World Academy of Science, Engineering and Technology
International Journal of Chemical and Materials Engineering
Vol:16, No:8, 2022

Accelerated Ageing of Unidirectional Flax Fibers Reinforced Recycled Polypropylene Composites

Lara Alam, Laetitia Van-Schoors, Olivier Sicot, Benoit Piezel, Shahram Aivazzadeh

***Abstract*—**Over the last decades, worldwide environmental awareness has grown due to the depletion of raw material resources and global warming. This awareness has prompted the development of new products more environmentally friendly. Among these products are biocomposite materials reinforced with natural fibers. The main challenge in developing the use of biocomposites in exterior applications is the lack of knowledge about their durability and the evolution of their mechanical and physicochemical properties in the long term. The aim of this work is to study the photooxidation of unidirectional (UD) composites based on recycled matrix. For this purpose, UD flax fiber composites based on recycled polypropylene were prepared by thermocompression. An accelerated aging test was carried out using a xenon arc WeatherOmeter. The consequences of UV exposure on the chemical composition and morphology of the surface of composites as well as on their tensile mechanical properties have been reported. The results showed that accelerated aging had a significant effect on the surface of these composites while it had little impact on their mechanical properties.

***Keywords*—**Flax fiber, photooxidation, physico-chemical properties, recycled polypropylene, tensile properties.

I. Introduction

IN recent years, an increased interest in composites reinforced with natural fibers has grown due to the challenges posed by petroleum products and the need to find renewable materials. Flax fibers as a reinforcement for composites have found their way into various applications such as automotive, aeronautics, construction, sports and leisure [1], [2]. This is due to their lightness, low cost, low energy of production and high specific mechanical properties [3]. Virgin polypropylene has been widely studied as a matrix in natural fiber composites [4]-[6]. However, with the accumulation of plastic waste in nature and the depletion of petroleum resources, it is necessary to replace virgin plastics in composites with recycled plastics.

The use of natural fiber composites in exterior applications has been limited due to the lack of knowledge about their durability compared to synthetic fiber composites. Most research has investigated the durability and the photooxidation aging of composites reinforced with short fibers or wood flour [4]-[7]. However, there are few studies on long natural fiber composites. Moreover, there is limited research on the study of photo-oxidative weathering of recycled polypropylene used as a matrix in natural fiber composites [8]. Such a study of the consequence of photodegradation on the mechanical and physicochemical properties of UD flax fibers composites with recycled polypropylene matrix is the focus of this work.

The exposure of polypropylene (PP) to solar UV radiation causes its photodegradation which is well studied in the literature [9], [10]. Photooxidation causes significant chemical changes to the surface of PP. Chemical groups are formed such as hydroperoxides and carbonyl products due to the decomposition reactions of all the chromophoric species introduced during the manufacture of PP [11]. In addition, during photooxidation, chain scission reactions dominate due to the reactive tertiary carbon of PP [12]. The chains thus formed are shorter with high mobility. They rearrange to form new crystals and therefore cause a significant change in the surface microstructure [13]. On the other hand, flax fibers can also undergo photodegradation. The phenolic group, lignin, of natural fibers has a high sensitivity to UV radiations [14]. Its photo-oxidation is mainly responsible for changes in the color of composite surfaces. The formation of yellowing color is due the photooxidation of lignin that leads to paraquinone chromophoric groups. The reduction of these latter to hydroquinones leads to photobleaching [15].

The investigation of the impact of photooxidation on the variations of chemical and mechanical properties of virgin PP composites has been widely reported in the literature [7], [16], [17]. The degree of degradation depends on several parameters such as the intensity of the UV irradiation, the temperature, the exposure time, the moisture content as well as the type of polymer. Homekiew et al. [8] have studied the surface morphology of rubber wood flour composites with virgin and recycled PP naturally aged for 360 days. At the end of aging, composites with recycled PP matrix presented higher cracking on surface compared to those with virgin matrix. They explained this difference by the lower viscosity of composites based on recycled PP. Recycled PP can be exposed to different reprocessing conditions which can affect its properties. Ghahri et al. [18] showed that the melt flow index (MFI) of the virgin PP increased five times with five extrusions. During multiple extrusions, the molecular weight of PP decreases due to chain scission which results in a reduction in viscosity. They also reported a decrease in flexural strength and flexural modulus of 65% and 46% respectively. In addition, recycled plastics exhibit a darker color than virgin plastics due to the color of the waste itself or the addition of pigments. Butilina et al. [19]

Lara Alam is with DRIVE Research Laboratory, University of Burgundy Franche-Comté and CPDM Research Laboratory, University of Gustave Eiffel, France (corresponding author, e-mail: lara.alam@univ-eiffel.fr).

Laetitia Van-Schoors is with CPDM Research Laboratory, University of Gustave Eiffel, France (e-mail: Laetitia.van-schoors@univ-eiffel.fr).

Olivier Sicot, Benoit Piezel and Shahram Aivazzadeh are with DRIVE Research Laboratory, University of Burgundy, France (Olivier.sicot@u-bourgogne.fr benoit.piezel@u-bourgogne.fr shahram.aivazzadeh@u-bourgogne.fr).

noted that pigments with darker colors are more capable of increasing the stability of wood composites with recycled PP against exterior weathering. Similarly, Du et al. [20] reported that carbon black was found to be the most effective among all pigments in providing the highest color stability.

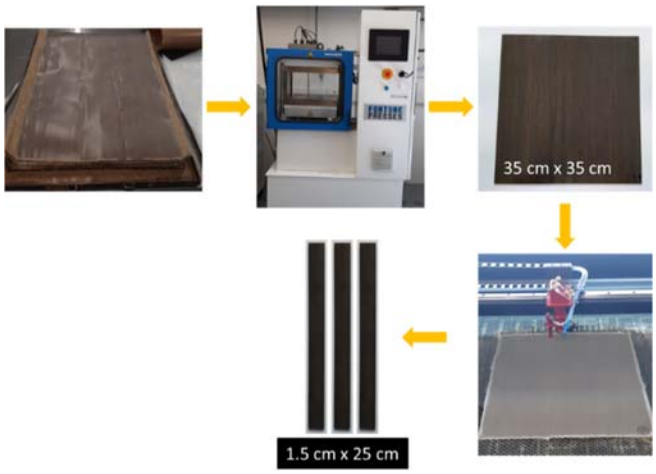

Fig. 1 rPP/flax composite fabricated by thermocompression process

The aim of this work is to investigate the influence of accelerated photooxidative aging on the mechanical and physicochemical properties of UD composites reinforced with flax fibers. This study focuses mainly on the use of a PP matrix from agricultural waste. Moreover, it seeks to provide information on the aging of UD composites intended to be used in structural applications.

II. Experimental

A. Materials

UD flax fibers were used as reinforcement in this work. FlaxTape110 sheets were supplied by Lineo with an areal weight of 110 g/m². The fibers are linked together by pectins and without any weft yarn.

Recycled PP (rPP) from agricultural plastic waste was chosen as matrix. Granules was produced by ADIVALOR. The MFI measured was about 6.0 ± 0.4 g/10 min at 230 °C. Polymer rolls from rPP pellets were formed by extrusion-calendaring process. The films obtained have a thickness of 110-120 µm. rPP films were compatibilized with 5 wt% of Polybond 3200 a PP grafted with maleic anhydride (PPgMA) purchased from ADDIVANT. The MFI was 115 g/10 min at 190 °C. The coupling agent was used to improve the interfacial adhesion between hydrophilic flax fibers and hydrophobic PP.

B. Manufacturing of Composites

Before fabrication of composites, flax fibers sheets were conditioned at 50 ± 1% of relative humidity and 23 ± 1 °C for 1 week. The film stacking process was used to fabricate the UD composites using the thermocompression method. Each composite is formed by 13 polymer films and 12 UD flax fiber tapes placed in a metallic mold to which a thermocompression cycle was applied. The mold was first heated up to 190 °C at 15 °C/min. It is then maintained at this temperature for a duration of 3 min with a pressure rate of 3.3 bar/min to reach 10 bars. After the consolidation step, the composite is cooled at a rate of 15 °C/min under 10 bars maintained until the end of the thermocompression cycle. The dimensions of the fabricated composites were 2.1 mm x 350 mm × 350 mm with a fiber content of 37%. The samples were cut from the composite plates to the required dimensions using a laser cutting machine (Fig. 1).

C. Accelerated Aging

Composite samples were exposed to xenon arc lamp using a WeatherOmeter CI3000 from Atlas. One side of specimens was exposed to UV radiations. The aging test was applied without water spray. The irradiance was fixed at 0.70 W/m² at 340 nm. The chamber temperature was set at 38 ± 2 °C, the black panel temperature was 63 ± 5 °C, and the test was performed at 65 ± 5% relative humidity for a total exposure of 504 hours. Samples were characterized after 96 h, 240 h, 408 h and 504 h of exposure.

III. Characterization

A. FTIR Spectral Analysis

For surface chemical analysis of the composites, a Nicolet™ iS20 FTIR spectrometer was used in Attenuated Total Reflection (ATR) mode. The infrared spectra were the average of 32 scans and measured in the range 400-4000 cm^{-1} with a 4 cm^{-1} resolution. The peaks were normalized with 2916 cm^{-1} which changes little during ageing [5].

B. Surface Morphology

The surface morphology of composites before and after aging was observed by a FEI Quanta 400 Scanning Electron Microscope (SEM) with an acceleration voltage of 10 kV. Prior to the analysis, the surfaces were coated with carbon.

C. Color Measurements

A Ci4200 spectrophotometer in CIELAB color system was used to measure the surface color of composites. The two coordinates L* and b* were measured at five different positions on each specimen. L* represents the lightness coordinate which varies from 0 to 100. A higher value of L* indicates an increase in lightness. b* is the chromaticity coordinate which varies from blue to yellow. A higher value of b* indicates an increase in yellowness.

D. Tensile Properties

Tensile characterization of UD flax composites was carried out according to ISO 527-5 standard using an MTS Criterion C45 machine with a 100 KN load cell. The machine is equipped with a clip-on extensometer with a 50 mm gauge length. The crosshead speed was 2 mm/min.

IV. Results and Discussions

The consequences of UV exposure on the chemical composition and morphology of the surface of rPP/flax composites as well as on their tensile mechanical properties will

be reported.

A. Chemical Surface Characteristics

Infrared spectroscopy is used to determine the chemical composition of the surface of the materials studied. Fig. 2 shows that before ageing, no peak characteristic of flax fibers appears in the spectrum of the composite. This indicates that on the surface, the rPP matrix covers the flax fibers well. Moreover, the spectrum of rPP/lin shows not only PP peaks [19] but also ethylene peaks (2838 cm^{-1} and 720 cm^{-1}) [21]. The presence of ethylene in the recycled matrix can refer to the polyethylene coming from the waste itself.

The absence of peaks in the range of 3400-3100 cm^{-1} and 1800-1500 cm^{-1} for the hydroxyl groups (-OH) and carbonyl (C=O)-vinyl (C=C) groups, respectively [5] proves that neither rPP films nor rPP/flax composites have undergone thermooxidation during their manufacture. Furthermore, this indicates that, during its first life, the rPP matrix has not undergone thermooxidation or photooxidation. The appearance of these peaks in the spectrum of composites aged for 504 h implies a photodegradation of their surface. These observations suggest that the rPP matrix has undergone photooxidation. The decomposition of hydroperoxides groups and β chain scission of alkoxy radicals are responsible for the formation of carbonyl groups, while the photolysis of the latter is responsible for the formation of vinyl groups through Norrish-II reaction [22]. The appearance of peaks of lignin and cellulose, chemical components of flax fiber, in the range 1650-1500 cm^{-1} refer to the presence of fibers at the surface [15]. Most likely, these fibers have undergone degradation during exposure to UV radiations. This leads to the contribution of the formation of additional carbonyl groups and new chromophore groups such as quinones [14].

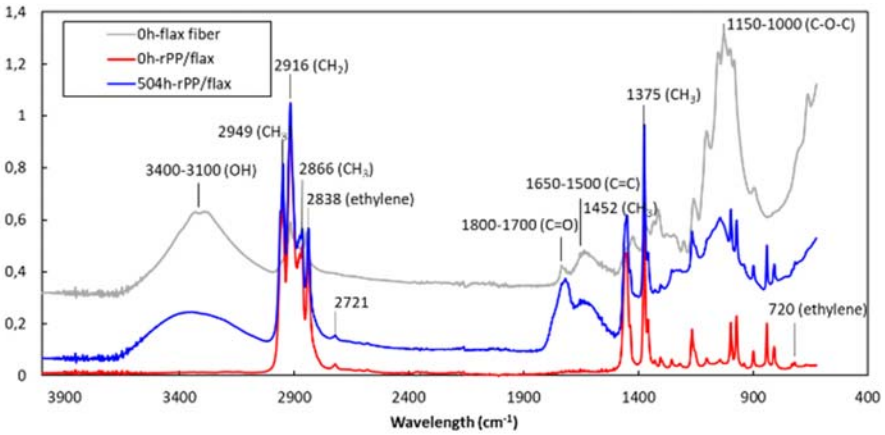

Fig. 2 IR surface spectra of flax fibers, unaged and aged rPP/flax

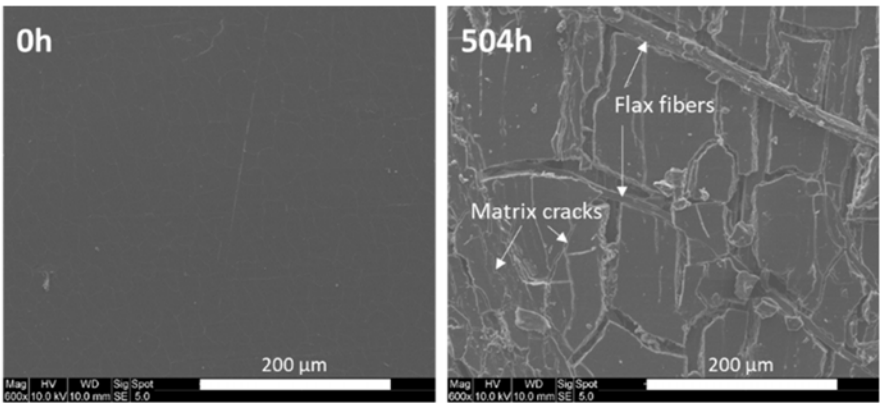

Fig. 3 SEM images of composite before and after 504 h of aging

B. Surface Morphology of Composites

Before aging, the surface of rPP/flax composites is free from voids and smooth (Fig. 3). It also shows good covering of the flax fiber by the rPP matrix. After 504 h of aging, the surface presents a network of cracks with an appearance of flax fibers on the surface. These results corroborate those obtained by IR spectroscopy where the characteristic flax fiber peaks appear on the spectra after 504 h of aging. These cracks are the result of surface photooxidation. This photooxidation leads to the formation of new chemicals, as discussed earlier, resulting from the chain scission reactions. The latter leads to the formation of shorter and more mobile chains. According to [13], these chains can be rearranged in a more organized way to form new crystals. This increase in surface density creates internal stress. Once the surface layer can no longer withstand it, cracks form and grow to form a network towards the end of aging.

C. Color Analysis

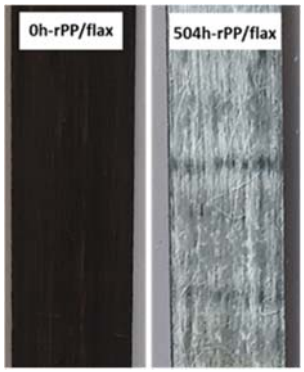

Fig. 4 Visual appearances of the surface of of rPP/flax before and after aging

From Fig. 4, the composites surface discoloration can be clearly seen after 504 h of aging. Prior to exposure, the surfaces of the composites showed the black color of the rPP matrix. Fig. 5 summarizes the results of the two color parameters L* and b* which confirm this discoloration. The b* parameter experienced a decrease in yellowness. This decrease is essentially due to the photooxidation of the chemical component, lignin, of flax fibers [17]. Indeed, the results found with IR spectroscopy and SEM images showed the appearance of flax fibers on the surface. Therefore, under UV radiation, lignins photodegrade to form paraquinone chromophoric structures which then undergo a reduction to give the hydroquinones resulting in photobleaching of the surface [15]. In addition, the increase in the L* parameter (increase in lightness) is also attributed to the photodegradation of flax fibers as well as to the scratch whitening mechanism of thermoplastic due to the formation of cracks on the surface as shown by SEM images [23].

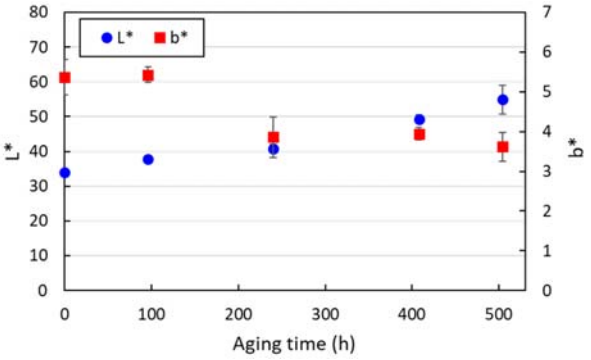

Fig. 5 Changes of L* and b* parameters of rPP/lin composites as a function of exposure time

D. Tensile Properties

The stress-strain curve of unaged and aged rPP/flax UD composites is presented in Fig. 6. As reported in the literature, the composites exhibit a nonlinear behavior which can be assimilated to a bilinear behavior [24]. The primary elastic modulus E1 can be calculated from the initial linear part estimated between the deformation of 0.015% and 0.1%. The second modulus E2 can be calculated between the deformation 0.3% and 0.6%. Such a choice of linear part is supported by the literature for natural fiber UD composites [25]. It is interesting to note that at the initial state, composites with recycled matrix have good mechanical tensile properties compared to those with virgin matrix according to the literature [26]. The tensile strength at rupture is about 247.9 ± 16.8 MPa and the two tensile moduli E1 and E2 are 26.4 ± 1.5 GPa and 19.5 ± 1.0 GPa respectively.

At the end of aging, the tensile mechanical properties remain relatively unaffected by UV aging (Fig. 3). A decrease of approximately 7% is noted for the tensile strength and the deformation at break while the two tensile moduli show almost no variation with the exposure time. This can be explained by the fact that the stiffness of UD composites is mainly dominated by the properties of flax fibers which seem to photodegrade only on the surface as shown previously with IR spectroscopy, SEM analysis and colorimetry. This implies that the photodegradation was limited on the surface, thus leaving the overall composites little affected.

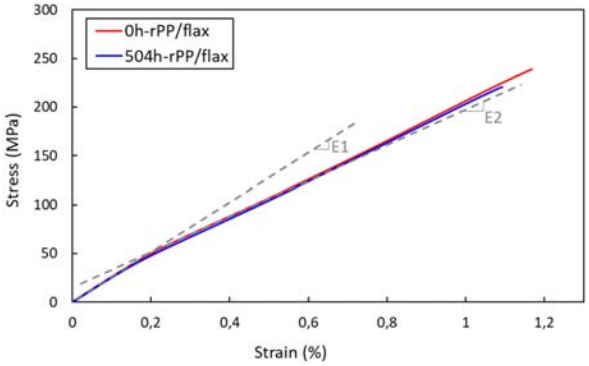

Fig. 6 Stress-strain curve of tensile test before and after aging

V. Conclusion

UD composites reinforced with flax fibers and based on rPP from agricultural waste have been prepared by thermocompression. They were then subjected to photooxidative aging under continuous exposure to UV radiations for 504 h. Analysis by IR spectroscopy showed, at initial state, a good encapsulation of flax fibers by the matrix. At the end of aging, the formation of new chemical groups on the surface indicated the photodegradation of the PP matrix and flax fibers. SEM analysis clearly verified this degradation by the appearance of cracks and flax fibers on the surface of composites. In addition, the surface photobleaching found with colorimetric analysis confirmed the photodegradation of surface flax fibers. Despite surface degradation, rPP/lin composites showed high mechanical resistance against photooxidation. It seems that the consequences of photooxidation were limited on the surface leaving the bulk of composites unaffected. The overall result encourages the use of recycled matrix in UD natural fiber composites for exterior semi-structural application.

ACKNOWLEDGMENT

This work is supported by the Bourgogne Franche-Comté region-France and Gustave Eiffel University.

REFERENCES

[1] C. Baley, A. Bourmaud, et P. Davies, « Eighty years of composites reinforced by flax fibres: A historical review », *Composites Part A: Applied Science and Manufacturing*, vol. 144, p. 106333, mai 2021, doi: 10.1016/j.compositesa.2021.106333.

[2] D. Mathijsen, « The renaissance of flax fibers », *Reinforced Plastics*, vol. 62, nº 3, p. 138-147, juin 2018, doi: 10.1016/j.repl.2017.11.020.

[3] C. Baley et A. Bourmaud, « Average tensile properties of French elementary flax fibers », *Materials Letters*, vol. 122, p. 159-161, mai 2014, doi: 10.1016/j.matlet.2014.02.030.

[4] R. Seldén, B. Nyström, et R. Långström, « UV aging of poly(propylene)/wood-fiber composites: UV Aging of Poly(propylene)/Wood-Fiber Composites », *Polym Compos*, vol. 25, nº 5, p. 543-553, oct. 2004, doi: 10.1002/pc.20048.

[5] L. Soccalingame *et al.*, « Reprocessing of artificial UV-weathered wood flour reinforced polypropylene composites », *Polymer Degradation and Stability*, vol. 120, p. 313-327, oct. 2015, doi: 10.1016/j.polymdegradstab.2015.07.013.

[6] M. D. H. Beg et K. L. Pickering, « Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites », *Polymer Degradation and Stability*, vol. 93, nº 10, p. 1939-1946, oct. 2008, doi: 10.1016/j.polymdegradstab.2008.06.012.

[7] D. Scida *et al.*, « Hygrothermal/UV Aging Effect on Visual Aspect and Mechanical Properties of Non-Woven Natural-Fiber Composites », *Journal of Renewable Materials*, vol. 7, nº 9, p. 865-875, 2019, doi: 10.32604/jrm.2019.06609.

[8] C. Homkhiew, T. Ratanawilai, et W. Thongruang, « Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubberwood flour », *Industrial Crops and Products*, vol. 56, p. 52-59, mai 2014, doi: 10.1016/j.indcrop.2014.02.034.

[9] D. J. Carlsson et D. M. Wiles, « The Photooxidative Degradation of Polypropylene. Part I. Photooxidation and Photoinitiation Processes », *Journal of Macromolecular Science, Part C: Polymer Reviews*, vol. 14, nº 1, p. 65-106, janv. 1976, doi: 10.1080/15321797608076113.

[10] A. François-Heude, E. Richaud, E. Desnoux, et X. Colin, « A general kinetic model for the photothermal oxidation of polypropylene », *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 296, p. 48-65, janv. 2015, doi: 10.1016/j.jphotochem.2014.08.015.

[11] D. J. Carlsson, A. Garton, et D. M. Wiles, « Initiation of Polypropylene Photooxidation. 2. Potential Processes and Their Relevance to Stability », *Macromolecules*, vol. 9, nº 5, p. 695-701, sept. 1976, doi: 10.1021/ma60053a002.

[12] D. M. Philip, J. Attwood, D. A. Hulme, et D. P. Shipton, « Evaluation of Weathering in Mixed Polyethylene and Polypropylene Products », p. 113, mars 2004.

[13] M. S. Rabello et J. R. White, « Crystallization and melting behaviour of photodegraded polypropylene– 1. Chemi-crystallization », p. 9.

[14] A. Cogulet, P. Blanchet, et V. Landry, « Wood degradation under UV irradiation: A lignin characterization », *Journal of Photochemistry and Photobiology B: Biology*, vol. 158, p. 184-191, mai 2016, doi: 10.1016/j.jphotobiol.2016.02.030.

[15] L. Soccalingame, D. Perrin, J.-C. Bénézet, et A. Bergeret, « Reprocessing of UV-weathered wood flour reinforced polypropylene composites: Study of a natural outdoor exposure », *Polymer Degradation and Stability*, vol. 133, p. 389-398, nov. 2016, doi: 10.1016/j.polymdegradstab.2016.09.011.

[16] C. Badji, J. Beigbeder, H. Garay, A. Bergeret, J.-C. Bénézet, et V. Desauziers, « Exterior and under glass natural weathering of hemp fibers reinforced polypropylene biocomposites: Impact on mechanical, chemical, microstructural and visual aspect properties », *Polymer Degradation and Stability*, vol. 148, p. 104-116, févr. 2018, doi: 10.1016/j.polymdegradstab.2017.12.015.

[17] Y. Peng, R. Liu, J. Cao, et Y. Chen, « Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin, and cellulose », *Applied Surface Science*, vol. 317, p. 385-392, oct. 2014, doi: 10.1016/j.apsusc.2014.08.140.

[18] S. Ghahri, S. K. Najafi, B. Mohebby, et M. Tajvidi, « Impact strength improvement of wood flour-recycled polypropylene composites », *J. Appl. Polym. Sci.*, vol. 124, nº 2, p. 1074-1080, avr. 2012, doi: 10.1002/app.34015.

[19] S. Butylina, M. Hyvärinen, et T. Kärki, « A study of surface changes of wood-polypropylene composites as the result of exterior weathering », *Polymer Degradation and Stability*, vol. 97, nº 3, p. 337-345, mars 2012, doi: 10.1016/j.polymdegradstab.2011.12.014.

[20] H. Du, W. Wang, Q. Wang, Z. Zhang, S. Sui, et Y. Zhang, « Effects of pigments on the UV degradation of wood-flour/HDPE composites », *J. Appl. Polym. Sci.*, p. n/a-n/a, 2010, doi: 10.1002/app.32430.

[21] M. Hamzah *et al.*, « Surface chemistry changes and microstructure evaluation of low density nanocluster polyethylene under natural weathering: A spectroscopic investigation », *J. Phys.: Conf. Ser.*, vol. 984, p. 012010, mars 2018, doi: 10.1088/1742-6596/984/1/012010.

[22] Y. Lv *et al.*, « Outdoor and accelerated laboratory weathering of polypropylene: A comparison and correlation study », *Polymer Degradation and Stability*, vol. 112, p. 145-159, févr. 2015, doi: 10.1016/j.polymdegradstab.2014.12.023.

[23] S.-S. Choi, H.-S. Chung, Y.-T. Joo, B.-K. Min, et S.-H. Lee, « Analysis of the whitening phenomenon of a thermoplastic elastomer article by UV weathering », *Polymer Testing*, vol. 30, nº 4, p. 415-419, juin 2011, doi: 10.1016/j.polymertesting.2011.02.010.

[24] T. Cadu, L. Van Schoors, O. Sicot, S. Moscardelli, L. Divet, et S. Fontaine, « Cyclic hygrothermal ageing of flax fibers' bundles and unidirectional flax/epoxy composite. Are bio-based reinforced composites so sensitive? », *Industrial Crops and Products*, vol. 141, p. 111730, déc. 2019, doi: 10.1016/j.indcrop.2019.111730.

[25] P. M. Giuliani, O. Giannini, et R. Panciroli, « Characterizing flax fiber reinforced bio-composites under monotonic and cyclic tensile loading », *Composite Structures*, vol. 280, p. 114803, janv. 2022, doi: 10.1016/j.compstruct.2021.114803.

[26] C. Baley *et al.*, « Flax/PP manufacture by automated fibre placement (AFP) », *Materials & Design*, vol. 94, p. 207-213, mars 2016, doi: 10.1016/j.matdes.2016.01.011.