheometry test of Figure 8, the images of Figure 9 correspond, from left to right, to filler contents of 0 %wt, 30-40 % wt and to 42 % wt. The adequate viscosity for processing the composites required a filler concentration inferior to 40% wt, the critical concentration for this system. These results justify the selection of concentrations between 30 and 40 %wt for the filler, and the remaining 60-70% wt for the polymeric matrix, to carry on the optimization process of the composites using variable concentrations of coupling agents. The selected compositions are described in Table 2.

Fig. 9 – Appearance of the materials inside the plastograph mixer along the process of optimization of composites:

It should be mentioned that the blends prepared during the optimization process had, at the end of each test, an excessive concentration of wood particles. Therefore, in order to test the most favourable combinations of components, the composites of Table 2 had to be prepared individually.

Table 2 – Chemical composition of the composites: relative content of HDPE HMA 035, Fine pine wood particles and PE-g-MA as coupling agent (E226 for probes A-J and E265 for probe J*).

Probe	HDPE HMA 035 (% wt)	Pine Wood (% wt)	E226/E265* (% wt)
A	100	0	0
B	60	40	0
C	55	40	5
D	50	40	10
E	45	40	15
F	65	35	0
G	55	35	10
H	70	30	0
I	60	30	10
J	50	30	20
J*	50	30	20

Synthesis of composites

The synthesis of composites with the compositions described in Table 2 was conducted using the plastograph mixer so that torque and temperature could be monitored as exemplified in Figure 10.

In the example of Figure 10, the first two peaks of the torque profile correspond to the addition of HDPE, followed by PE-g-MA. After stabilization of the mixed polymers, the wood particles were added in three steps, letting the torque stabilize in between. The growing viscosity of the melted blend agrees with the increase of filler content. Moreover, compared to the graphics of the optimization process, each step of the torque profile denotes a higher stabilization of the blend because of the preliminary addition of the coupling agent. The temperature profile shows a decrease at each moment of material addition into the chamber, but a gradual increase as the concentration of sawdust was augmented.

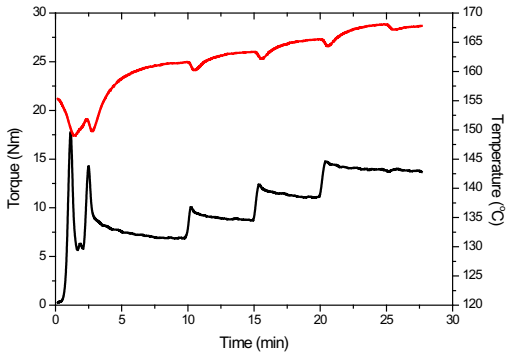

Fig. 10 – Example of the monitoring process by torque rheometry of the synthesis of composite G.

Each composite of Table 2 was also analysed using FTIR, DSC-TGA and SEM.

Figure 11 illustrates the FTIR results obtained with composite G that contains 55% HMA 035, 35% Fine wood particles and 10% E-226 as coupling agent. The FTIR spectrum of the composite shows all the most intense peaks from each component. The bands at 600, 1030, 1240, 1640 and the broad band at 3356 cm^{-1} clearly originate from the pine wood whereas the narrow peaks at 725, 1471, 2842 and 2917 cm^{-1} are from the HDPE polymer. The small intensity band at 1731 cm^{-1}, typically from a carbonyl stretching vibration, may be originated from the coupling agent since maleic anhydride should absorb at that wavenumber [15,18,21,38].

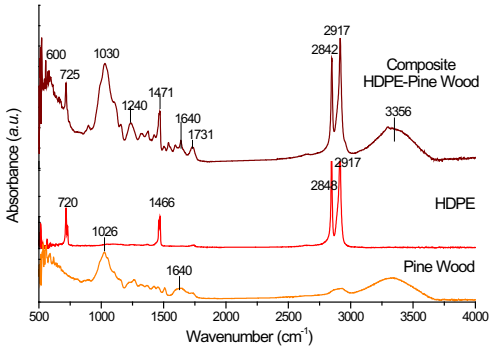

Figure 11 – Vibrational spectra of composite G compared to those of its main components (HDPE and pine wood particles).

The DSC-TGA results from most of the probes of Table 2 is presented in Figures 12 and 13 separating data from weight loss and heat flow to simplify the observation of the graphics. The reference sample, probe A which is 100 % composed of HMA 035, is included for comparison. The probe samples B, D, F, G and J represent samples with 40, 35 and 30% of wood particles but the corresponding weight loss that occurred around 300-350 ºC in all samples was, according to Figure 12, 5-10% inferior to the expected values. Since this technique requires just a few milligrams of material for each sample, the fragments under analysis had to contain wood particles inferior to the medium size range of each category. This means that the polymeric percentage was higher in the analysed samples.

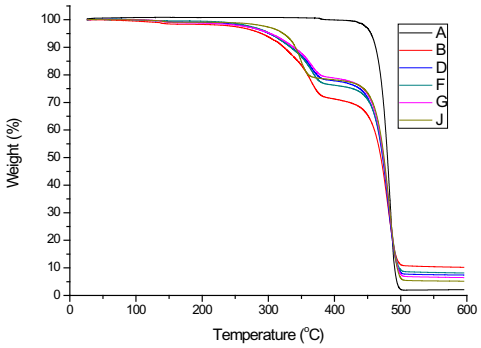

Figure 12 – TGA results from probes A, B, D, F. G and J.

As for DSC the results show that the transitions observed in the reference sample also occurred in the composite probes, namely softening, melting and degradation around 50, 140 and 450 ºC. Moreover, all samples from composites also presented an endothermic peak between 300 and 350 ºC, which corresponded to the degradation of the wood component of the composite. The obtained data did not allow observing any energetic advantage regarding the use of coupling agents in some of the probes. This may be due to the low content of maleic anhydride in E-226 and E-265 as previously discussed.

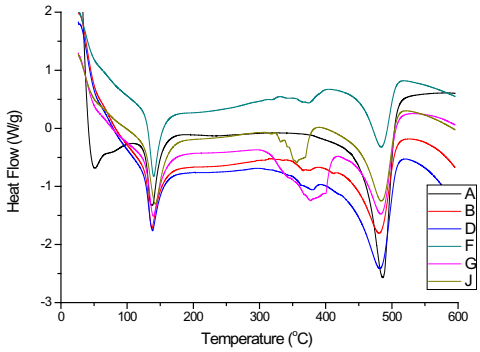

Figure 13 – DSC results from probes A, B, D, F. G and J.

The composites were also characterized regarding microstructure trough SEM analysis. The G probe depicted in Figure 14 shows that that the wood particles were evenly distributed in the composite matrix. At high magnification, the surface characteristics of the wood particles were clearly distinguished from the polymeric matrix and a strong interfacial adhesion between these components could be explained as resulting from the observed physical interaction, as well as from the chemical bonding resulting from the use of E-226. All the other samples that contained a high percentage of coupling agent showed similar features regarding the enhanced interfacial adhesion as compared to samples without that component.

The mechanical properties of the composites A-J containing variable contents of HMA 035, wood particles and E-226, and of J* probe that is similar to J but contains E-265 instead of the latter coupling agent, were evaluated through tensile tests. The corresponding stress-strain curves are presented in Figures 14-17 and the results are summarized in Table 3. The stress at maximum load of the reference sample, probe A, is similar to the value reported in the technical date sheet but the obtained strain value was much inferior to the supplied value.

Table 3: Mechanical properties of the WPC produced.

Probe	Stress at Maximum Load (MPa)	Strain at Maximum Load (%)
A	28.5	2.96
B	23.8	0.57
C	21.3	0.75
D	23.5	0.78
E	23.1	0.95
F	23.7	1.23
G	21.8	1.11
H	20.3	1.29
I	19.8	1.04
J	22.0	0.89
J*	25.4	1.65

From Figure 14, where composites containing 30, 35 and 40% wt of wood particles and without coupling agent are compared, it can be concluded that, in general, with the increase of the wood particles content, the stiffness of the composites increase since higher values of the filler content correspond to higher tensile strength values and lower strain values. The probe B, in particular, shows higher stiffness since the obtained curve is almost linear and fracture occurs at very low deformation extent. Conversely, the composite containing less filler content shows the higher deformation and lower stress at maximum load. This trend concerning the filler content was also reported in the literature [9,20,34,39,40].

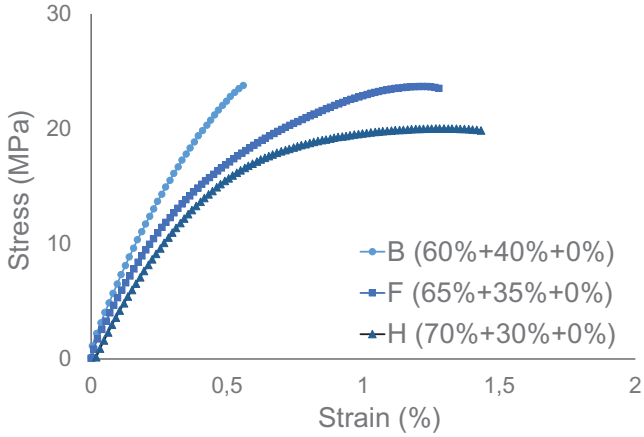

Fig. 14 - Influence of wood particle content on the composites mechanical behaviour for a PE-g-MA content of 0 wt.%.

Comparing probes I, G and J, with 30, 35 and 40 % wt filler content but with 10% wt of coupling agent E-226, the behaviour observed in Figure 15 is similar to that reported in Figure 14, with the exception of the lower deformation extent of all probes. This may be attributed to the effect of the coupling agent in enhancing the interfacial adhesion of the composite components, causing the fracture to occur earlier in the test. Nevertheless for the highest filler content, 40 % wt, the opposite trend is observed: with the addition of 10% wt of PE-g-MA an increment of the composite strain is obtained without loss of tensile strength [9,20,34,39,40].

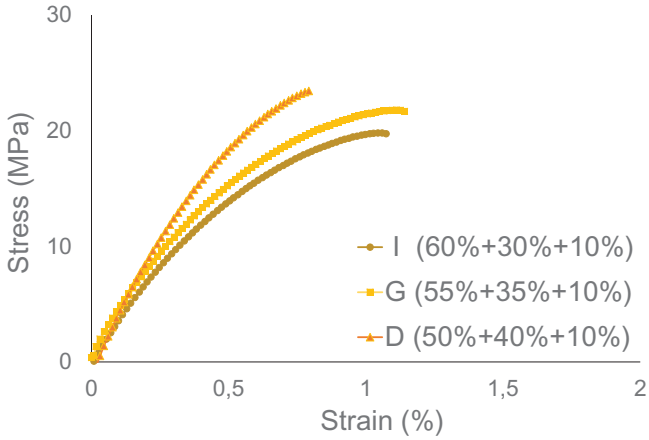

Fig. 15 - Influence of the filler content on the composites mechanical behaviour for a PE-g-MA content of 10 wt.%.

Concerning to the influence of PE-g-MA content on the composites mechanical behaviour, Figure 16 represents the stress-strain curves obtained for the composites produced with 40 % wt wood particles and different contents of E-226. The increasing content of this coupling agent leads to higher strain values without significant loss of tensile stress values. This corresponds to an increase in the toughness of the composites.

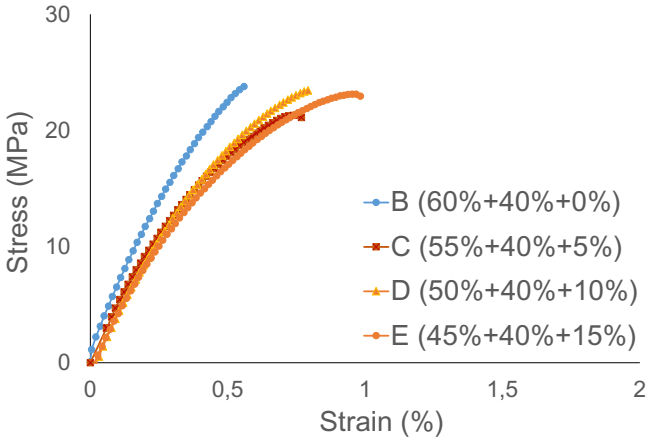

Fig. 16 - Influence of PE-g-MA content on the composites mechanical behaviour for a wood particle content of 40 wt.%.

In Figure 17, the stress-strain curves compare composites containing 30% wt of wood particles and E-226 as coupling agent, as well as E-265 for one of the probes (J*). It is interesting to perceive that the effect of E-226 is similar to that described for other filler contents. As the coupling agent content increases, the strain is reduced probably due to higher interfacial adhesion in the respective composites. However, the addition of E-265 reveals a different behaviour and the J* probe achieves the highest stress, as well as highest strain values of all studied composites. This corresponds to the sample with the greater toughness, that is, the one with better performance for absorbing loading forces.

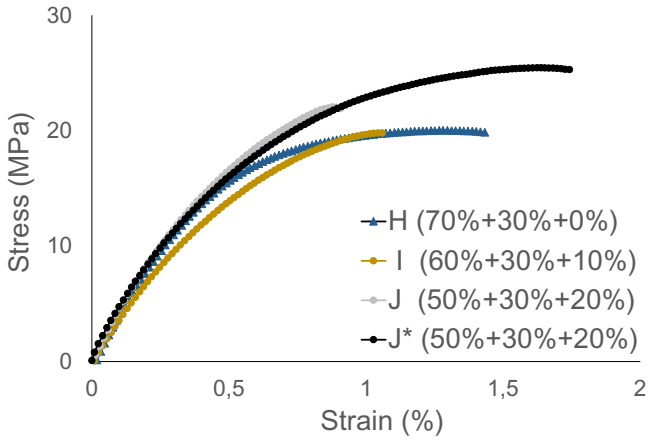

Fig. 17 - Influence of PE-g-MA content and type (E-226, E-265) on the composites mechanical behaviour for a wood particle content of 30 wt.%.

The water contact angle and the swelling results of the composites are expressed in Table 4. Whereas the first parameter reflects the wettability of the surface of the composites, the latter shows the water retention in the core of the materials. As expected, the reference sample (probe A, 100% HDPE) has a water contact angle superior to 90º, equal to 94º, denoting a hydrophobic surface, and a very reduced mass variation (0.2 %) after immersion in water. The surfaces of most of the composites (B, C, D, E, F, H and I) have some hydrophilic character due to their high content in wood particles, reflected in contact angle values around 77º-84º. The swelling of these composites agrees with that tendency since their mass variation reaches 10% relative to the initial value. Interestingly, probes G, J and J* have higher contact angle values than probe A, meaning that their surface is more hydrophobic than the isolated polymer. These same probes have also the lower mass variation values (3, 4 and 3% respectively), meaning that the absorbed water was very low for composites with 30 to 35 % wt wood particles. The reason for this hydrophobic behaviour is based on the high content of coupling agent of these samples. The effect of increasing the interfacial

adhesion between the wood particles and the polymeric matrix, besides causing an increase in the tensile strength of the composites, also increases the density of the materials, offering more resistance to the surface contact and core entrance of water molecules inside the composites.

Table 4- Water contact angle and swelling of the composites

Probe	Angle (º)	Mass variation (%)
A	94	0.2
B	77	10.0
C	78	7.0
D	84	5.5
E	82	6.0
F	84	9.0
G	107	3.0
H	79	9.0
I	88	7.5
J	98	4.0
J*	120	3.0

The methodology which was followed from the start of this work involved two main stages, as represented in Figure 18. The first stage concerned the selection and characterization of the raw materials and preliminary treatment procedures to ensure that their inherent variables would be controlled throughout the whole study. It involved diverse optimization tests to narrow the range of possible raw materials or, more precisely, to determine with accuracy which particular properties were more adequate for the composites. In the second stage, the optimization continued with further tests applied to a limited range of combinations of components. The Medium and Coarse fractions of the wood residues were discarded and only the Fine fraction passed from the first to the second stage. The range of wood particles concentrations was limited to values between 30 and 40% wt and the HDPE polymer, preferably HMA 035 for the mentioned filler contents, varied between 60 and 70%. The effect of different coupling agents, with concentrations of 5, 10, 15 or 20% wt was also considered, meaning that these percentages were reflected in the subtraction of the same amounts of HDPE. The detailed characterization of all the combinations described in Figure 18 enabled determining chemical, physical and mechanical properties of the composites, collecting valuable information to better adapt each WPC to a final product, considering also its processing technology.

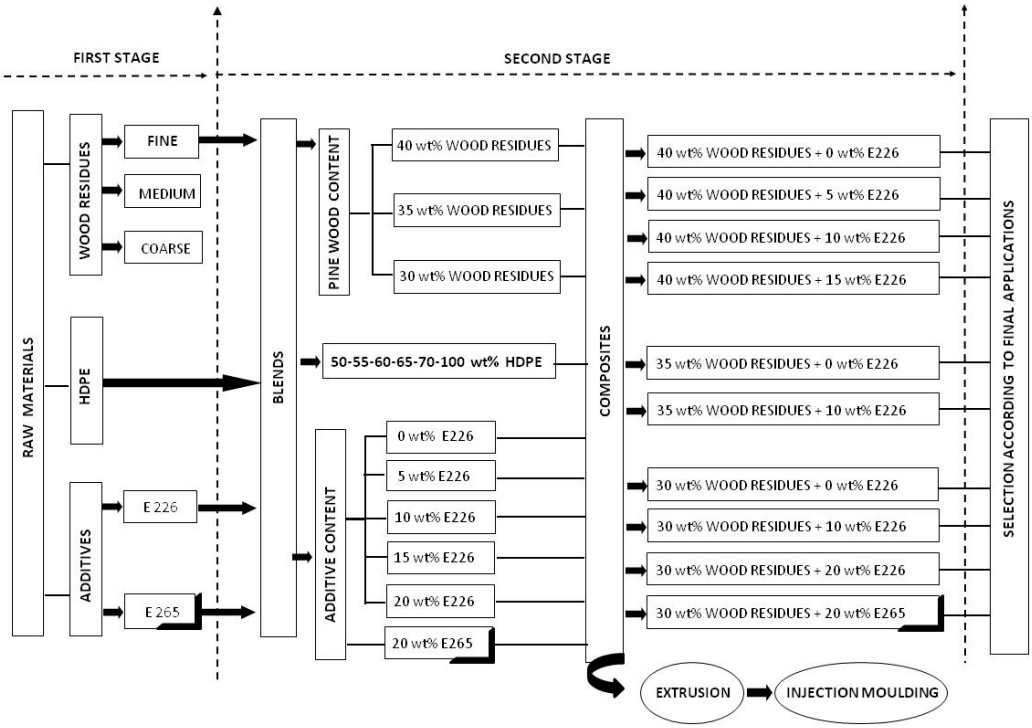

Fig. 18 – Diagram representing the methodology for qualitative and quantitative selection of components to obtain the projected composites.

5. Conclusions

From the objective of synthesising a WPC for an innovative shading system, this study enabled the implementation of a methodology to search for the most adequate properties of composites made of pine wood residues in a matrix of HDPE and PE-g-MA. The composites were optimized and characterized using FTIR, DSC-TGA, SEM, torque rheometry, tensile testing, measurements of water contact angle and water absorption capacity through diverse standard tests. These techniques were used to access the chemical composition, thermal behaviour, microstructure, viscosity, mechanical properties, surface wettability and swelling of the composites.

The results showed that the composites with better properties for the projected application were made of 55% wt HMA 035, 35% wt Fine wood particles and 10% wt E-226. This proportion of components originates a composite that can be processed by extrusion and has enough mechanical strength (22 MPa) to be applied as a shutter unit from a shading system. The high mechanical strength derives from the high filler content and also from the good interfacial adhesion, which was caused by the addition of the coupling agent. The bonding between the composite components, corroborated by SEM observations, contributes not only to the mechanical properties, but also to the augmented resistance against water, as shown by the hydrophobic behaviour of the material surface and low water absorption in immersion tests.

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