Assessment of the natural fiber reinforced bio-polyethylene composites flexural macro and micromechanical properties

One of the most common load modes is flexure. The paper measures and models the flexural strength and modulus of a bio-polyethylene reinforced with thermos-mechanical fibers from corn stover. Moreover, the authors use modified rules of mixtures to evaluate the contribution of the reinforcements to the properties of the composite. It was found a high impact of coupling agent content on the strength of the composites, and materials with a 6% of such agent and 50% of reinforcement increased 181% the strength of the matrix, and 464% its modulus. The obtained values are noticeable higher than polypropylene and some of its composites. Micromechanics analysis shows that the effect of natural fiber reinforcement on the flexural properties of a bio-based PE is similar to the effects on a polyolefin. Thus, the use of fully bio-based composites can be proposed as a substitute for some oil-based polymers, partially bio-based materials, and their composites.

Keywords: Biocomposites; injection molding, micromechanical analysis; flexural properties; natural fibers; Interface analysis

Introduction

The literature shows that we are under a global context of climate emergency and efficient solutions are required to reduce energy and fossil materials consumption to protect the environment (Ripple et al. 2019; Gills and Morgan 2020). Nowadays, the use of oil-based plastics by the industry is widely extended. This is mainly due to its properties such as specific strength and durability, as well as its low cost and its suitability to be used in automated manufacturing. However, the consumption of fossil resources, GHG emissions, and the inadequate management of end-of-use products represent critical environmental impacts (Sohn et al. 2020; Chae and An 2018). The interest in bioplastics grew as a consequence of worldwide regulations for the use of oil-based plastic materials in response to the impact they generate (Shin et al. 2020;

European Commission 2018). One of the alternatives has been the production of biopolymers, similar to oil-based ones, but based on renewable resources (Siracusa and Blanco 2020; Spierling et al. 2018). Thus, it is possible to find alternative commercial bioplastics with almost the same properties as oil-based plastics but with a reduced carbon footprint. One of these materials is bio-based polyethylene (BioPE) produced from ethanol obtained from sugar cane (Brodin et al. 2017; Iwata 2015).

A common practice to increase the mechanical properties of a polymer is preparing composite materials and use of fibers as reinforcements. In this sense, natural fibers have shown high potential as strengthening and stiffening materials when used as reinforcement for thermoplastics (Yildirim et al. 2020; Hamouda et al. 2017). At the same time, the use of natural fibers decreases the percentage of polymer in the composite. (Tarrés, Vilaseca, et al. 2019; Joshi et al. 2004). Properties of a composite material depend on several factors including the properties of the matrix, the intrinsic properties of the reinforcements, and the interface between such phases (Tarrés, Hernández-díaz, and Ardanuy 2021; Zhou, Fan, and Chen 2016). The intrinsic properties of the fibers are mainly determined by their origin (wood fibers, annual plants, agroforestry residues, or recycled fibers) (Serra-Parareda et al. 2021; Albert Serra et al. 2019), as well as the treatments used to obtain the reinforcements (chemical, semi-chemical, thermo-mechanical or mechanical treatments) (Delgado-Aguilar et al. 2018). The interfacial adhesion between the natural fibers and the plastic matrix is hindered by the opposite polarities of the two phases (Sepe et al. 2018; Rouger and Mutje 1984). The hydrophilic nature of the fibers can be reduced by chemical treatments (Singha and Rana 2012), although the use of coupling agents is a highly cited strategy (Dányádi et al. 2007; Mohanty, Verma, and Nayak 2006). The literature shows that the addition of a coupling agent such as polyethylene grafted maleic anhydride

(MAPE) is effective in creating a strong interface between natural fibers and polyethylene (Mohanty, Verma, and Nayak 2006). Previous research showed that the identical chemical structure of bio-polyethylene and polyethylene allows a good blend between the polyethylene chains of MAPE and BioPE (Tarrés and Ardanuy 2020; Mekonnen et al. 2013).

In addition, corn (Zea mays L.) is one of the more widespread crops in the world with a volume of 1100 million tons during 2019/20 (Žilić et al. 2022). Apart from being an important source of food, corn is used for the production of corn starch. However, these crops generate low-value lignocellulosic residues in the shape of stalks, leaves, and husks that are usually left or incinerated in the fields resulting in the emission of CO_2. Approximately 40% of corn production is made up of cobs, stalks, and leaves (Miranda et al. 2018). To date, little effort has been focused on recovering this biomass for upcycling applications. The use of this agricultural residue as a reinforcement for the production of BioPE-based composite materials would mean the reduction of greenhouse gas emissions, would give value to this residue, and would increase the sustainability of the industry.

In previous papers, some of the authors researched the tensile properties of corn fiber-reinforced Bio-PE composites (Tarrés and Ardanuy 2020; Tarrés, Hernández-díaz, and Ardanuy 2021). These papers show that these composites can reach noticeable tensile properties, in line with polyolefin. Nonetheless, semi-oriented short fiber-reinforced composites are anisotropic and show different properties depending on the direction of the load. Thus, differences between tensile and flexural properties are expected. Moreover, flexural loads are more common than a purely tensile state of loads for real product applications. In that sense, if the materials have to be proposed for applications in automotive, construction, product design, or packaging, where other authors have shown interest, the flexural properties of the materials have to be known (Hamouda et al. 2019). To the best knowledge of the authors, there is extensive literature devoted to the preparation of natural fiber reinforced polyolefin, but the papers where a bio-Polyethylene is used as a matrix are scarce.

The main objective of this work is to analyze the mechanical and micromechanics flexural properties of composite materials obtained with different percentages of MAPE coupling agent and reinforcement that have been modeled. Knowing these properties is essential to proposing bio-based materials as an alternative to oil-based polymers.

Composite materials preparation and characterization

Corn stover supplied by Fundació Mas Badia (La Tallada d'Empordà, Spain) was ground using a mill equipped with a 5 mm sieve and then subjected to a thermo-mechanical process with steam-water at 180°C for 15 minutes, with a liquid to the dry raw material ratio of 6:1. Finally, the lignocellulosic material was defibrated using Sprout-Waldron equipment (Andritz, Spain) to achieve better individualization and dispersion of the fibers within the polymeric matrix. The obtained fibers were stored at 80ºC for 24h to remove moisture. These fibers, together with the bio-polyethylene, and the polyethylene grafted maleic anhydride (MAPE), were mixed in different proportions (weight/weight) using a Gelimat kinetic mixer (Dusatec, New Jersey, USA). Bio-based polyethylene SHA7260, with a molecular weight of 61.9 g/mol, was purchased from Braskem (Sao Paulo, Brazil). The coupling agent was MAPE Fusabond MB100D acquired from Eastman Chemical Products (San Roque, Spain).

The materials were mixed at 210 °C and 3000 rpm for 2 minutes. The mixtures were cooled before being ground using a blade mill to obtain pellets to be used in the injection-molding machine. Finally, obtained pellets were dried and stored at 80°C for at least 24 hours before injection. The injection process of the composites was carried out on an Arburg 220M 350-90U injection machine (Lossburg, Germany) obtaining specimens with the dimensions required in the standard ASTM D790. The specimens were conditioned in a climatic chamber (Dycometal, Spain) at 50% relative humidity and 23°C for at least 48 hours as indicated in ASTM D618.

The flexural test allows measuring the flexural strength, the elastic modulus in the elastic region, and the maximum bending deformation. It was performed using a TM 1122 universal testing machine (Instron, USA) at a constant speed of 2 mm/min according to ASTM D790. The resulting flexural properties are the mean of at least 5 experiments.

Models and theoretical formulations

Modified rule of mixtures

Rules of mixtures are linear functions where the independent variables are the volume fractions of the phases and the dependent variable a mechanical property of the composite material. These models are attractive because are elegant and easy to handle mathematically. A modified rule of mixtures for the flexural strength of a semi-aligned short fiber-reinforced composite has the following form:

$$\sigma_f^C = f_c \cdot \sigma_f^F \cdot V^F + (1 - V^F) \cdot \sigma_f^{M^*} \quad (1)$$

where σ_f^C is the flexural strength of the composite, σ_f^F is the intrinsic fiber flexural strength, $\sigma_f^{M^*}$ is the contribution of the matrix to the flexural strength of the composite and is the matrix flexural stress at the point of maximum deformation of the composite. To account for the impact of the orientation and morphology of the fibers and the strength of the interface, a coupling factor (f_c) is added to the equation. The coupling factor is the product of two factors, the first factor (χ_1) considers the loss of properties due to fiber orientation in the composite. On the other hand, the second factor (χ_2) ponders the fiber-matrix interface and the length of the fibers. χ_2 can be obtained through the critical length of the reinforcements according to the shear lag model (Tucker and Liang 1999). Then, the fibers present in the reinforcement, with a length distribution, are divided into subcritical fibers, and supercritical fibers. The shear lag model considers that the matrix transmits stress to the fibers (reinforcement) through the interface by shear loads. Therefore, the critical length of a fiber is the length at which the center area of the fiber endures a load equal to its intrinsic strength. Critical length can be calculated by the following equation:

$$L_c^F = \frac{d^F . \sigma_t^F}{2. \tau} \tag{2}$$

where d^F is the fiber diameter and τ is the interfacial shear strength. Once the value of L_c^F is obtained, it is compared with the mean length of the fibers (L_F) and χ_2 can be obtained. If the mean fiber length (L_F) is lower than the critical fiber length (L_c^F), equation (3) can be applied; otherwise, equation (4) is applied.

$$\chi_2 = \frac{L^F}{2. L_c^F} \tag{3}$$

$$\chi_2 = 1 - \frac{L_c^F}{2. L^F} \tag{4}$$

A modified rule of mixtures for the flexural modulus of the composites can be formulated with the following form:

$$E_f^C = \eta_e \cdot E_f^F \cdot V^F + (1 - V^F) \cdot E_f^M \tag{5}$$

where E_f^C and E_f^M are the flexural moduli of the composite and matrix, respectively. E_f^F is the intrinsic modulus of the reinforcement and η_e is an efficiency factor that accounts for the impact of the reinforcement orientation and morphology, being the product of an orientation efficiency factor (η_0) and a length efficiency factor (η_l).

Equations 1 and 5 can be used to obtain the intrinsic properties of the reinforcements from the experimental values of the matrix and the composites. Nonetheless, the coupling factor and the efficiency factor remain unknown, and the equations cannot be solved. Then, a rearrangement of equations 1 and 5 gives rise to a fiber flexural strength factor (FFSF) and a fiber flexural modulus factor (FFMF), which represent the contribution of the reinforcement to the flexural strength and modulus of the composites:

$$\mathrm{FFSF} = \frac{\sigma_f^C - \left(1 - V^F\right) \cdot \sigma_f^{M^*}}{V^F} = f_c \cdot \sigma_f^C \tag{6}$$

$$\mathrm{FFMF} = \frac{E_f^C - E_f^M \cdot \left(1 - V^F\right)}{V^F} = \eta_e \cdot E_f^F \tag{7}$$

Results and discussion

Flexural properties

Table 1 shows the flexural properties of BioPE and its composites. The table shows the impact of coupling agent (MAPE) contents on the flexural strength (σ_f^C), deflection at failure (D_f^C), strain at failure (ε_f^C), and flexural modulus (E_f^C). The table adds the standard deviations.

Insert Table 1 Here.

The percentage of coupling agents and the percentage of reinforcement had noticeable effects on the flexural properties of the materials. In a recent article, some of the authors evaluated the impact of coupling agents over tensile properties. It was found that tensile strength increased up to 6% of MAPE, and higher coupling agent percentages decreased such property (Tarrés and Ardanuy 2020). This is not the case for flexural strength, which increased with MAPE percentages up to 8%. Further MAPE percentages were not tested because a material with increased flexural strength but with diminished abilities to sustain tensile loads was uninteresting as multipurpose material. The main differences between a flexural and a tensile load can be found in the sections of the specimens under load. While in the case of tensile load all the specimen section is submitted to such tensile loads, in the case of the flexural specimen, more or less half of the section is under tensile and the other half under compression. Taking into account the anisotropy of short fiber reinforced composites due to the orientation of the reinforcements being not random and the morphology of the fibers changing in diameter and length noticeably, differences between the behavior of specimens under tensile and flexural loads can be expected.

Figure 1 shows the effect of MAPE and reinforcement percentages on the flexural strength of the composites.

Insert Figure 1 Here

In all the cases, the flexural strength of uncoupled materials is higher than BioPE's (21.25 MPa). The figure shows how a 2% MAPE content had a noticeable impact on the flexural strength of the materials containing 40% of corn stalk fibers (CSF) or more. Materials with lower CSF contents showed increases in their flexural strength but were not so noticeable. This can be linked to the number of available OH groups. The presence of MAPE provokes two different reactions inside the composite materials. On the one hand, PE chains of the coupling agent entangle and co-crystallize with the BioPE matrix. On the other hand, maleic anhydride groups create chemical bonds with the OH groups on the fiber surface. The higher the percentage of reinforcement, the higher the available OH groups on the surface of such fibers. As the percentage of MAPE increases, the effect on the flexural strength of the composites is higher, especially for materials adding 20% of CSF or more. In the case of the composite reinforced with a 10% of CSF a 4% of MAPE increased the flexural strength of the uncoupled composite, but higher MAPE contents delivered variable results. This can be caused by a saturation of the OH groups or by self entanglement of MAPE. It must be taken into account that the percentage of MAPE is measured against the percentage of reinforcement and thus, the higher the presence of CSF, the higher the presence of MAPE. On the other hand, Composites with 40 and 50% of CSF increased continuously their flexural strength with MAPE contents. Nonetheless, this increase is not linear. Figure 1 adds a regression curve for the evolution of the flexural strength of the composite reinforced with a 50% of CSF. The flexural strength of such materials increased quickly for 2 to 6% MAPE contents. The increase of flexural strength slowed down for 8% MAPE content. Materials with a 6% of MAPE, and CSF percentages up to 40%, show a linear progression of their flexural strength. This indicates the presence of a strong interface.

In the case of the flexural modulus, the effect of MAPE on such property cannot be corroborated (Figure 2).

Insert Figure 2 Here.

The flexural modulus of the composites for the same CSF percentage showed a little variation in their values regarding MAPE content. Only the materials with 30% of CSF showed notable differences between the moduli at different MAPE contents. Nonetheless, such differences cannot be linked to the presence of MAPPE. The rest of the materials show almost horizontal regression lines. This is in line with the literature that corroborates a limited effect of coupling agents and the interface strength over the modulus of a composite. Being the modulus a fundamental property of a material, the absence of noticeable changes in the modulus of the materials against MAPE content indicated that the structure of the material has not been dramatically changed.

Attending to the data obtained during this study and the prior studies on tensile properties, a 6% of MAPE is proposed to obtain materials that deliver high tensile and flexural properties. In all the cases, the stiffening effect of CSF is more noticeable than its strengthening effect.

Figure 1 shows how the flexural strength of the materials with a 6% of MAPE increased linearly for CSF contents in the range from 10 to 40%. The material that adds 50% of CSF returned a flexural strength lower than the predicted by a linear model. The materials with 10 to 50% CSF contents increased the flexural strength of the matrix a 41%, 815, 130%, 161%, and 181%, respectively. All the values were higher than the flexural strength of polypropylene (PP) (26.07 MPa).

In the case of the flexural modulus, adding a rigid phase to the composite increases the rigidity of such material, and this is reflected in the increase of the flexural modulus of the composites against CSF content (Figure 2). The materials that added 6% of MAPE increased 120%, 182%, 320%, 385%, and 464% the modulus of the matrix for 10 to 50% CSF contents, respectively. Thus, adding 6% of MAPE and 10 to 50% of CSF to a BioPE allows the obtention of materials with flexural strengths and moduli higher than PP. The evolution of the flexural modulus of the materials in the range from 10 to 40% of CSF is linear (Figure 2). This is an indication of a good dispersion of the reinforcements in the matrix (Granda et al. 2016). The composites with 50% of CSF returned modulus a bit lower than the expected of linear evolution, indicating the increasing difficulties of obtaining a good dispersion or the formation of fiber bundles (Granda et al. 2016).

Nonetheless, the increase of the flexural strength and the modulus produces a decrease in the toughness and an increase in the embrittlement of the materials. Naturally, the embrittlement of the materials is reflected by the increase of the flexural modulus and the decrease of the strain at failure of the materials. As specified in ASTM D790, the strain at failure was computed from the deflection at failure using:

$$\varepsilon_f^C = \frac{6 \cdot D \cdot d}{L^2} \tag{8}$$

Where D is the maximum deflection at the center of the specimen, L is the supports span (52.6mm for the tests), and d is the depth of the specimen (3.1 mm mean depth). Figure 3 shows the evolution of the strain at the failure of the materials.

Insert Figure 3 Here.

The figure shows how the ability of the material to deform without breaking decreases with the percentage of reinforcement. The use of MAPE has little effect on the flexural modulus but increases the flexural strength. Thus, the use of MAPE allows higher deformations. In this case, MAPE has a toughening effect, increasing the area below the stress-strain curve.

The amount of deformation a material can sustain will be a very important parameter to establish if the materials can be used for industrial purposes, In a majority of cases, products are designed having into account the maximum acceptable deformation, and seldom the ultimate strength (Oliver-Ortega et al. 2018). Besides, increasing the toughness of a material has a direct effect on its impact properties.

Micromechanics modeling of flexural properties

The main purpose of micromechanics is to know the effect of the changes of phase contents on the mechanical properties of the composites, understanding such materials as heterogeneous. To evaluate the contributions of the phases the authors propose using modified rules of mixtures for the flexural strength (Equation 1) and modulus (Equation 5) for short semi-aligned fiber-reinforced composites. The values for the contributions of the matrix at different strains were obtained from a regression curve of the stress-strain diagram, represented by equation 9:

$$\sigma_f^{M^*} = -0.0011 \cdot \left(\varepsilon_f^C\right)^5 + 0.0245 \cdot \left(\varepsilon_f^C\right)^4 - 0.1544 \cdot \left(\varepsilon_f^C\right)^3 - 0.4361 \cdot \left(\varepsilon_f^C\right)^2 + 7.8506 \cdot \left(\varepsilon_f^C\right)^1 - 0.4173 \qquad (9)$$

The fiber volume fraction (V^F) for the composites adding 10 to 50% of CSF are 0.068, 0.141, 0.218, 0.304 and 0.395. The coupling factor may show values between 0 and 1 and composites with strong interfaces show coupling factors between 0.18 and 0.2 (Fu and Lauke 1996).

In equation 5, the modulus efficiency factor (η_e) usually shows values of around 0.5 for these kinds of composite materials (Serrano et al. 2014; López et al. 2012).

As mentioned in a previous section, equations 1 and 5 cannot be solved to obtain the intrinsic properties of the reinforcement due to the presence of the coupling and efficiency factors. Nonetheless, the net contributions of the fibers to the flexural strength and modulus are $f_c \cdot \sigma_f^C$, and $\eta_e \cdot E_f^C$, respectively. Thus, equations 1 and 5 can be solved to obtain such contributions at different fiber volume fractions. These values can be plotted against fiber volume fractions and then a regression line for these points can be obtained (Equations 6 and 7). The slope of such a line gives an idea of the strengthening (FFSF) or stiffening (FFMF) capabilities of the reinforcement. Figure 4 shows the FFSF and the FFMF for the CSF-reinforced BioPE composites.

Insert Figure 4 Here.

The figure shows the contribution of the fibers for uncoupled and coupled at 6% of MAPE composite materials. Figure 4a shows the importance of a strong interface to obtain good contributions of the fibers to the flexural strength of the composites. FFSF for uncoupled and coupled composites were 73.886 and 133.84, respectively. This means that adding 6% of MAPE increases to 86% the strengthening ability of CSF. Glass fibers, hemp fibers, and coupled and uncoupled alfa fibers as PP reinforcement returned FFSFs of 383.5, 202.26, 335.13, and 173.01, respectively (Tarrés, Soler, et al. 2019; Vilaseca et al. 2020). In this case, CSF fibers as BioPE reinforcement show strengthening capabilities noticeably lower than other natural fibers. It must be taken in account that the surfaces of referred fibers are richer in cellulose content than corn fiber surfaces and thus, the impact of the coupling agent over the strength of the interface is lower.

Figure 5b shows the limited effect of MAPE over the stiffening abilities of CSF. Coupled and uncoupled composites returned almost the same FFMF. For comparison purposes, glass fiber, cotton fibers, and stone groundwood fibers, as PP reinforcement returned FFMFs of 26.45, 12.60, and 11.83, respectively (A. Serra et al. 2019; Oliver-Ortega et al. 2018). CSF as BioPE reinforcement returns similar values to other natural fibers. Thus, the stiffening effect of CSF over a BioPE is comparable to other natural fibers as polyolefin reinforcement. Having into account that nowadays there are examples of the use of natural fiber reinforced polyolefin composites in the automotive, construction, and product design industries there is the possibility of substituting such oil-based polymers with bio-based ones.

Conclusions

Composite materials from Bio-PE and thermos-mechanical fibers from corn stover were prepared and tested under flexural loads. The results showed that the flexural strength and modulus of the composites were similar to or higher than commodities like polyolefin and its composites. The use of coupling agents was necessary to ensure strong interfaces between the matrix and the reinforcements and also to increase the elongation at the break of the materials.

The micromechanics study of flexural properties indicates that the interface between the bio-polyethylene matrix and corn stover fibers obtained by thermomechanical treatments can be improved by the incorporation of a coupling agent. The incorporation of a 6% coupling agent and 40% corn stover fibers led to a 143% and 385% increase in flexural strength and flexural modulus, respectively. However, the micromechanics study also revealed a lower reinforcing ability of the fibers from this agricultural residue concerning glass fibers or other natural fibers from annual plants. The effect of the percentages of fibers on the flexural properties of the composites was similar to other natural fibers as polyolefin reinforcement. Thus, it seems possible to change from partially bio-based composites to fully bio-based ones.

Obtained flexural properties, in line with polyolefins like polypropylene and high-density polyethylene, allows proposing BioPE / CSF composites as suitable substitutes for such commodities. Nonetheless, any use must have into account the increase of the viscosity of the composites over the matrices, the reduction of the allowed deformations, and the possible effect of water absorption on the properties of the materials. Thus, a complete technical analysis of the use of the materials must be produced. Moreover, the impact of water absorption is a future line of research, as well as the impact properties of the materials. Besides, the environmental impact of the composites has to be measured based on a life-cycle analysis.

References

Brodin, Malin, María Vallejos, Mihaela Tanase Opedal, María Cristina Area, and Gary Chinga-Carrasco. 2017. “Lignocellulosics as Sustainable Resources for Production of Bioplastics – A Review.” *Journal of Cleaner Production* 162. Elsevier Ltd:

646–64. doi:10.1016/j.jclepro.2017.05.209.

Chae, Yooeun, and Youn Joo An. 2018. “Current Research Trends on Plastic Pollution and Ecological Impacts on the Soil Ecosystem: A Review.” *Environmental Pollution* 240. Elsevier Ltd: 387–95. doi:10.1016/j.envpol.2018.05.008.

Dányádi, Lívia, Tünde Janecska, Zoltán Szabó, Gábor Nagy, János Móczó, and Béla Pukánszky. 2007. “Wood Flour Filled PP Composites: Compatibilization and Adhesion.” *Composites Science and Technology* 67 (13): 2838–46. doi:10.1016/j.compscitech.2007.01.024.

Delgado-Aguilar, M., H. Oliver-Ortega, J. Alberto Méndez, J. Camps, F.X. Espinach, and P. Mutjé. 2018. “The Role of Lignin on the Mechanical Performance of Polylactic Acid and Jute Composites.” *International Journal of Biological Macromolecules* 116. doi:10.1016/j.ijbiomac.2018.04.124.

European Commission. 2018. “A European Strategy for Plastics in a Circular Economy.” https://ec.europa.eu/commission/publications/factsheets-european-strategy-plastics-circulareconomy_%0Aen.

Fu, S-Y, and B Lauke. 1996. “Effects of Fiber Length and Fiber Orientation Distributions on the Tensile Strength of Short-Fiber-Reinforced Polymers.” *Composites Science and Technology* 56: 1179–90.

Gills, Barry, and Jamie Morgan. 2020. “Global Climate Emergency: After COP24, Climate Science, Urgency, and the Threat to Humanity.” *Globalizations* 17 (6). Taylor & Francis: 885–902. doi:10.1080/14747731.2019.1669915.

Granda, L. A., F. Espinach, J. A. Méndez, F. Vilaseca, M. Delgado-Aguilar, and P. Mutjé. 2016. “Semichemical Fibres of Leucaena Collinsii Reinforced Polypropylene: Flexural Characterisation, Impact Behaviour and Water Uptake Properties.” *Composites Part B: Engineering* 97: 176–82. doi:10.1016/j.compositesb.2016.01.035.

Hamouda, Tamer, Ahmed H. Hassanin, Ali Kilic, Zeki Candan, and Mehmet Safa Bodur. 2017. “Hybrid Composites from Coir Fibers Reinforced with Woven Glass Fabrics: Physical and Mechanical Evaluation.” *Polymer Composites* 38 (10): 2212–20. doi:10.1002/pc.23799.

Hamouda, Tamer, Ahmed H. Hassanin, Naheed Saba, Mustafa Demirelli, Ali Kilic, Zeki Candan, and Mohammad Jawaid. 2019. “Evaluation of Mechanical and Physical Properties of Hybrid Composites from Food Packaging and Textiles Wastes.” *Journal of Polymers and the Environment* 27 (3). Springer US: 489–97. doi:10.1007/s10924-019-01369-3.

Iwata, Tadahisa. 2015. “Biodegradable and Bio-Based Polymers: Future Prospects of Eco-Friendly Plastics.” *Angewandte Chemie - International Edition* 54 (11): 3210–15. doi:10.1002/anie.201410770.

Joshi, S V, L T Drzal, A K Mohanty, and S Arora. 2004. “Are Natural Fiber Composites Environmentally Superior to Glass Fiber Reinforced Composites?” *Composites Part a-Applied Science and Manufacturing* 35 (3): 371–76. doi:10.1016/j.compositesa.2003.09.016.

López, Joan Pere, Pere Mutjé, M.A. Pèach, N.E. El Mansouri, Sami Boufi, and Fabiola Vilaseca. 2012. “Analysis of the Tensile Modulus of Polypropylene Composites Reinforced with Stone Groundwood Fibers.” *BioResources* 7 (1): 1310–23.

Mekonnen, Tizazu, Paolo Mussone, Hamdy Khalil, and David Bressler. 2013. “Progress in Bio-Based Plastics and Plasticizing Modifications.” *Journal of Materials Chemistry A* 1 (43): 13379–98. doi:10.1039/c3ta12555f.

Miranda, M. T., F. J. Sepúlveda, J. I. Arranz, I. Montero, and C. V. Rojas. 2018. “Analysis of Pelletizing from Corn Cob Waste.” *Journal of Environmental Management* 228 (September). Elsevier: 303–11. doi:10.1016/j.jenvman.2018.08.105.

Mohanty, Smita, Sushil K. Verma, and Sanjay K. Nayak. 2006. “Dynamic Mechanical and Thermal Properties of MAPE Treated jute/HDPE Composites.” *Composites Science and Technology* 66 (3–4): 538–47. doi:10.1016/j.compscitech.2005.06.014.

Oliver-Ortega, Helena, José Alberto Méndez, Rafel Reixach, Francesc X Espinach, Mònica Ardanuy, and Pere Mutjé. 2018. “Towards More Sustainable Material Formulations: A Comparative Assessment of PA11-SGW Flexural Performance versus Oil-Based Composites.” *Polymers* 10 (4): 440. doi:10.3390/polym10040440.

Ripple, William, Christopher Wolf, Thomas Newsome, Phoebe Barnard, William

Moomaw, Philippe Grandcolas, William Ripple, et al. 2019. "World Scientists ' Warning of a Climate Emergency To Cite This Version : World Scientists ' Warning of a Climate Emergency." *Bioscience*. https://hal.archives-ouvertes.fr/hal-02397151/document.

Rouger, J., and P. Mutje. 1984. "Correlation between the Cellulose Fibers Beating and the Fixation of a Soluble Cationic Polymer." *British Polymer Journal* 16 (2): 83–86.

Sepe, R., F. Bollino, L. Boccarusso, and F. Caputo. 2018. "Influence of Chemical Treatments on Mechanical Properties of Hemp Fiber Reinforced Composites." *Composites Part B: Engineering* 133 (January). Elsevier Ltd: 210–17. doi:10.1016/j.compositesb.2017.09.030.

Serra-Parareda, Ferran, Fabiola Vilaseca, Francesc X. Espinach, Pere Mutjé, Marc Delgado-Aguilar, and Quim Tarrés. 2021. "Stiffening Potential of Lignocellulosic Fibers in Fully Biobased Composites: The Case of Abaca Strands, Spruce Tmp Fibers, Recycled Fibers from Onp and Barley Tmp Fibers." *Polymers* 13 (4): 1–20. doi:10.3390/polym13040619.

Serra, A., Q. Tarrés, M. Chamorro, J. Soler, P. Mutjé, F.X. Espinach, and F. Vilaseca. 2019. "Modeling the Stiffness of Coupled and Uncoupled Recycled Cotton Fibers Reinforced Polypropylene Composites." *Polymers* 11 (10). doi:10.3390/polym11101725.

Serra, Albert, Quim Tarrés, Miquel Llop, Rafel Reixach, Pere Mutjé, and Francesc X. Espinach. 2019. "Recycling Dyed Cotton Textile Byproduct Fibers as Polypropylene Reinforcement." *Textile Research Journal* 89 (11): 2113–25. doi:10.1177/0040517518786278.

Serrano, A., F. X. Espinach, J. Tresserras, R. del Rey, N. Pellicer, and P. Mutje. 2014. "Macro and Micromechanics Analysis of Short Fiber Composites Stiffness: The Case of Old Newspaper Fibers-Polypropylene Composites." *Materials and Design* 55. Elsevier Ltd: 319–24. doi:10.1016/j.matdes.2013.10.011.

Shin, Sun Kyoung, Namil Um, Yong Jun Kim, Na Hyeon Cho, and Tae Wan Jeon. 2020. "New Policy Framework with Plastic Waste Control Plan for Effective Plastic Waste Management." *Sustainability (Switzerland)* 12 (15). doi:10.3390/su12156049.

Singha, A. S., and Raj K. Rana. 2012. “Natural Fiber Reinforced Polystyrene Composites: Effect of Fiber Loading, Fiber Dimensions and Surface Modification on Mechanical Properties.” *Materials and Design* 41: 289–97. doi:10.1016/j.matdes.2012.05.001.

Siracusa, Valentina, and Ignazio Blanco. 2020. “Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly(ethylene Terephthalate) (Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications.” *Polymers* 12 (8). MDPI AG: 1641. doi:10.3390/polym12081641.

Sohn, Yu Jung, Hee Taek Kim, Kei Anne Baritugo, Seo Young Jo, Hye Min Song, Se Young Park, Su Kyeong Park, et al. 2020. “Recent Advances in Sustainable Plastic Upcycling and Biopolymers.” *Biotechnology Journal* 15 (6): 1–16. doi:10.1002/biot.201900489.

Spierling, Sebastian, Carolin Röttger, Venkateshwaran Venkatachalam, Marina Mudersbach, Christoph Herrmann, and Hans Josef Endres. 2018. “Bio-Based Plastics - A Building Block for the Circular Economy?” *Procedia CIRP* 69: 573–78. doi:10.1016/j.procir.2017.11.017.

Tarrés, Quim, and Mònica Ardanuy. 2020. “Evolution of Interfacial Shear Strength and Mean Intrinsic Single Strength in Biobased Composites from Bio - Polyethylene and Thermo - Mechanical Pulp - Corn Stover Fibers.” doi:10.3390/polym12061308.

Tarrés, Quim, David Hernández-díaz, and Mònica Ardanuy. 2021. “Interface Strength and Fiber Content Influence on Corn Stover Fibers Reinforced Bio-polyethylene Composites Stiffness.” *Polymers* 13 (5): 1–14. doi:10.3390/polym13050768.

Tarrés, Quim, Jordi Soler, José Ignacio Rojas-Sola, Helena Oliver-Ortega, Fernando Julián, F. Xavier Espinach, Pere Mutjé, and Marc Delgado-Aguilar. 2019. “Flexural Properties and Mean Intrinsic Flexural Strength of Old Newspaper Reinforced Polypropylene Composites.” *Polymers* 11 (8): 1–13. doi:10.3390/polym11081244.

Tarrés, Quim, Fabiola Vilaseca, Pedro J. Herrera-Franco, F. Xavier Espinach, Marc Delgado-Aguilar, and Pere Mutjé. 2019. “Interface and Micromechanical Characterization of Tensile Strength of Bio-Based Composites from Polypropylene and Henequen Strands.” *Industrial Crops and Products* 132 (February). Elsevier: 319–26. doi:10.1016/j.indcrop.2019.02.010.

Tucker, Charles L., and Erwin Liang. 1999. “Stiffness Predictions for Unidirectional Short-Fiber Composites: Review and Evaluation.” *Composites Science and Technology* 59 (5): 655–71. doi:10.1016/S0266-3538(98)00120-1.

Vilaseca, Fabiola, Ferran Serra-Parareda, Eduardo Espinosa, Alejandro Rodríguez, Pere Mutjé, and Marc Delgado-Aguilar. 2020. “Valorization of Hemp Core Residues: Impact of NaOH Treatment on the Flexural Strength of PP Composites and Intrinsic Flexural Strength of Hemp Core Fibers.” *Biomolecules* 10 (6). Multidisciplinary Digital Publishing Institute: 823. doi:10.3390/biom10060823.

Yildirim, M., T.A. Negawo, A. Kilic, and Z. Candan. 2020. “Development and Characterization of Hybrid Composites from Sustainable Green Materials.” *Green Materials* 9 (4): 1–10.

Zhou, Yonghui, Mizi Fan, and Lihui Chen. 2016. *Interface and Bonding Mechanisms of Plant Fibre Composites: An Overview*. *Composites Part B: Engineering*. Vol. 101. Elsevier Ltd. doi:10.1016/j.compositesb.2016.06.055.

Žilić, Slađana, Valentina Nikolić, Burçe Ataç Mogol, Aytül Hamzalıoğlu, Neslihan Göncüoğlu Taş, Tolgahan Kocadağlı, Marijana Simić, and Vural Gökmen. 2022. “Acrylamide in Corn-Based Thermally Processed Foods: A Review.” *Journal of Agricultural and Food Chemistry*. doi:10.1021/acs.jafc.1c07249.