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A B S T R A C T

Lignocellulosic fibres such as hemp fibres have emerged as an attractive alternative to nonrenewable fibers in the reinforcements in polymer composites. These fibres are subjected to pretreatment prior fibre extraction. In hemp industry, the retting is the first treatment applied to the plant after harvesting in order to separate the fibres from the central woody part of the stem. This treatment is needed to be more understood because of its importance for the development of high-performance hemp biocomposites. In this study, the influence of field retting treatment and lab-scale retting treatment of hemp fibres harvested at the end of flowering (EF) and at the seed maturity (SM) respectively, on hemp fibres /polypropylene biocomposites was investigated. The results highlight that, regardless the harvest period (initial state of the fibres) and type of retting, the thermal stability of biocomposite increased gradually with retting duration due to the increase of thermal stability of the fibres. The decomposition temperature of the fibres harvested at EF and SM increased from 335 °C and 352 °C, respectively to 350 °C and 368 °C for fibres that retted during five weeks. Tensile strength and Young's modulus of the biocomposites reinforced with fibres harvested at EF increase gradually until reaching a maximum (5 weeks) (46.0 ± 1.9 MPa and 4072 ± 196 MPa respectively), and then tends to decrease with a prolonged field retting (42.9 ± 1.6 MPa and 3627 ± 188 MPa respectively). In contrast, for biocomposites reinforced with fibres harvested at SM and retted in accelerated conditions, the tensile strength and Young's modulus decreased rapidly from 44.9 ± 2.2 MPa and 3732 ± 291 MPa for unretted fibres to 39.9 ± 2.6 MPa and 3327 ± 183 MPa for five week retted fibres.

Keywords:
Hemp fibres
Polypropylene
Retting temporal dynamics
Biocomposites
Thermal properties
Mechanical properties

1. Introduction

Due to environmental consideration and economic factors, plant fibres reinforced polymer composites (biocomposites) have acquired a remarkable interest over last decades. They are developed in many sectors, such as in building (decking), naval, automobile (interior equipment, cowls), and sports (surfboard) as an alternative of conventional fibers (e.g. glass or carbon) reinforced composites materials (Joshi et al., 2004; Pappu et al., 2019; Muthuraj et al., 2019). Besides their excellent mechanical properties and their lightening structures (Bledzki and Gassan, 1999; Bourmaud et al., 2018), these plant fibres reinforced composites, can reduce the environmental impact (Joshi et al., 2004), can be recycled while keeping the original properties (Bourmaud and Baley, 2007), and their processing do not damage the processing equipment as natural fibres causes less surface abrasion. However, the incompatibility of these fibres with the polymer matrix and the variation of their quality in term of the morphology, chemical composition, physical and mechanical properties greatly reduce their high use as reinforcement in polymers for structural application (Bledzki and Gassan, 1999; Bourmaud et al., 2018).

Hemp plant fibres are one of the species that are used as reinforcement in polymers. These fibres are located at the periphery of the hemp stems in form of bundles containing several elementary fibres that are assembled together by an interface of amorphous polysaccharides (cementing compounds e.g. pectins) (Crônier et al., 2005). Each unitary fibre (or elementary fibre) is composed of concentric cylindrical walls and has a complex structure that contains the microfibrils of cellulose as basic units and matrix of amorphous polysaccharide including pectins, hemicelluloses and lignin (Bledzki and Gassan, 1999; Bourmaud et al., 2018; Väisänen et al., 2019). The variation of amount of hemp fibres substances has an impact on their intrinsic mechanical properties (Bourmaud et al., 2013; Marrot et al., 2013) that play a key role in mechanical performance of final composite. In addition, the presence of some substances such as pectins and

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waxes, that bind the fibres together, can prevent the hydroxyl groups of cellulose from interacting with polar polymer matrix. Therefore, removing these substances and separating the fibres to obtain individual fibres or smaller fibres bundles, are needed to improve interfacial bonding between fibres and matrix in order to enhance the mechanical performance of final composite (El Mechtali et al., 2015; Li et al., 2009; Martin et al., 2013; Sisti et al., 2016).

For this aim, many pre-treatments of the fibres have been developed in order to improve the intrinsic properties of the fibre and the adhesion between the fibre and matrix: i) Chemical treatment, using silane, alkaline, acetylation ethylenediaminetetraacetic acid (EDTA) and ethylene diamine tetra (methylene phosphonic acid) (EDTMPA) increases the compatibility between fibres and matrix (Bledzki et al., 2008; Cantero et al., 2003; Islam et al., 2010; Liu et al., 2016), ii) Enzymatic treatment, (e.g. endo-polygalacturonase, hemicellulases) (Liu et al., 2016; Nykter et al., 2008) inducing a cleaner fibre's surface, helps to improve the mechanical properties of fibre reinforced composites and iii) steam explosion (Kukle et al., 2011; Thomsen et al., 2006; Vignon et al., 1997). Although these methods are reported in literature, the most widely used pretreatment in the hemp industry is field retting (also known as dew-retting) thanks to its low cost and ease of use (application) (Sisti et al., 2018). The field retting treatment consists of cutting and spreading out the hemp plants on the field after harvesting, so that the microorganisms (fungi and bacteria) colonize the stems (Djemiel et al., 2017; Ribeiro et al., 2015) producing a range of polysaccharide-degrading enzymes, especially pectinolytic which remove the components in the middle lamella (pectic substance) and allow the cortex fibres to be progressively separated (Akin et al., 2007; Henriksson et al., 1997). This treatment is weather-dependent and is performed in empirical way in the field which leads to a variation of the hemp fibres quality in term of division state of the fibres, chemical, thermal and mechanical properties (Goudenhooft et al., 2018; Mazian et al., 2018; Placet et al., 2017; Réquilé et al., 2018). Indeed, field retting can be considered as an advantage or an inconvenience depending of its degree. Therefore, it is necessary to control this treatment in order to avoid under or over retting.

Therefore, the objective of this work is to assess the influence of two types of retting (a field retting on one side and an accelerated retting performed in lab-scale pilot units on the other side), the retting duration (up to 11 weeks) and the harvesting period (end of flowering (EF) and seed maturity (SM)) on the properties of a polypropylene/30 wt% hemp fibres. Thermal stability and microstructure were surveyed using thermogravimetry analyses (TGA) and differential scanning calorimetry (DSC), respectively. Scanning electron microscopy observations were carried out on the tensile fracture surfaces after mechanical test.

2. Materials and methods

2.1. Raw materials

2.1.1. Hemp cultivation and sampling

Hemp (*Cannabis sativa L.*, Cultivar 'Santhica 27') was sown at a rate of 30 kg/ha on 10th May, 2017 in the south of France (N 44.130673°, E 4.315895°) by CIVAM Chanvre Gardois (Le Bouquet, France). The hemp plants were harvested manually at the end of flowering (EF) (21th august, 2017), and at the seed maturity (SM) (26th September, 2017) (Fig. 1). The stems lengths at EF and SM are 1.56 m and 1.58 m, respectively.

2.1.2. Retting conditions

After each harvest period, the plants were subjected to specific retting treatments.

- The plants harvested at the end of flowering were left in the field for retting (Fig. 2A).
- The plants harvested at the seed maturity were retted using two designed lab-scale pilot units (Fig. 2B). Two equivalent lab-scale pilot units were used for performing the retting in controlled conditions, especially in terms of humidity and air speed. These lab-scale pilot units consist of two parts: i) the upper part that is transparent in polymethyl methacrylate (PMMA). The dimensions of this part are 1 m (length) x1 m (width) x45 cm (height). ii) the lower part is in polyvinyl chloride (PVC) with dimensions of 1 m (length) x1 m (width) x25 cm (height), filled with gravel / clay balls and containing 15 cm of soil retrieved directly from the field were the hemp was sown. The ventilation of this lab-scale pilot unit is ensured by suction of the air through a perforated surface. The air speed sweeping the surface of the soil is representative of a calm time, 0.2 $m.s^{-1}$. Intermittent watering of the soil and of the stems dropped and lined on the soil surface is preformed 4 times for 24 h to maintain the relative humidity at around 75%.

2.1.3. Weather conditions

During field retting of the stems harvested at the end of flowering, the monitoring of the temperature and the relative humidity was realized using the hygro-buttons sensors (Progesplus, Carquefou, France) which are put in contact with the soil in the field. In addition, daily average precipitation data were acquired from Météo France (meteorological station Méjannes-le-Clap). For retting in the lab-scale pilot units, these parameters were followed using thermo-hygrometer Kimo.

Fig. 3A shows the weather conditions during field retting of plants harvested at the end of flowering. During this field retting, the weather was hot, except two last weeks of treatment. Indeed, the average maximum and minimum temperature between the 1 st week and the 9th week are 40.2 °C and 17.5 °C, respectively, while during two last weeks of this period, they decreased to 26.3 °C and 7.1 °C, respectively. As concern the retting conditions for the stems harvested at SM and retted in the lab-scale pilot unit (Fig. 3B), the temperature and relative humidity are homogeneous. The relative humidity and the temperature are around of 75% and between 10–20 °C, respectively, throughout treatment.

2.1.4. Matrix

The polymer used as a matrix for manufacturing of composite materials is a polypropylene (PP, grade H733-07) with a melt flow rate of 7.5 g/10 min (230 °C, 2.16 kg) provided by Braskem (Brazil). In order to improve the compatibility between the matrix and the reinforcements, 1 wt% maleic anhydride grafted polypropylene (MA-g-PP, Orevac CA100) with 1 wt% grafting rate purchased from Arkema (France), was added as coupling agent. A hemp fibres loading of 30 wt% was chosen.

2.1.5. Composite material processing

The fibres and the coupling agent (MA-g-PP) have been dried before processing for 24 h at 60 °C in a vacuum to eliminate residual water. Granules of PP and MA-g-PP were mixed with hemp fibres using a twin-screw micro-compounder (DSM Xplore, microcompounder, Geleen, The Netherlands, 15cm3) with the temperatures profile of 180 °C (feeder) – 180 °C (middle screw) - 200 °C (die) and a screw speed of 80 rpm.

The extruded pellets were dried for 3 days at 60 °C, then injected molded using IM15 Zamak Mercator machine (Skawina, Poland) with a barrel temperature of 195 °C. Molded samples are tensile dogbones specimens corresponding to the ISO 527-2 type-1BA to obtain ISO ½ dogbone specimens. Table 1 gives the different biocomposites for each selected growth stage. An additional biocomposite was elaborated without MA-g-PP in the case of hemp fibres harvested at SM period and unretted, so called later R0PPSMref.

2.2. Experimental methods

2.2.1. Biocomposite thermal stability

The thermal stability of biocomposites was analyzed using a Perkin-Elmer Pyris-1 thermal analysis system. Samples of about 10 mg were

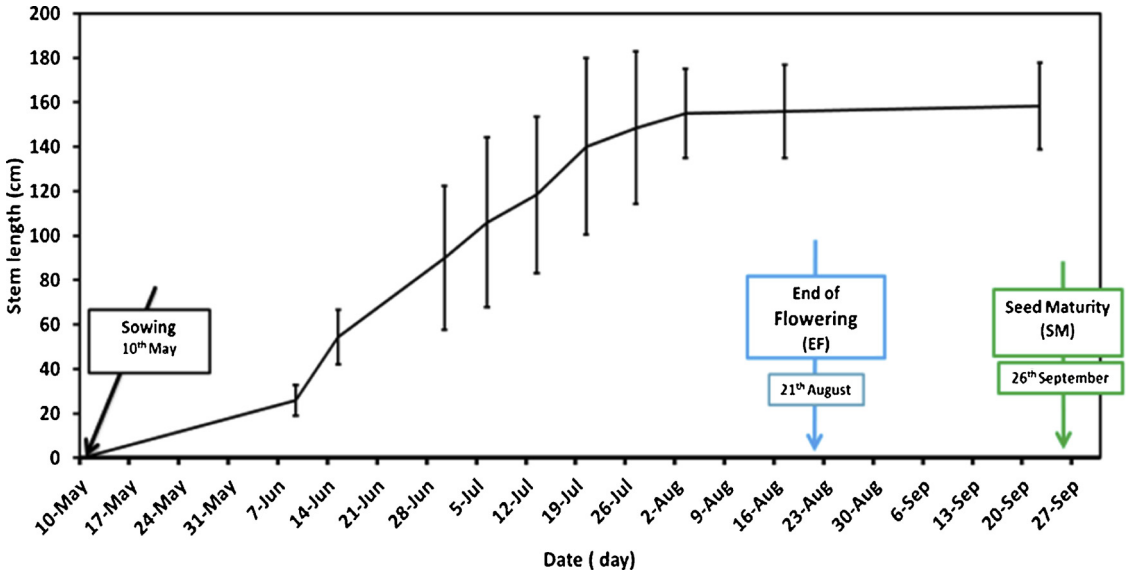

Fig. 1. Hemp stem length during growth.

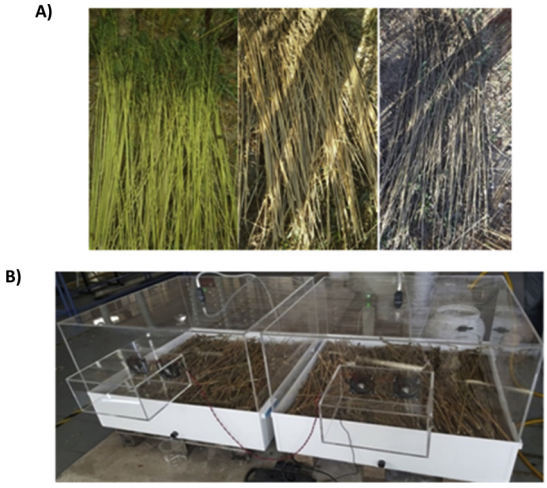

Fig. 2. A) Field retting (left: non-retted stems; middle: 3 weeks retted stems; right: 9 weeks retted stems). B) Lab-scale pilot units used for a controlled and accelerated retting.

heated in nitrogen from 30 °C to 700 °C at the rate of 10 °C.min^{-1}. The mass variation was recorded as a function of temperature. A differential thermogravimetric analysis (DTGA) curve was collected from the TGA analysis.

2.2.2. Mechanical characterization of biocomposites

Before mechanical test, biocomposites were conditioned for 3 days at 23 ± 2 °C and 50 ± 10% RH. Then, tensile test characterization was performed in the same hygrothermal conditions on ISO ½ dog-bone samples. A Zwick TH 0101 apparatus machine equipped with an extensometer Zwick "clip-on" for the determination of the Young's modulus was used. The displacement speed was set to 1 mm.min^{-1} for the tensile modulus measurements, and 20 mm.min^{-1} for the break property measurements. The tests were carried out at least four times for each specimen to evaluate the reproducibility.

2.2.3. Microstructure characterization of biocomposites

The crystallinity behavior of biocomposites was assessed through differential scanning calorimetry (DSC, Perkin Elmer) using a Q100 TA Instruments® equipped with a cooling attachment, under a nitrogen atmosphere. The measurements were performed under nitrogen atmosphere at a 20 mL.min^{-1} flow. Two heating steps from 30 °C to 220 °C at 10 °C/min with an intermediate cooling step at 10 °C/min were carried out. Samples of about 10 mg were analyzed in standard aluminum DSC pans. Melting enthalpy was determined from the 1 st and 2nd heating steps.

The crystallinity ratio was calculated according to the equation below:

$$\chi_{C1} = \frac{\Delta H_{m1}}{W \times \Delta H_{m100\%}} \times 100 \quad (1)$$

$$\chi_{C2} = \frac{\Delta H_{m2}}{W \times \Delta H_{m100\%}} \times 100 \quad (2)$$

Where ΔH_{m1} and ΔH_{m2} are the melting enthalpy obtained from the 1 st and 2nd heating steps, respectively. W is the PP content by weight and ΔH_{m100} is the estimated melting enthalpy of a fully crystalline PP (209 J.g-1) (Sperling, 2005).

2.2.4. Microscopic observations

After the mechanical tests, microscopic observations of the tensile fracture surfaces were carried out. The samples were sputter-coated with a thin layer of gold, and then analyzed through environmental scanning electron microscope (ESEM) Quanta FEG 200 (FEI Co.)

3. Results and discussion

3.1. Color of stems after different types of retting

The visual assessment of the stems and fibres color has been carried out during field retting and lab-scale retting of the stems harvested at the end of flowering and seed maturity, respectively. It can be observed in the photograph (Fig. 4), that the color of stems and fibres changes during plant growth from light green to yellow. This color variation is related to decomposition of the chlorophyll that is responsible of green color and the partial retention of carotenoids which emit yellow color (Hörtensteiner, 2004; Matile, 2000; Merzlyak and Gitelson, 1995).

During field retting of hemp stems harvested at EF, the color of fibres and stems change gradually and slowly from light green for unretted samples (R0EF), yellow for low retted samples (R1EF to R3EF), yellow with the presence of grey and black spot for medium retted samples (R4EF and R5EF) and black for highly retted samples (R9EF and R11EF). In contrast, for the samples of SM, the color changes rapidly from yellow (R0SM) to black after one week of retting. This

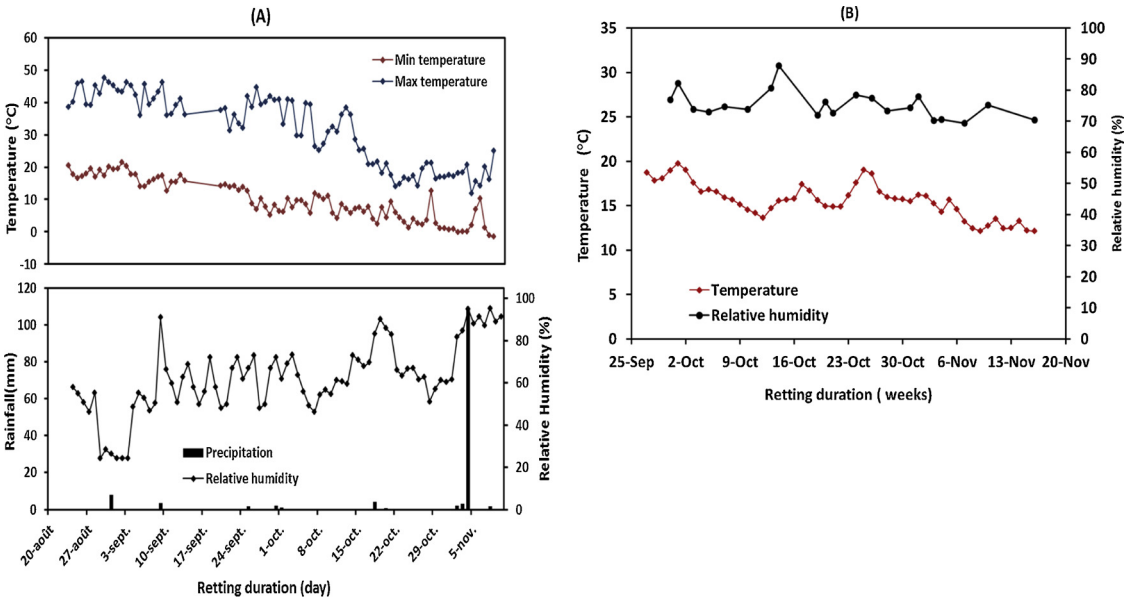

Fig. 3. Daily weather conditions (minimum and maximum temperature, relative humidity and precipitation) (A) during field retting of stems harvested at EF and (B) during artificially/controlled retted stems harvested at SM in lab-scale pilot unit.

Table 1
The performed biocomposites.

Retting time (day)	0	7	21	35	77
Retting time (week)	**0**	**1**	**3**	**5**	**11**
Samples name	R0PPEF	–	R3PPEF	R5PPEF	R11PPEF
	R0PPSM	R1PPSM	R3PPSM	R5PPSM	–

indicates that the retting in the lab-scale pilot was fast due to the homogeneous distribution of temperature and relative humidity which are favorable conditions for a rapid development of microorganisms at the stems surface (Bleuze et al., 2018; Mazian et al., 2018).

3.2. Evolution of biocomposite thermal stability with hemp fibre retting

Thermogravimetric analysis (TGA) was carried out in order to assess the impact of retting on the thermal performance of biocomposite. Fig. 5 presents the curves of TGA and corresponding DTGA respectively

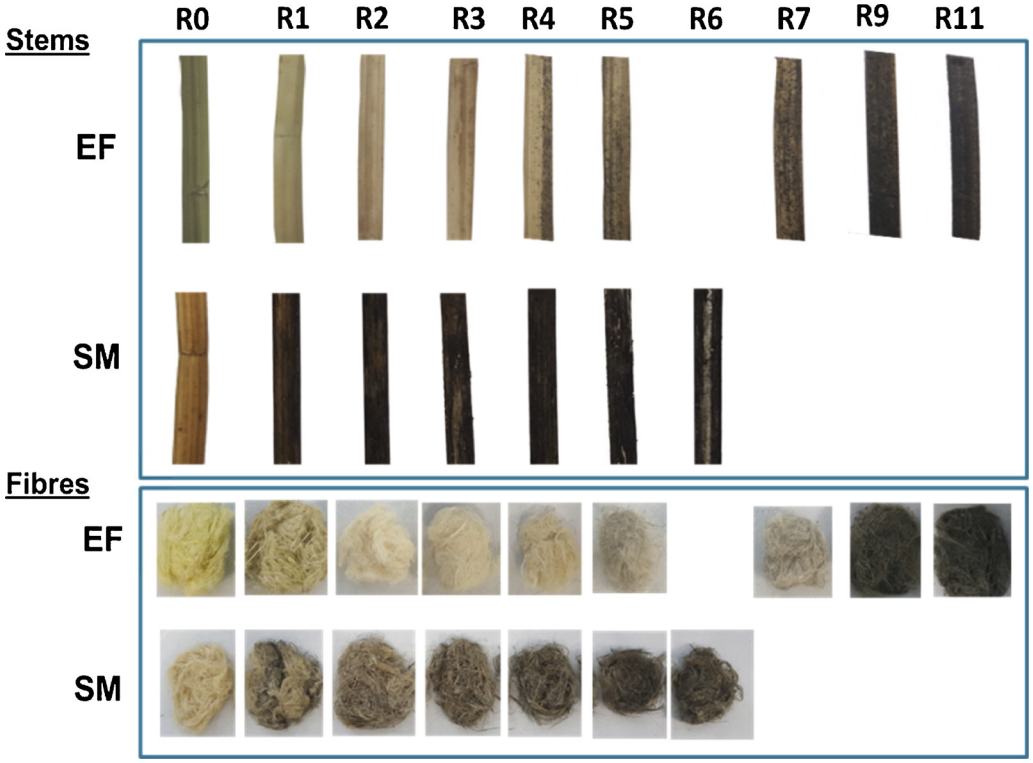

Fig. 4. Color change during field retting of the stems harvested at EF and during lab-scale retting of the stem harvested at SM. Corresponding color change of the fibres.

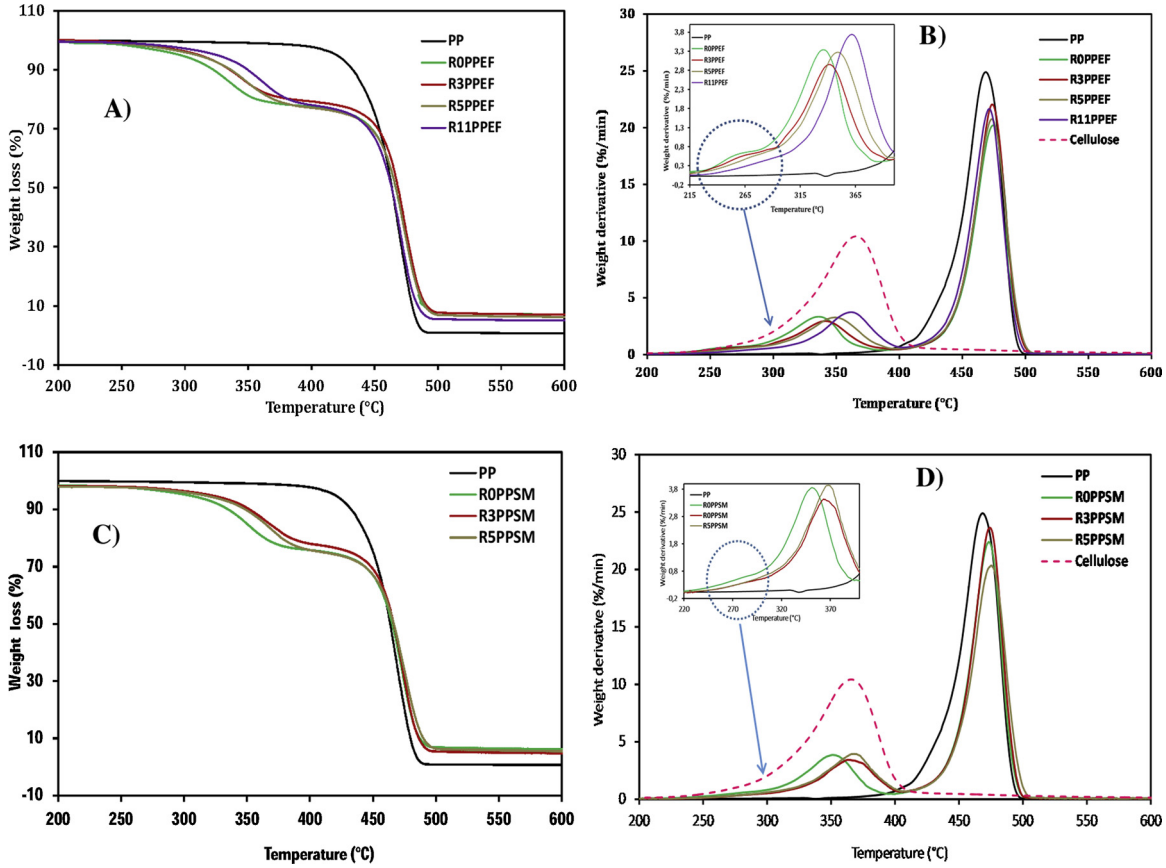

Fig. 5. TGA (A) and DTGA (B) curves of neat PP and biocomposites with fibres harvested at EF (R0PPEF) and field retted at different times (R3PPEF, R5PPEF and R9PPEF). TGA (C) and DTGA (D) curves of neat PP and biocomposites with fibres harvested at SM (R0PPSM) and field retted at different times (R3PPSM, R5PPSM and R9PPSM).

of neat PP and of biocomposites, with fibres harvested at the EF period and then field retted, and with fibres harvested at SM period and artificially retted in the lab-scale pilot unit.

The thermal degradation curve of neat PP gives evidence of a single weight-loss region located at 460 °C. However, the biocomposites degradation occurs in three stages process, where the first stage at about 200–280 °C is associated to the degradation of non-cellulosic components (pectins and hemicelluloses), the second stage at 340–380 °C is attributed to the decomposition of major component of fibres (cellulose) and the third stage at around 460–470 °C is related to the decomposition of polymer matrix.

As concerns the biocomposites with fibres harvested at EF period and field retted (Fig. 5A), TGA curves show different thermal behaviors according to retting duration. From the derivative of the weight loss as a function of temperature (Fig. 5B), it can be seen on one hand that the increase of retting duration leads to an increase of thermal stability in the 200–400 °C temperature range corresponding to both non-cellulosic (pectins and hemicelluloses) and cellulose decompositions. On the other hand, it can be observed that, the portion of the pectins and hemicelluloses gradually decreased (peak intensity at around 220–280 °C) with the retting duration owing to the microorganisms activity (Bleuze et al., 2018; Mazian et al., 2018) which leads to an increase of cellulose degradation temperature until reaching the same temperature of the degradation of pure cellulose. Indeed, the removal of non-cellulosic component induces a higher structural order of cellulose that contains strong intramolecular and molecular hydrogen bonds that requires a higher degradation temperature to be broken-down (Kabir et al., 2013; Ouajai and Shanks, 2005). The cellulose degradation temperature shifts from 335 °C for R0PPEF to 342 °C for R3PPEF, 350 °C for R5PPEF and then to 360 °C for R11PPEF.

As concerns the biocomposites with the fibres harvested at SM period and retted in the lab-scale pilot unit (Fig. 5C and D), the same behavior is observed. The degradation temperature of the fibres increases with retting due to an increase of cellulose degradation temperature increases from 352 °C for R0PPSM, to 364 °C for R3PPSM and 368 °C for R5PPSM. This variation led to an improvement of thermal stability of biocomposite.

Besides the thermal stability changes with retting duration, these results also allowed to highlight that the initial state according to plant growth is not similar. The fibres harvested at the seed maturity had fewer portions of non-cellulosic components and present higher temperature degradation of cellulose (352 °C for R0PPSM) compared to the fibres harvested at end of flowering (335 °C for R0PPEF). This means that at the seed maturity, the cellulose fraction of fibres is higher than that of fibres harvested at end of flowering. This initial difference is remaining all along the retting process (342 °C for R3PPEF compared to 364 °C for R3PPSM and 350 °C for R5PPEF compared to 368 °C for R5PPSM).

3.3. Change in biocomposite microstructure with hemp fibre retting

The crystallinity degree and the melting temperature for neat PP and the biocomposites were determined from the first and the second heating ramps (Fig. 6 and Table 2). The melting enthalpy measured at first heat ramp is linked to the initial crystallinity which depends on the thermal background of the sample i.e. the processing steps. In the second ramp, the thermal background of the sample does not furthermore significantly influence the crystallization and retting treatment could only have an impact on the melting enthalpy measured in this ramp.

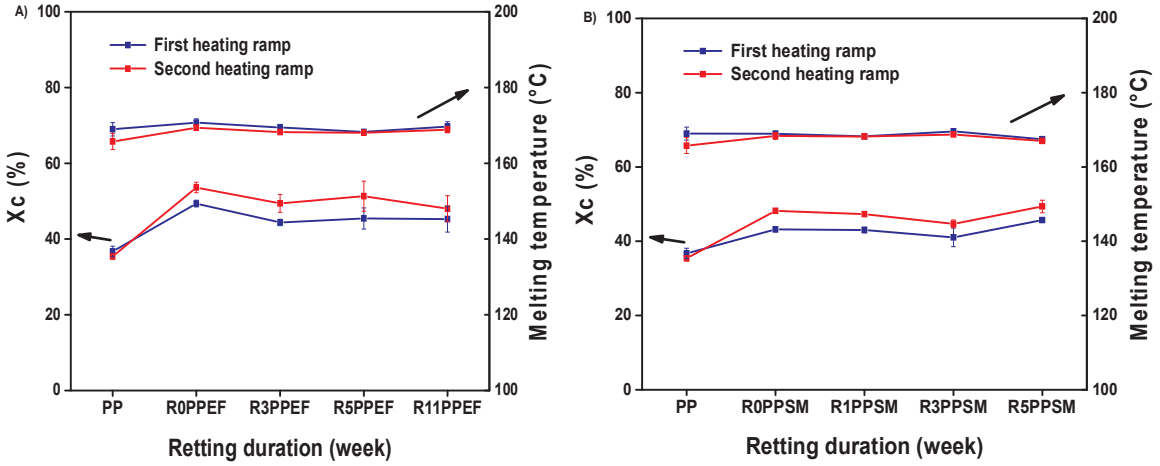

Fig. 6. Evolution of the crystallinity degree and the melting temperature A) of neat PP and biocomposites with fibres harvested at EF (R0PPEF) and field retted at different times (R3PPEF, R5PPEF and R11PPEF), B) of neat PP and biocomposites with fibres harvested at SM (R0PPSM) and retted in the lab-scale pilot unit at different times (R1PPSM, R3PPSM and R5PPSM).

Table 2
DSC analysis results.

	1 st Heating ramp			2nd heating ramp		
	ΔH_{m1} (J.g-1)	X_{c1} (%)	T_m (°C)	ΔH_{m2} (J.g-1)	X_{c2} (%)	T_m (°C)
PP	76.7 ± 2.9	36.7 ± 1.3	168 ± 1.7	73.9 ± 1.5	35.3 ± 0.7	166 ± 2.1
R0PPEF	71.1 ± 1.2	49.4 ± 0.9	171 ± 0.9	77.3 ± 1.9	53.6 ± 1.4	169 ± 0.5
R3PPEF	63.9 ± 1.2	44.4 ± 0.9	169 ± 0.8	71.2 ± 3.4	49.4 ± 2.3	168 ± 0.2
R5PPEF	65.5 ± 4.0	45.4 ± 2.8	168 ± 0.4	74.0 ± 5.7	51.3 ± 3.9	168 ± 0.3
R11PPEF	65.2 ± 4.9	45.3 ± 3.4	170 ± 1.3	69.2 ± 4.9	47.9 ± 3.6	169 ± 0.7
R0PPSM	62.2 ± 0.9	43.2 ± 0.7	169 ± 0.7	69.5 ± 0.2	48.2 ± 0.1	168 ± 0.9
R1PPSM	62.0 ± 1.1	43.0 ± 0.8	168 ± 0.2	68.1 ± 0.7	47.2 ± 0.5	168 ± 0.2
R3PPSM	59.2 ± 3.6	41.0 ± 2.5	170 ± 0.3	64.4 ± 1.5	44.6 ± 1.0	169 ± 0.2
R5PPSM	65.8 ± 0.7	45.7 ± 0.5	167 ± 0.2	71.1 ± 2.4	49.3 ± 1.7	167 ± 0.1

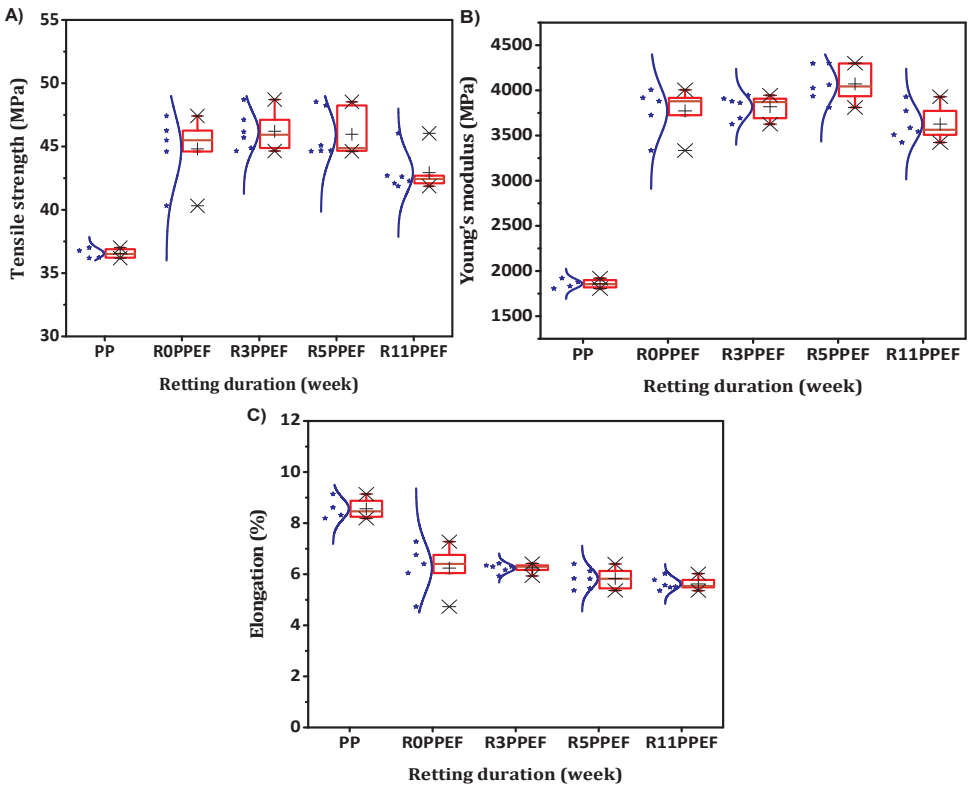

Fig. 7. Results of tensile strength (A), Young's modulus (B), and elongation at break (C) for neat PP and the biocomposites with fibres harvested at end of flowering (R0PPEF) and field retted at different retting durations (R3PPEF, R5PPEF and R11PPEF). The back crosses and red line correspond to the means and medians, respectively.

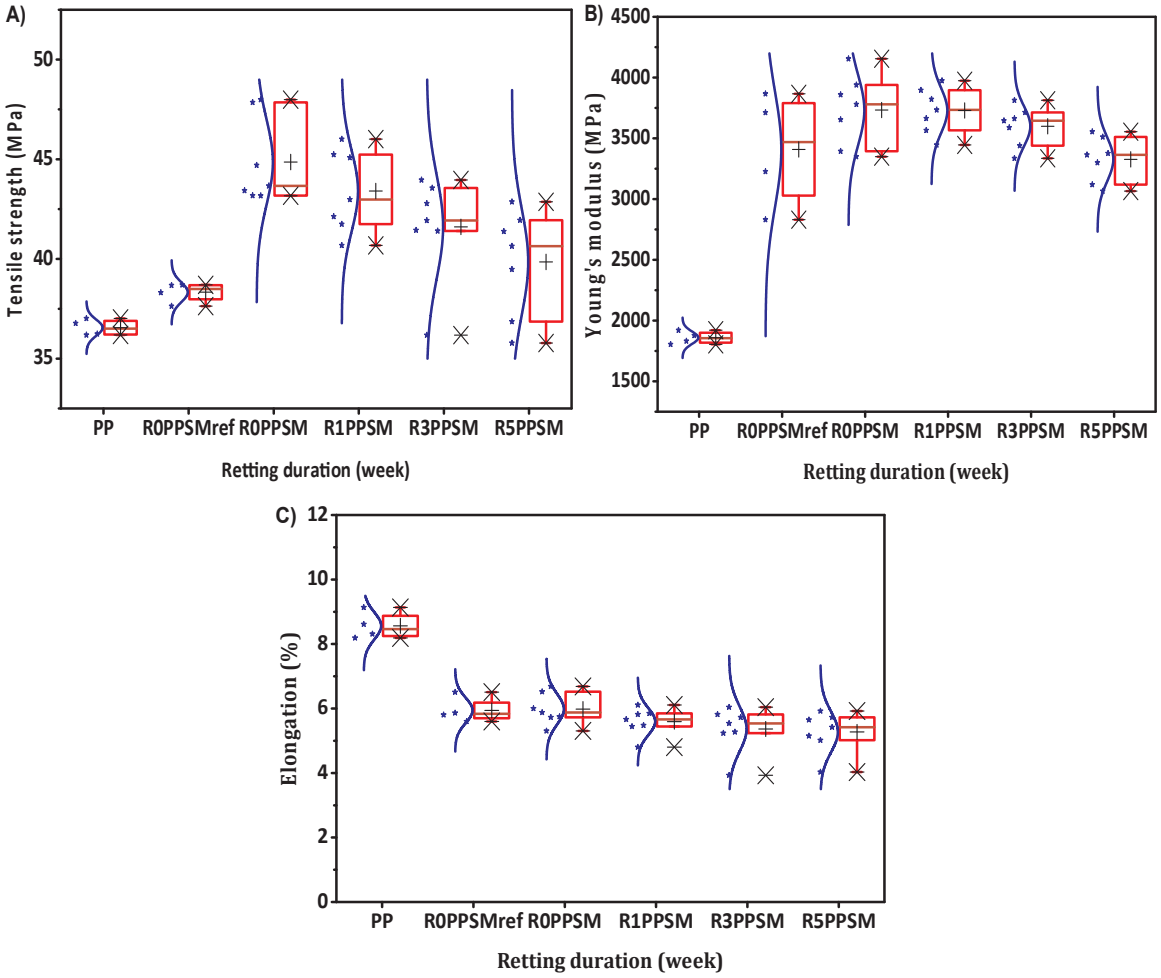

Fig. 8. Results of tensile strength (A), Young's modulus (B), and elongation at break (C) for neat PP and biocomposites with fibres harvested at seed maturity (R0PPSM with MA-g-PP and R0PPSMref without MA-g-PP) and retted in the lab-scale pilot unit at different retting durations (R1PPSM, R3PPSM, R5PPSM). The back crosses and red line correspond to the means and medians, respectively.

Table 3
Results of tensile strength, Young's modulus, and elongation at break for neat PP and the biocomposites.

	Young's modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PP	1859 ± 51	36.6 ± 0.4	8.6 ± 0.4
R0PPEF	3772 ± 265	44.8 ± 2.7	6.2 ± 1.0
R3PPEF	3818 ± 129	46.2 ± 1.5	6.2 ± 0.2
R5PPEF	4072 ± 196	46.0 ± 1.9	5.8 ± 0.4
R11PPEF	3627 ± 188	42.9 ± 1.6	5.6 ± 0.2
R0PPSMref	3409 ± 472	38.3 ± 0.5	5.9 ± 0.4
R0PPSM	3732 ± 291	44.8 ± 2.2	5.8 ± 0.5
R1PPSM	3729 ± 186	43.4 ± 2.0	5.6 ± 0.4
R3PPSM	3599 ± 163	41.6 ± 2.6	5.4 ± 0.7
R5PPSM	3327 ± 183	39.9 ± 2.6	5.3 ± 0.6

Nevertheless, a comparison of crystallinity ratio of neat PP and biocomposite shows clearly higher values for the biocomposite. This observation explained that the fibres act also as a nucleating agent for the crystallization and the partial crystalline growth of PP, as already shown in the literature (Amash and Zugenmaier, 2000; Arbelaiz et al., 2006).

Regarding the effect of retting on the crystallinity ratio, no trend could be observed either for composites with retted fibres harvested at EF or for composites with retted fibres harvested at SM. Indeed, for the first run, the crystallinity ratio of R0PPEF, R3PPEF, R5PPEF and R11PPEF are 49%, 44%, 45% and 45% respectively. The crystallinity ratio of R0PPSM, R1PPSM, R3PPSM, and R5PPSM are 43%, 43%, 41% and 46%, respectively. This variation of the crystallinity could be related to the roughness change of fibres and processing impact during compounding of the fibres.

Results show also that crystallinity ratio is significantly higher in the second run than first one. Indeed, it varies from 54% for R0PPEF, to 49% for R3PPEF, 51% for R5PPEF, 48% for R11PPEF. As concern the composites reinforced with fibres retted in lab-scale pilot unit, their crystallinity ratio are 48% for R0PPSM, 48% for R1PPSM, 44% for R3PPSM and 51% R5PPSM. The results reveal also that the crystallinity ratio of composite reinforced with the fibres harvested at the end of flowering (R0PPEF) is slightly higher than that of composite with fibres harvested at the seed maturity (R0PPSM).

3.4. Evolution of biocomposite mechanical properties with the hemp retting

Tensile properties (Figs. 7 and 8; Table 3) have been analyzed for neat PP and biocomposites. Whatever the retting duration, the type of retting and the harvest period, the addition of hemp fibers to PP always has a positive effect, conferring a mechanical reinforcement to the polymer matrix with an increase in tensile strength and Young's modulus and a decrease in elongation at break. This highlights the capacity of hemp fibres reinforcement as largely exposed in literature (Badji et al., 2018; Martin et al., 2013).

As concerns the influence of MA-g-PP coupling agent, Fig. 8 reveals that the addition of the coupling agent has also a significant positive

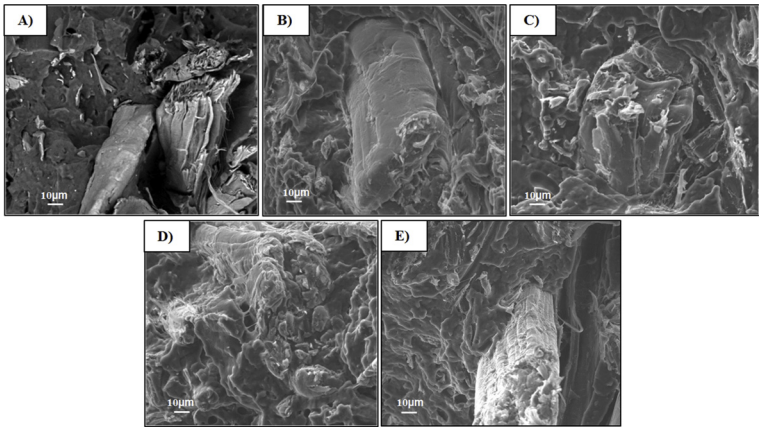

Fig. 9. Tensile fracture cross-sections of A) PP/unretted hemp fibres biocomposite without MA-g-PP, B) PP/unretted hemp fibres biocomposite with MA-g-PP, C) PP/field retted hemp fibre biocomposite with different retting durations: 3 weeks, D) 5 weeks and E) 11 weeks.

effect on the mechanical performance of biocomposite with an increase in tensile strength and Young's modulus and a decrease in elongation at break by comparing R0PPSMref (without MA-g-PP) and R0PPSM (with MA-g-PP) as already presented in literature (Bourmaud and Baley, 2007; Pracella et al., 2006; Sullins et al., 2017).

Regarding the fibres harvested at the end of flowering (Fig. 7), results show that the mechanical properties of the biocomposites increased slightly at the first stage of field retting (up to 5 weeks) and then tend to decrease with an extended field retting (11 weeks). The Young's modulus (Fig. 7B) increased gradually from 3772 ± 265 MPa for R0PPEF to 4072 ± 196 MPa for R5PPEF, and then decreased to 3627 ± 188 MPa for R11PPEF. A similar trend is observed for the tensile strength (Fig. 7A), with a slight increase from 44.8 ± 2.7 MPa (mean value) for R0PPEF to 46.2 ± 1.5 MPa for R3PPEF, and then a decrease with a prolonged retting duration to 42.9 ± 1.6 MPa for R11PPEF. The strain at break (Fig. 7C) tends to decrease slightly with increasing of retting duration from 6.2 ± 1.0 %, (R0PPEF) to 5.8 ± 0.4 %, (R3PPEF) and 5.6 ± 0.2 % (R5PPEF).

As concerns the fibres harvested at seed maturity and retted under controlled conditions in the lab-scale pilot unit (Fig. 8), results show that the Young's modulus remain stable after one week of retting (~3700 MPa for R0PPSM and R1PPSM), then reduced to 3599 ± 163 MPa and 3327 ± 183 MPa after 3 weeks and 5 weeks of retting (R3PPSM and R5PPSM), respectively. The tensile strength decreased gradually during retting, from 44.8 ± 2.2 MPa for R0PPSM, to 43.4 ± 2.0 MPa, 41.6 ± 2.6 MPa, and 39.9 ± 2.6 MPa for R1PPSM, R3PPSM R5PPSM, respectively. No significant change of the strain at break is observed with increasing of retting duration since it varies from 5.8 ± 0.5 % (R0PPSM) to 5.6 ± 0.4 %, 5.4 ± 0.7 %, and 5.3 ± 0.6 % for R1PPSM, R3PPSM and R5PPSM, respectively.

These results indicate clearly that mechanical properties of biocomposites differ according to the harvest period and the type of retting. Indeed, the mechanical properties of biocomposites with the fibres harvested at SM decreased rapidly after one week of controlled retting, whereas for the biocomposites with the fibres harvested at EF, they decreased only at the end of retting. This could be explained by the retting types performed for each harvest period. Indeed, the stems harvested at EF were field retted under dry weather conditions which leads to a slow variation of fibres characteristics, while the stems harvested at SM and retted under wet conditions in laboratory result a rapid change of the fibres characteristics. In our previous study in agreement with literature, it has been demonstrated that intrinsic properties of the fibres (e.g. fibres mechanical properties) change during retting. The first stage of retting treatment results in an improvement of the mechanical properties of fibres due to the removal of non-cellulosic compounds which leads to an increase of the cellulose fraction and of the cellulose crystallinity (Mazian et al., 2018). However, when the fibres are highly retted (over-retted), their structure changes by a high degradation of non-cellulosic compounds or even by microbial degradation of cellulose (Placet et al., 2017). Therefore, in this case, the mechanical properties of the fibres decreased which results in lower tensile properties of the composites. The behavior of mechanical properties of the biocomposites during retting pursue to mechanical properties of the fibres.

It can be concluded that the mechanical properties of the biocomposite are governed by the quality of hemp fibre which depends also on retting duration and the weather conditions. In dry weather conditions, a long period of retting (5 weeks) is required for obtaining the highest mechanical properties. In contrast, under wet conditions and homogeneous distribution of humidity (75%), the prolonged field retting must be avoided.

3.5. *Effect of retting on fibre/matrix interfacial adhesion*

Fig. 9A and B show the fracture cross-sections of PP/unretted hemp fibre biocomposite without MA-g-PP and with MA-g-PP/respectively. Fig. 9C, D and E correspond to fracture cross-sections of PP/field retted hemp fibres biocomposites with different retting durations, i.e. 3, 5 and 11 weeks respectively.

Without MA-g-PP, micro spaces (voids) can be observed at the interfacial zone, indicating a poor adhesion between fibres and matrix. In contrast, by adding MA-g-PP, a better adhesion seems to be involved (ex. Fig. 9B). These observations are in agreement with the results of Pracella et al. (2006) and Bourmaud and Baley (2007).

As concerns the influence of retting on the adhesion of the fibres through the matrix, Fig. 9B, C, D and E show a significant adhesion of the fibres to the matrix and no pull out phenomena. This good adhesion of the fibres through the matrix could be not only related to coupling agent used, but also to degradation of interfibrillar cementing components (pectins) during retting. Li et al. (2009), have reported that removal of non-cellulosic compounds leads to a separation of the fibres which bring a better adhesion between fibre and matrix because of higher surface contact and increased rugosity and an increase of mechanical properties of final material.

4. Conclusion

The present study revealed the influence of the retting on PP/hemp fibres biocomposites properties. Whatever the harvest period and retting type, the thermal stability of the biocomposites improves with retting duration due the enhancement of thermal stability of fibres. Indeed, the increase of retting duration induces a removal of non-cellulosic materials (pectins and hemicellulose) leading to a progressive increase of the degradation temperature of cellulose that is a major

compound of the fibre. The fibres harvested at SM exhibit a better thermal stability compared to that of the fibres harvested at EF, due to the high cellulose fraction present in the fibres at plant maturity. The retting has no effect on the crystallinity of biocomposites, since no trend has been clearly observed.

In the case of field retted fibres, the tensile properties of biocomposites (tensile strength and Young's modulus) increased during retting to a threshold value (after 5 weeks) and decreased at the end of retting. As concerns the accelerated retted fibres in the lab-scale pilot unit, the tensile properties decreased rapidly with increasing of retting duration. The removal of non-cellulosic materials and increasing of cellulose fraction at beginning of retting bring better tensile performances of the biocomposite. However, increasing of retting duration leads to a high degradation of non-cellulosic materials, or even to the cellulose degradation which result in lower tensile properties of biocomposites. Knowledge of retting mechanisms will allow to a significant contribution in optimizing the biocomposites properties.

Declaration of Competing Interest

The authors declare that he has no conflict of interest

Acknowledgements

The authors would like thank the "CIVAM Chanvre Gardois association (Le Bouquet, France)" for their collaboration to conduct this study.

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