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Mechanical and interfacial properties of wood and bio-based thermoplastic composite

Fabien Sliwa [a,c,*], Nour-eddine El Bounia [a], Fatima Charrier [b], Gérard Marin [c], Frédéric Malet [d]

[a] Canbio, Hélioparc, 2 Av. du Président Angot, 64053 Pau Cedex 09, France
[b] IPREM-EPCP, UMR CNRS 5254, Université de Pau et des Pays de l'Adour, IUT des Pays de l'Adour, 40004 Mont de Marsan Cedex, France
[c] IPREM-EPCP, UMR CNRS 5254, Université de Pau et des Pays de l'Adour, Hélioparc, 2 Av. du Président Angot, 64053 Pau Cedex, France
[d] ARKEMA CERDATO, PSM 27470 Serquigny, France

ABSTRACT

The aim of this investigation was to study a new family of wood polymer composites with thermoplastic elastomer matrix (pebax® copolymers) instead of commonly used WPC matrices. These copolymers are polyether-b-amide thermoplastic elastomers which present an important elongation at break and a melting point below 200 °C to prevent wood fibers degradation during processing. Moreover these polymers are synthesized from renewable resources and they present a hydrophilic character which allow them to interact with wood fibers. We have used two pebax® grade with different hardness and three types of wood fibers, so the influence of the matrix and wood fibers characteristics were evaluated. Composites were produced using a laboratory-size twin screw extruder to obtain composite pellets prior to injection moulding into tensile test samples. We have evaluated fibers/matrix interaction by differential scanning calorimetry (DSC), infrared spectroscopy (IRTF) and scanning electron microscopy (SEM). Then, the mechanical properties, through tensile test, were assessed. We also observed fibers dispersion into the matrix by tomography X. DSC, IRTF and SEM measurements confirmed the presence of strong interface interactions between polymer and wood. These interactions lead to good mechanical properties of the composites with a reinforcement effect of wood fibers due also to a good dispersion of fibers into the matrix without agglomerate.

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1. Introduction

The use of raw materials derived from renewable resources has grown rapidly in recent years in both industrial applications and research works. Natural fiber reinforced polymer attracted attention because of their low cost, low density, low abrasion and good specific mechanical properties. The utilization of vegetable fibers is driven by growing market trends in terms of environmental impact. The most common composites with natural fibers are made with Polyolefin (polyethylene PE and polypropylene PP) and polyvinyl chloride (PVC) matrices and wood fibers as reinforcement. PVC based composite has grown due to its superior performance and excellent weatherability compared to polyolefins [1–4], however PVC is subject of discussion regarding to its environmental impact notably due to the heavy metals stabilizers which can be used and its low recycling rate.

In previous investigations [1,2,5–12] it has been shown that the properties of WPCs depend on several factors such as the characteristics of matrix and fillers, the fractional composition of wood fillers, chemical interaction between wood fibers and polymer, humidity absorption and processing conditions. One of the main issues is the compatibility between fibers and the polymer. The hydrophilic character of wood fibers contrasts with the hydrophobic character of the matrices, leading to poor adhesion between matrices and fibers. That is why to obtain good mechanical properties it is necessary to use polar polymers or polymers with groups able to interact with wood fibers. The compatibilization between fibers and matrices have to be improved. The main solutions to improve mechanical properties, resistance to water absorption and fibers dispersion are the use of coupling agents, pre-treatment of wood fiber and/or the polymer through surface coating treatment or graft co-polymerization.

Another difficulty from a technological point of view is the low thermal resistance of wood fibers, their thermal degradation begins around 200 °C. This temperature depends on the wood species and composition. Therefore to avoid this thermodegradation it is necessary to use a matrix with a relatively low melting point [12–17].

In order to overcome the constraint reported previously for the elaboration of WPC, we have selected pebax® copolymers as

* Corresponding author at: Canbio, Hélioparc, 2 Av. du Président Angot, 64053 Pau Cedex 09, France.
  E-mail address: fabien.sliwa@laposte.net (F. Sliwa).

matrix. Pebax® is polyether-b-amide thermoplastic elastomers which confer good specific mechanical properties such as a high elongation at break. Moreover it has a melting point below 200 °C helping to prevent wood fibers degradation and a hydrophilic character which enables it to interact with wood fibers. Pebax® copolymer consists of rigid polyamide segments, acting as physical cross links, and flexible polyether segments, its properties depend on the polyether/polyamide ratio [18–22].

Furthermore, another reason to select this polymer is that it comes from renewable resources. This is a good point as our final objective is to elaborate a composite mainly issued from natural resources: bio-based composites.

Thanks to its properties, such as elastomeric behavior, high elastic recovery and hydrophilic character, pebax® defined as a technical polymer. This is why, contrary to most of WPCs based on polyolefins or PVC matrices, one can imagine very specific and technical applications for this composites. Furthermore, due to the hydrophilic character, it is expected that the use of a compatibilizing agent is not needed.

In the present work, we have firstly studied the interaction between wood fibers and pebax® matrices using differential scanning calorimetry, infrared spectroscopy and scanning electron microscopy. The objective was to evaluate the compatibility between filler and matrix. Therefore, the mechanical properties of composites have then been evaluated. Tensile tests and hardness tests have been carried out to obtain Young modulus, elongation at break and hardness of composites.

Remark : In this paper, the terms "fiber" or "flour" will be used to talk about wood fillers.

2. Experimental

2.1. Materials

The raw materials used in this study were three types of wood flour and two grades of pebax®. The wood flours (WFs) characteristic are summarized in Table 1.

The first wood flour (WF1) was supplied by Rettenmaier (Spruce wood referenced C120 [23]).

The second wood flour (WF2) come from Maritime Pine which has been ground and sieved at a laboratory scale in the Sylvadour Laboratory, Mont de Marsan, University of Pau and Pays de l'Adour (France).

The third wood flour (WF3) is a Maritime Pine wood produced at an industrial scale by Canbio (1 tonne) in order to have a representative and homogenous sample.

Pebax® 25R53 SP01 and pebax® 55R53 SP01 copolymers were supplied by Arkema (CERDATO, Serquigny, France) in powder form. In this article, copolymers will be respectively quoted as pebax®25 and pebax®55. Pebax® is a hard/soft bloc-copolymer. The hard phase is a polyamide and the soft one is a polyether. The two copolymers were selected in order to have two hardness levels and a melting points below 200 °C. Pebax®25 and pebax®55 have

respectively a tensile moduli of 15 MPa and 145 MPa and melting temperatures of 136 °C and 167 °C.

2.2. Processing

2.2.1. Compounding

Before compounding, WFs were dried at 105 °C during 6 h and pebax® at 60 °C under vacuum during 5 h. The two components WFs and pebax® were dry-blended prior to extrusion. Then, compounding was carried out using a laboratory-size twin screw extruder (Thermo Scientific, Eurolab 16) in order to produce homogeneous pellets with different levels of filler content (from 10 to 50 wt.%, WFs). The extruder barrel temperature ranged from 90 °C to 170 °C (die temperature).

2.2.2. Molding

Prior to injection molding, the pellets were dried during 16 h at 80 °C. Then, dumbbell tensile test samples (ISO 527-2, type 1A) were injected using a 65-ton DK injection molder. The mold temperature was set at 15 °C and the barrel profile temperature of the injection machine ranged from 160 °C to 200 °C depending on composites wood filler content.

2.3. Testing and analysis

2.3.1. Differential scanning calorimetry (DSC)

Matrix and composites were analyzed with a nonisothermal differential scanning calorimetry analyzer (DSC) from TA instruments (Q100) to access their thermal properties: melty (T_f) and cristally (T_c) temperatures, and fusion/crystallization enthalpies H_c and H_f.

The samples were heated up to 210 °C at 10 °C min^{-1} and held for 1 min at this temperature. Then, the samples were cooled at 10 °C min^{-1} from 210 °C to −60 °C. A second heating is performed at 10 °C min^{-1} from −60 °C to 210 °C. All the experiments were carried out in sealed pans under dry nitrogen environment.

2.3.2. IR spectroscopy

FTIR spectroscopy was conducted to analyze of interaction between wood and matrix. For each sample, 200 scans were recorded in absorbance units from 4000 to 700 cm^{-1}. Spectra were obtained using attenuated total reflectance mode (ATR). Composite surfaces analyzed were in contact with a ZnSe crystal with a 45° angle of incidence. At least three replicate samples were analyzed.

2.3.3. Scanning electron microscopy

The fractured surface of composites, obtained by cryo-breakage under liquid nitrogen, was examined using an environmental scanning electron microscopy (ESEM). The advantage of using ESEM is that coating metallization of composites surfaces is not needed for analysis.

Surface characteristics were analyzed at 25 kV accelerating voltage. The objective of this analysis was to study the interfacial morphology of the composites and interaction between wood and matrix.

2.3.4. Mechanical properties: tensile test

The tensile tests were conducted according to ISO 527-2 on an Instron universal testing machine with 5 kN load cell, using dumbbell sample type 1A. A crosshead speed of 1 mm min^{-1} was used for Young modulus determination and 50 mm min^{-1} for the evaluation of elongation at break. All the mechanical measurements were carried out at took temperature (23 °C +/1 °C) and relative humidity of 50 ± 5% . It should be noted that the mechanical property results of the composites reported in this work are the average of five independent specimens.

Table 1
Wood fibers characteristics.

Characteristics	Lignocel C120	Maritim pine wood	Maritim pine wood
Reference	WF1	WF2	WF3
Wood species	Spruce	Maritim pine	Maritim pine
Particle size range (µm)	60–450	60–1000	0–600
Cellulose (%)	∼50	∼42	∼42
Lignin (%)	∼25	∼28	∼28
Hemicellulose (%)	∼25	∼27	∼27

2.3.5. Tomography

In order to visualize wood flour dispersion and their size, composites samples were examined using a high-resolution computed tomography system. The dimension of examined volume of all samples were $(3.6–3.8) \times (2.8–3.8) \times (0.94–1.43)$ mm^3.

3. Results and discussion

3.1. Study of polymer–wood interactions

We will focus ourselves on the result obtain for the composites pebax®25 and wood flour WF1. A similar feature was observed for the others composites pebax®25/WF2, WF3 and pebax®55/WF1.

The first analysis performed to evaluate interaction polymer–wood is differential scanning calorimetry (DSC). The objective is to investigate wood addition influence on thermodynamic transitions of the matrix: crystallization and melting.

Only the crystallization process was affected by wood addition, hence, we will only present the crystallization results in this part of our work.

On the Fig. 1, a thermogram related to cooling after a first heating scan of pebax®25 and composites containing 10–50 wt% wood flour.

Pebax®25 shows three crystallization peaks, two of them are related to polyamide phases (peaks at T_{c1} 48 °C and T_{c2} 67 °C) the third is associated with polyether phase at −13 °C. It has been reported in the literature that the two peaks for polyamide segments are related to two crystalline phases. It is also reported that crystallization enthalpy and temperature (H_c and T_c) of pebax® copolymer depend on the polyether/polyamide ratio [18,20,24].

In order to compare neat copolymer to composite we have normalized ΔH_c since only the polymer participate to the crystallization process. There is no significant change for polyether phase. For polyamide phase ΔH_c shows a little decrease when the wood content increases. This effect is linked to the interactions between wood and polymer: chains of polymer bounded to the wood are excluded from crystallization process, that is why there is a little decrease of ΔH_c [13,25,26].

We can also note a change of crystallization temperatures T_c of polyamide phase for composites but not for the polyether phase. The introduction of wood leads to a decrease of 5 °C of the T_{c1} crystallization temperature and an increase of 10 °C of T_{c2} crystallization temperature for polyamide phase of pebax® in composites. From these first results, we show an influence of wood on polyamide phase of pebax® structuration. It can be also concluded that wood flour play a role of nucleating agent.

In order to confirm these results, we have prepared a polyamide/wood flour composite. Polyamide 11 which compose the
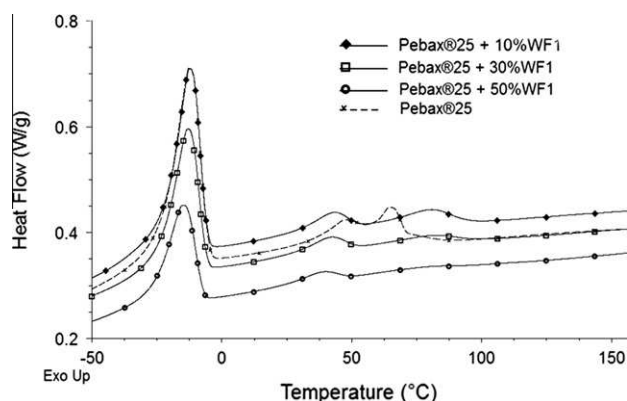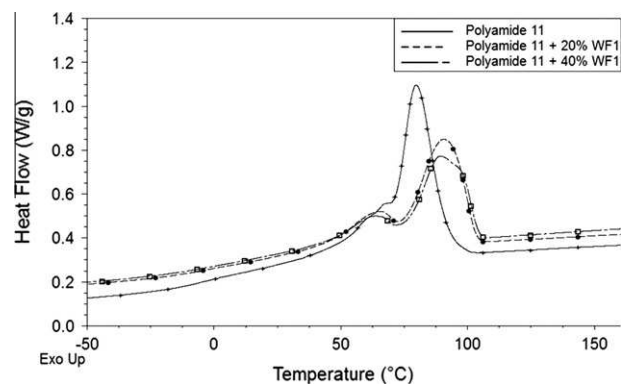
Fig. 2. DSC crystallisation thermograms of polyamide 11 and composites with 20% and 40% of wood.

polyamide phase of pebax®25 was chosen as matrix. Two polyamide/wood composites with 20 wt% and 40 wt% WF1 content were evaluated by DSC following the same procedures as exposed before. The crystallization thermograms are exposed on Fig. 2 below.

As previously noticed for composites with pebax®25 matrix we observe the same change in the composites crystallization temperature. We confirm that wood fibers have an influence on polyamide crystallization (T_{c1} decreases and T_{c2} increases), wood flours play a role of a nucleating agent [25–27].

From all the DSC measurements, we can conclude that wood addition have an influence on polyamide phase of pebax®. Therefore, we demonstrate an interaction between wood and polyamide.

To go further in understanding the interactions between wood and matrix, we have used FTIR analysis. IR spectra of pure components (pebax®25 and WF1) and composites with 10 wt% and 30 wt% wood are shown on Figs. 3 and 4. Changes in the 800–1800 cm^{-1} (Fig. 3) and 2600–3600 cm^{-1} (Fig. 4) regions, for needed interpretation.

Chemical groups attribution of IR absorbance bands of pebax® and wood are respectively given in Table 2.

From Figs. 3 and 4 composites spectra showed change compared to pure components notably for bands [E] [F] [B] at 3308, 3090 and 1539 cm^{-1} corresponding to NH groups of polyamide phase. Furthermore, we observe a new peak [B] at 1558 cm^{-1}.

Another significant modification is observed for the band [A] attributed to C=O groups of polyamide phase of pebax®. We can also note other changes of bands [C] [D] [G] corresponding respectively to C—O, CH$_2$ bending and CH$_2$ stretching groups of the matrix.

Fig. 1. DSC crystallization thermograms of pebax®25 and composites with 10%, 30% and 50% of wood.
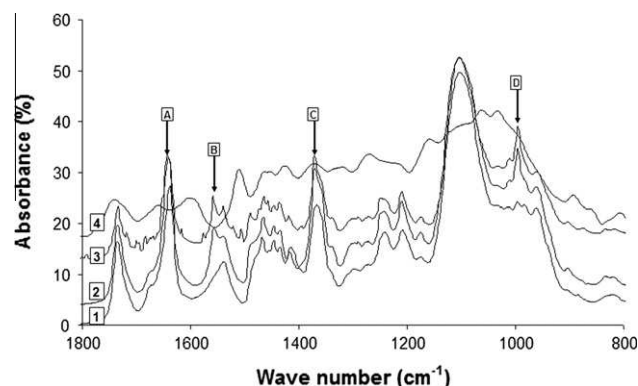
Fig. 3. IR spectra between 800–1800 cm^{-1} of (1) pebax®25, (2) composite pebax®25 + 10% WF1, (3) composite pebax®25 + 30% WF1 and (4) WF1.
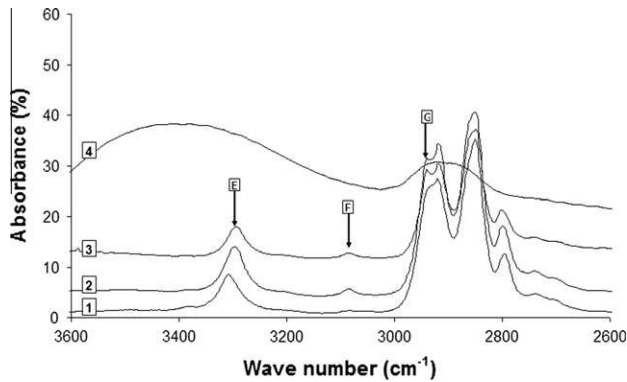
Fig. 4. IR spectra between 2600–3600 cm^{-1} of (1) pebax®25, (2) composite pebax®25 + 10% WF1, (3) composite pebax®25 + 30% WF1 and (4) WF1.

Table 2
Attribution of IR bands of pebax®25 [21,22] and wood [28–30].

Wave number (cm^{-1})	Chemical bonds	Wave number (cm^{-1})	Chemical bonds
3308	v_{as} (NH)	1415	v (C—N)
3090	v_s (NH)	1367	δ_s (CH$_2$)
2919	v_{as} (CH$_2$)	1241	v_{as} (C—O)
2850	v_s (CH$_2$)	1209	v_{as} (C—O)
1734	v (C=O) esters	1103	v_s (C—O)
1638	v (C=O) amides	998	v_s (C—O)
1539	δ (NH)	830	v_s (C—C)
1468	δ_{as} (CH$_2$)	721	γ_s (C—C)
3000–3700	v (OH)	1372	δ_{as} (C—H)
2920	v (CH)	1320	γ (CH$_2$)
1600–1740	v (C=O)	1270	δ_s (C—H)
1510	v (C=C)	1030, 1060	δ_s (C—O), δ_{as} (C—O)
1426	δ (CH$_2$)	890–1200	δ (OH)

All these spectral modifications could be explained by partial destruction of polyamide intermolecular hydrogen bonds and formation of new hydrogen bonds at the interfacial polymer–wood, notably between polar groups of the matrix (NH and C=O) and functional groups of wood (OH, C—O).

The existence of such interaction between wood and polymer, put in evidence by infrared spectroscopy, was previously reported in the literature [13,29,31,32]. The new peak at 1558 cm^{-1} for composites compared to the peak at 1539 cm^{-1} for the matrix is related to the formation of hydrogen bonds [33,34].

These results confirm the interaction between polyamide phase of pebax® and wood observed previously by DSC.

At this stage, we conclude that polyamide phase is in close contact with wood flour. The question is how this result is reflected in terms of adhesion fibers/matrix. To answer, scanning electron microscopy was used to investigate this fibers/matrix adhesion after cryogenic fracture of composites.

Figs. 5 and 6 show the morphological structures respectively for composites pebax®25 + 20%WF1 and pebax®25 + 40%WF1.

It is easy to observe the close contact between wood fibers and matrix. Wood fibers are embedded in the matrix with no gap between them. This is a proof of the strong adhesion that appeared at the contact zone between the polymer and wood due to the hydrogen interactions showed previously by IRTF [13,17]. Furthermore, wood particles are coated with the matrix and the failure occurs in the matrix and not at the filler's surface. Several studies in the literature have shown that when adhesion is not so good, there are voids around the wood particles and fiber pull-out is observed [32,35,36].

Hence, we confirm the good interaction between fibers and matrix for our composites. We will see in the next part of this paper if this result would lead to good mechanical performance of the composites.

3.2. Mechanical properties

Mechanical properties were evaluated on composites with the two matrices (pebax®25 and pebax®55) and the three wood fibers (WF1, WF2 and WF3). We will present in a first part the influence of wood addition on composites with the two matrices reinforced by the WF1 and in a second part, the influence of the three wood fibers on the pebax®25 matrix.

3.2.1. Tensile properties

We have analyzed the influence of wood addition on the two main tensile characteristics of pebax® matrices which are the Young modulus E and the elongation at break ε_r.

We can note on Fig. 7 an important increase of Young modulus E with wood content and a difference on composites behavior related to wood flours. This difference is being more pronounced at high wood content. The increase of the Young modulus with wood content is a phenomenon usually reported in the literature. This augmentation is linked to a higher wood modulus compared to the matrix and to a good matrix/wood interface quality. The differ-
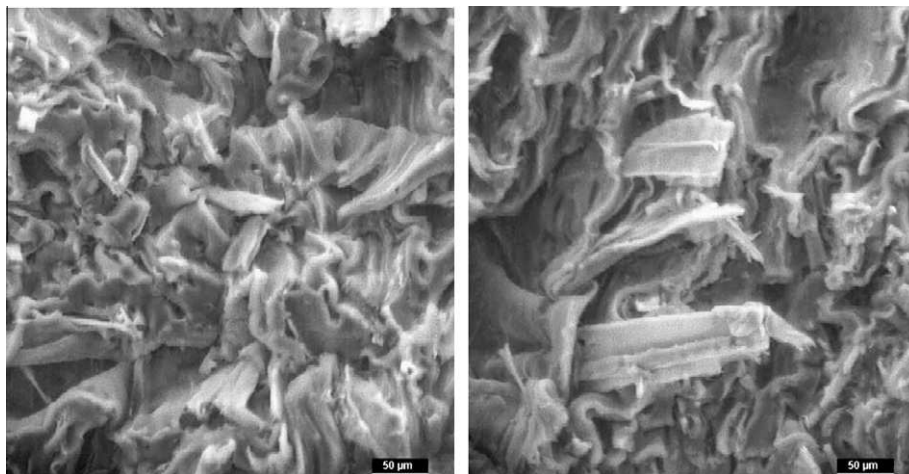

Fig. 5. SEM micrographs of cryogenic fracture surface of composite pebax®25 + 20% WF1.
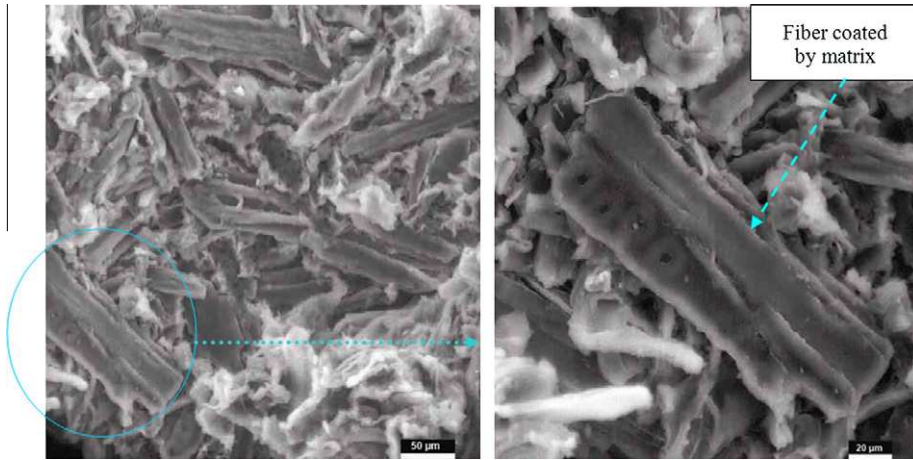
Fig. 6. SEM micrographs of cryogenic fracture surface of composite pebax®25 + 40% WF1.
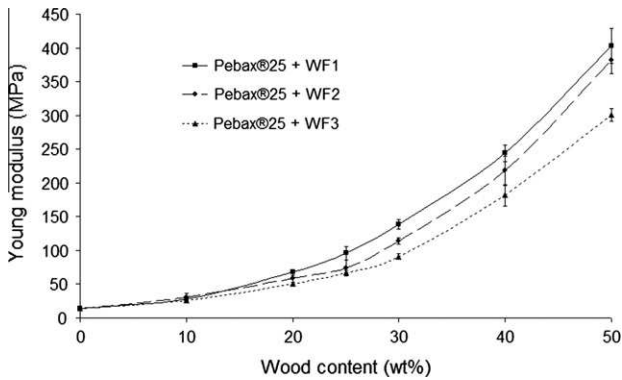

Fig. 7. Evolution of Young modulus versus wood content for composites with pebax®25 matrix and the three wood flours (WF1, WF2 and WF3).

ences observed between the three wood flours are mainly linked to a difference in particle size distribution [7,8,37,38].

However, if we compare our results to the literature on wood composites with different matrices such as PP, we can note a higher augmentation of the Young modulus. Indeed, with 50% of wood content, in the literature [8,39–41] it is reported an increase of the Young modulus between 300% and 800% while we have an increase between 2000% and 3000% for our composites. This difference is due to a high difference of matrices Young modulus but mainly to the good quality of wood/polymer interface for our composites.

On Fig. 8, we evaluate the influence of WF1 wood content on the Young modulus of the two matrices pebax®25 and pebax®55.
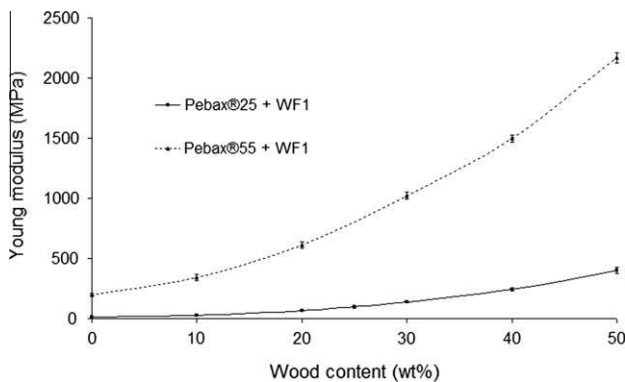

Fig. 8. Evolution of Young modulus versus wood content for composites with pebax®25 and pebax®55 matrices reinforced by WF1.

We can observe a significant difference between composites with the two matrices. Composites with pebax®55 matrix present higher modulus compared to composites with pebax®25 matrix. This can be partly due to a modulus 10 times higher for pebax®55 compared to pebax®25. In order to compare the composites we have to normalize the data by the matrix modulus, we will compare them after applying an empirical model.

To get a global interpretation of wood effect on E modulus, we have tried to model our results using different semi-empirical models such as Halpin–tsai, Quemada, Hirsh or Guth and Gold [42–47]. The best fitting (see Fig. 9) was obtained with a modified Guth and Gold model. In fact, we modified the quadratic terms k. It became an adjustable parameter which characterize the interaction between fibers and their reinforcing effect:

$$E = E_m(1 + 2.5\phi_v + k\phi_v^2) \tag{1}$$

E and E_m are respectively the Young modulus of composites and matrix.

Hence, the factor k can lead to a first quantifying approach of the differences between composites.

On one hand, with pebax®25 matrix, we confirm the observation presented bellow with the three wood fibers. Indeed, the factor k of composites with WF1 is higher than the one for WF2 and WF3, which is indicative of a higher reinforcing effect on modulus with WF1.

On the other hand, "k" is significantly lower for composites with pebax®55 matrix. This is indicative of a lower reinforcing effect for the pebax®55 matrix composites modulus. The explanation of this difference is attributed to a higher difference between the modulus of wood fibers and the modulus of the soft matrix pebax®25 compared to the difference between the pebax®55 and the wood fibers.

Fig. 10 presents the evolution of elongation at break ε_r versus wood content for all the composites.

As expected [8,31,39,40,48], for all the composites, we can observe a decrease of elongation at break (ε_r) when wood content increases. This phenomenon is widely reported in the literature for composites reinforced with particles.

On the graph presented above we will first compare composites with pebax®25 matrix and the three wood fibers. We can note a transition behavior between 20 wt% and 30 wt% of wood content. Composite behavior changes from an elastomeric one to a solid one. We can correlate this result with the morphology change observed with the SEM analysis.

In this transition area, we also observe a difference between composites with the three wood fibers. At 25 wt%, composites with WF3 present a higher elongation at break compared to composites
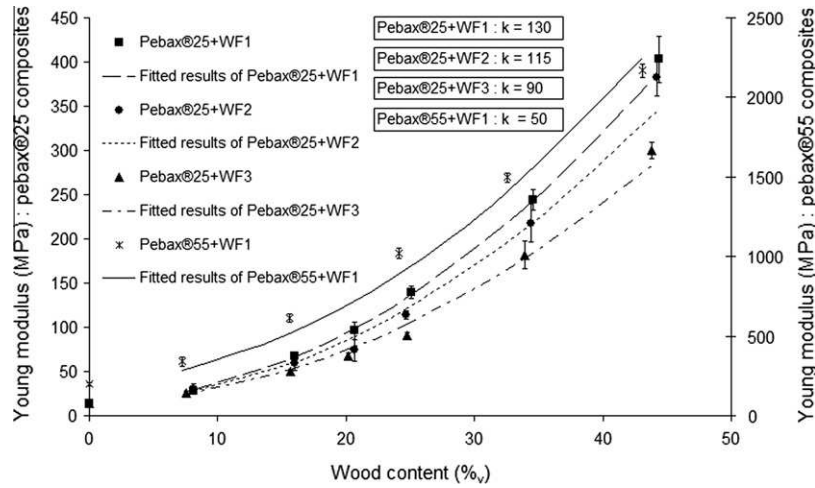
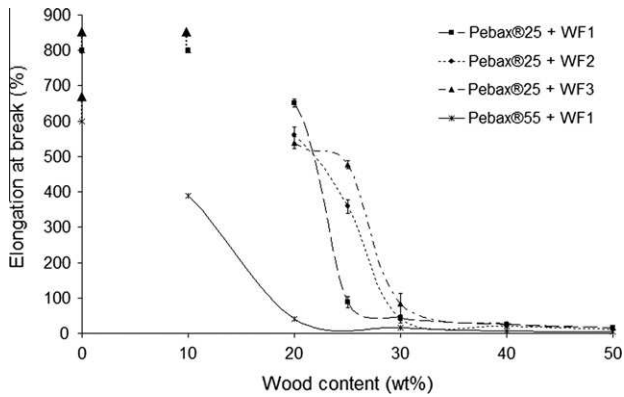**Fig. 9.** Young modulus versus wood content: Eq. (1).

Fig. 10. Evolution of elongation at break versus wood content.

with WF2 and significantly with WF1, although composites with WF3 have the lowest modulus. Hence, composites which keep their elastomeric character higher, in the transition 20–30%, have the lowest modulus. This difference between the three wood fibres

can be due to the difference in particle size. We will observe particles size later in this publication.

Previously, we compared composites with the two matrices and the WF1. At the same fiber content, ε_r is higher for composites with a pebax®25 matrix, which are more ductile. Furthermore, this difference leads to a change in the transition ductile/brittle comprised in this case between 10 wt% and 20 wt%, the elongation at break dropping from 400% to 40%. This difference is due to the more rigid character of the pebax®55 matrix as it contains more polyamide than pebax®25.

In order to better understand the mechanical results previously reported we performed tomography analysis on our composites. Tomography is an analysis not commonly used in wood composite area, but it is reported in different studies the advantages of using this analysis. It allows to observe wood fibers dispersion into the matrix without destruction of the sample, moreover it can also permit to rebuild the sample volume in three dimension (3D). This reconstruction is not easy and depends on the type software used [32,49,50]. Hence, we will only present the two dimension pictures.
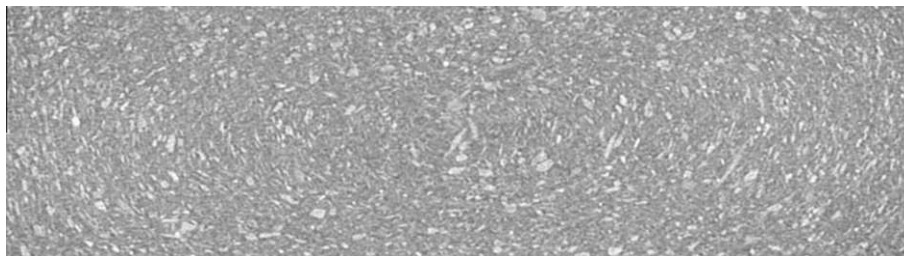

Fig. 11. Tomography picture of pebax®25 + 30% WF1: 8.9 × 2.5 mm.
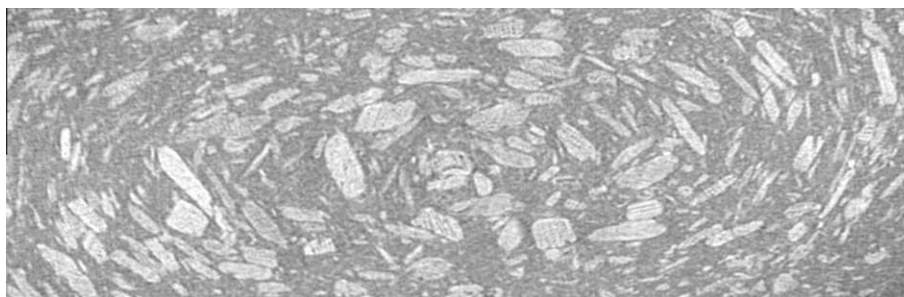

Fig. 12. Tomography picture of pebax®25 + 30% WF2: 8.6 × 2.8 mm.

Analysis have been done on composites with WF1 and WF2 at 20%, 30% and 50% of wood content. We will only present in this publication pictures with 30% of wood content (See Figs. 11 and 12).

We can note a good dispersion of fibers into the matrix without aggregates. This result along with good interface could explain the reason why we have good homogenous mechanical properties. We can also observe an orientation of particles on the sample side, and parallel to it. This orientation is due to material flow during injection moulding. Moreover, no void between matrix and particles is observed which is a sign of a good composite cohesion.

We can also easily confirm the particle size difference between the WF1 and WF2 which can explain the differences in mechanical properties. Indeed, with smaller particles the specific area increases leading to higher mechanical properties with the finest particles.

4. Conclusion

A new WPC made of a bio-based thermoplastic elastomer matrix and wood fiber is exposed in this study. We have characterized the matrix/wood interface by different analysis. First we have shown by SEM analysis a good coverage of wood fibers by the matrix sign of good adhesion. Then, we have demonstrated an interaction between wood particle and polyamide phase of pebax® by DSC and FTIR analysis.

The quality of this interaction matrix/filler leads to good mechanical properties, loads can be transferred from the matrix to the filler. For all the composites the Young modulus increases notably with wood content and can be described with an empirical law which permit to evaluate the influence of the different wood fibers and matrices of our study.

We have also shown a change in the mechanical behavior from elastomeric to less stretchable solid as wood content increases, with a step between 20 wt% and 30 wt%. If we want to keep the elongation properties of the matrix, wood content should be lower than 30 wt%.

Analysis by X-ray tomography demonstrated the good fiber dispersion which contributes to the improvement of mechanical properties. Furthermore, this analysis have permitted to confirm the difference of particles size between the wood fibers of our study which explain the variation of mechanical properties.

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